A scheme for the classification of explosions in the chemical process industry

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ABSTRACT

All process industry accidents fall under three broad categories—fire, explosion, and toxic release. Of these fire is the most common, followed by explosions. Within these broad categories occur a large number of sub-categories, each depicting a specific sub-type of a fire/explosion/toxic release. But whereas clear and self-consistent sub-classifications exist for fires and toxic releases, the situation is not as clear *vis a vis* explosions. In this paper the inconsistencies and/or shortcomings associated with the classification of different types of explosions, which are seen even in otherwise highly authentic and useful reference books on process safety, are reviewed. In its context a new classification is attempted which may, hopefully, provide a frame-of-reference for the future.

1. Introduction

A bewildering variety of accidents occur in process industry during the storage, manufacture, and transportation of chemicals. These range from minor innocuous leaks to catastrophic releases (like the ones occurred at Seveso and Bhopal), from the barely noticed tiny sparks to all-consuming fires, and from the plop of a bubble to earth-shattering explosions of the type witnessed at Feyzin [1,2], Mexico City [1,2], Vishakhapatnam [3], Sydney [4], and Buncefield [5], among hundreds of others [1,2,6–8]. The impact can also have a bewildering range, from causing temporary malfunctioning of a small component of an equipment to the demolition of an entire factory.

But, in broad terms, all process industry accidents can be classified under one or more of three categories: fire, explosion, and toxic release. Within these three broad categories fall numerous sub-categories which differ from each other in subtle as well as coarse ways. In order to forecast the likely accidents and to assess the likely consequences it is essential to properly classify the different sub-categories of accidents on the basis of their distinct attributes. Only with a proper understanding of the nature and the mechanism of each event can the consequence modelling be done effectively.

When studying the state-of-the-art of explosion modelling the authors were surprised to find that no self-consistent and/or com-

prehensive sub-classification of the different forms of explosions exists. Even the otherwise very authentic and exceedingly useful compendia, such as of Lees [1,2], CCPS [9,10], or the 'Yellow Book' prepared by TNO – The Netherlands Organization for Applied Scientific Research [11] – do not provide adequately clear and distinct sub-classification.

This aspect was put up for discussion by the authors during two recent international conferences, held at Pondicherry [12] and Tehran [13]. The participating scientists and safety professionals agreed that this indeed is the case.

In this paper the lacunae associated with the existing classifications of explosions are reviewed and a new classification is attempted which may, hopefully, provide a frame-of-reference for the future. This exercise assumes importance when it is recalled that of the three broad categories of accidents mentioned above, explosions cause the greatest proportion of losses in chemical process industry—an estimated 67.7% against 30.2% losses caused by fires and 2.1% by toxic releases [1,2].

2. The existing classifications

Among the most sought-after of all compendiums in the domain of process safety engineering is the *magnum opus* of the late Lees [1,2]; in it explosions have been classified as follows:

1. *Physical explosions*
   (a) Mechanical failure of pressure system
   (b) Overpressure of pressure system

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(c) Under-pressure of pressure system
(d) Over-temperature of pressure system
(e) Under-temperature of pressure system
2. *Condensed phase explosions*
  (a) High explosives
  (b) Ammonium nitrate
  (c) Organic peroxides
  (d) Sodium chlorate
3. *Vapour cloud explosions* (*VCEs*)
4. *Boiling liquid expanding vapour explosions* (*BLEVEs*)
5. *Confined explosions with reaction*
  (a) Explosion involving vapour combustion
  (b) Reactor explosions
  (c) Other explosions involving liquid phase reactions
6. *Vapour escapes into, and explosions in, buildings* (*VEEBs*)
7. *Dust explosions*

The problem one faces while following this classification is that its hierarchy of sets and sub-sets is unclear and overlapping. For example BLEVE, which is essentially a physical explosion, has been cited as a category separate from 'physical explosions'. Likewise vapour cloud explosions (VCEs) have been put in a different slot from 'vapour escapes into, and explosions in, buildings' (VEEBs) even though a VEEB is very similar in its mechanism to a VCE. Moreover the happenings 'c' and 'e' listed under *physical explosions* are, in true sense, implosions.

Another authentic manual from a highly reputed professional body: CCPS (Centre for Chemical Process Safety) of the AIChE (American Institute of Chemical Engineers), titled *Guidelines for Chemical Process Quantitative Risk Analysis* [10] lists 'Explosions' as follows:

1. Confined explosions
2. Vapour cloud explosions
3. Physical explosions
4. Dust explosions
5. Detonations
6. Condensed phase detonations
7. Missiles

Curiously it lists BLEVE, which is in reality the kind of explosion which is 'louder' than most other kinds of explosions, under 'Fires'! It is particularly surprising because one-fifth of all BLEVEs occur without causing any fire [14–16].

In another of the oft-used CCPS manual [9], the *logic diagram for explosion events* given on its page 128 (Fig. 1), creates the impression that 'physical explosions' and 'confined explosions' are two distinct categories, mutually exclusive. They aren't!

Moreover in the *logic diagram for physical explosion* of this manual, VCE has been included among physical explosions. But VCE is not a physical explosion; it is a chemical explosion.

Numerous other texts on explosions surveyed by us, which are otherwise exceedingly useful, either provide similar forms of misclassification [17–21], or no classification at all [11,22].

Before proceeding with a proposed new classification of explosions, it may be worthwhile to set the context by working at the definition of the term 'explosion'.

3. What is an explosion?

The word 'explosion' instantaneously conjures up the image of something coming apart with a bang. In day-to-day existence we also use the word to describe any sudden burst of energy: for example a tennis player *exploding* into a flurry of shots; a sprinter taking off *explosively*; a boxer *detonating* his left hook. We also use expressions like *as soon as the boss saw the quarterly report he simply exploded*. Or the more common types: *I can't tell my wife I will be late for dinner . . . she will explode*. The word has its origins in the Latin word *explodere* which means 'to drive off the stage by clapping' [23].

In more staid scientific language, the phenomenon of explosion has been defined in terms of an event's ability to generate massive overpressure. According to Lees [1,2], *an explosion is a sudden and violent release of energy*; the extent of violence depending on the rate at which energy is released. An inflated balloon or a car tyre, or a boiler heated to well above 100 °C all have energy stored under pressure. If this energy is released suddenly, it would cause a violent explosion. But if released slowly, the same extent of energy would be dissipated with no violence.

The Centre for Chemical Process Safety, American Institute of Chemical Engineers [9] defines explosion as a release of energy that causes a blast; a blast being a transient change in the gas density, pressure and velocity of the air surrounding an explosion point. Crowl and Louvar [24] make it shorter by labeling explosion as a rapid expansion of gases resulting in a rapidly moving pressure or shock wave. A highly perceptive definition has been given by F. M. Global [18]: *an explosion is a rapid transformation of potential physical or chemical energy into mechanical energy and involves the violent expansion of gases*.

To wit, an explosion is distinguished by the following characteristics:

(a) Sudden release of physically or chemically generated and stored energy.
(b) A shock wave/blast wave of significant magnitude, rapidly moving out from the explosion source.

Depending on the conditions of the blast, debris/flying fragments may originate from containment of the source of explosion, or materials in immediate contact with it. Cratering of the soil directly underneath the source may also lead to projectiles.
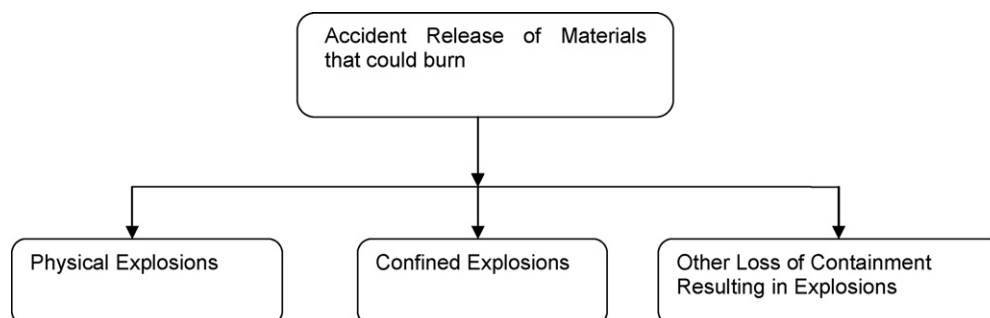

Fig. 1. Logic diagram for explosion events given in CCPS [9].

3.1. The general physical mechanism of an explosion

To see the relation between these various manifestations of an explosion and to better understand the differences between the various types of explosions treated in the next section, it may be helpful to recapitulate the general physical mechanism of an explosion. At the moment of explosion the energy which enables it, is present as a gas under pressure. The high pressure can be obtained by a pure, physical process (compression, heating) or by chemical conversion. The temperature of the gas may not necessarily be elevated, but often is; certainly so when the cause of high pressure is chemical conversion. 'Explosive' energy release with a rate as high as in explosions can in rare cases also take place by chemical reaction in solids, without formation of significant quantities of gas, but this kind of 'explosion' is not relevant to process safety.

The gas under pressure may instantaneously expand by bursting its containment, or may do so in the open air even when no containment is present in case its formation has been extremely rapid. Expansion of the gas causes a shock wave in the surrounding air. The mechanism of expansion can be modeled as a series of discrete compression waves which increase the pressure of the air outside the source while at the same time decreasing the pressure of the source and setting the air in motion in a direction turned away from the source (blast wind). Collision with ambient air molecules sets the latter in motion. A compression wave with its gradually rising pressure (isentropic compression) propagates with local sound velocity. This property depends on the molecule mean travel velocity and hence increases with temperature. Due to the compression in the wave the temperature of the air behind the wave increases and the subsequent waves move with higher velocities. They therefore tend to overtake the primary one, thus forming a wave characterized by a flat frontal pressure increase akin to the accelerating piston mechanism.

A shock wave can be seen as discontinuous – a jump-wise – increase in pressure, temperature and material velocity, propagating through a medium with the material velocity in the direction of the front. The propagation velocity of a shock front is therefore principally higher than of a sound wave. Unlike as in a compression wave the compression in a shock wave is non-isentropic. Obviously the initial shock peak strength depends on the intensity of the source. In a three-dimensional diverging expansion of the compressed gas in free air the shock peak is followed by rarefaction in which pressure, temperature and material velocity gradually decrease and at sufficient distance from the source pressure can even become temporarily sub-atmospheric. The entire wave of propagating shock and rarefaction together is called blast (Fig. 2). At further expansion the shock peak strength decreases continually and at last, diminishes to a sound wave. If the explosion happens to be occurring near the closed end of a pipe, the resultant shock wave does not diverge and so remains planar. This prolongs the duration of the high pressure; it eventually gets weakened due to the non-isentropic nature of the compression, but very slowly. As a result the pressure decay is much slower in a pipe.

Transfer of shock wave energy from one material to the other is optimal at equal acoustic impedance (product of density and sound velocity). A shock wave in air therefore reflects most of its energy when hitting a solid or a liquid surface. An explosion in the air near the ground results by the reflection in higher pressure at the ground surface than in free air at the same distance from the source.

When the compressed gas is confined, at the moment of explosion the containment ruptures, and often is shattered. The resulting fragments are subjected to pressure difference and drag and are therefore propelled in the direction of the shock wave. There is a lot more to shock waves: their reflection and diffraction at solid (or liquid) surfaces and interactions with each other but these aspects are not pertinent to the classification of explosions.
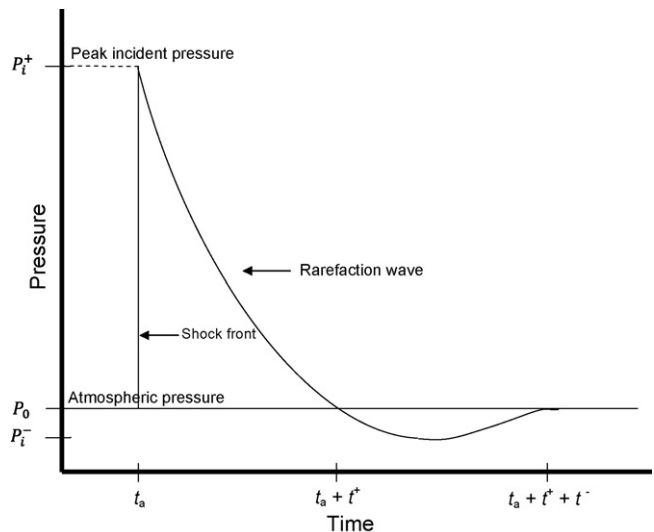

Fig. 2. Blast wave led by a shock and followed by a rarefaction wave; t_a, t^+ and t^- represent times of peak incident pressure, positive phase duration and negative phase duration, respectively.

Unfortunately it is not possible to assign precise cut-off values for the 'suddenness' of energy release, magnitude of the blast, or speed of shock wave below which an event will not be an explosion and above which it would [2,24–26]. This is because a lot depends on numerous other factors which may aggravate or diffuse a potentially explosive situation. For example under identical conditions of rate of pressure rise a vessel weakened at some part by corrosion or fatigue may explode while another vessel of identical rated strength may hold on. Likewise a vapour cloud meeting with some type of obstacles in its path may explode while another vapour cloud of identical material density and size meeting with different types of obstacles may not [27,28].

In summary, only two broad generalizations can be made:

(a) When the pressure build-up in any vessel or conduit exceeds the ability of the container to withstand the pressure, an explosion may result.
(b) When in an unconfined space, the rate of pressure rise due to the energy conversion process substantially exceeds the ability of the space to diffuse the pressure rise, an explosion may result.

4. Types of explosions

As mentioned earlier, one encounters a wide variety of explosions, in terms of nature as well as magnitude, ranging from what we get if a water droplet accidentally falls on hot oil in the kitchen, to firecrackers; a bursting bubble to earth-shaking blasts; a 0.22 gunshot to nuclear bombs. But, in essence, only three kinds of energy are associated with all explosions: physical, chemical, and nuclear. Of these, only the first two are encountered in process industries as also in day-to-day existence. We would, therefore, dwell further only on these two. In addition this classification being specific to explosions which occur in chemical process industry in the course of process operations, and during the storage and transport of associated chemicals, we have omitted external happenings such as a lightening strike, sabotage, earthquake, etc., which may cause an explosion. Hence the first order of the proposed classification (Fig. 3) comprises of two categories: physical explosion and chemical explosion.
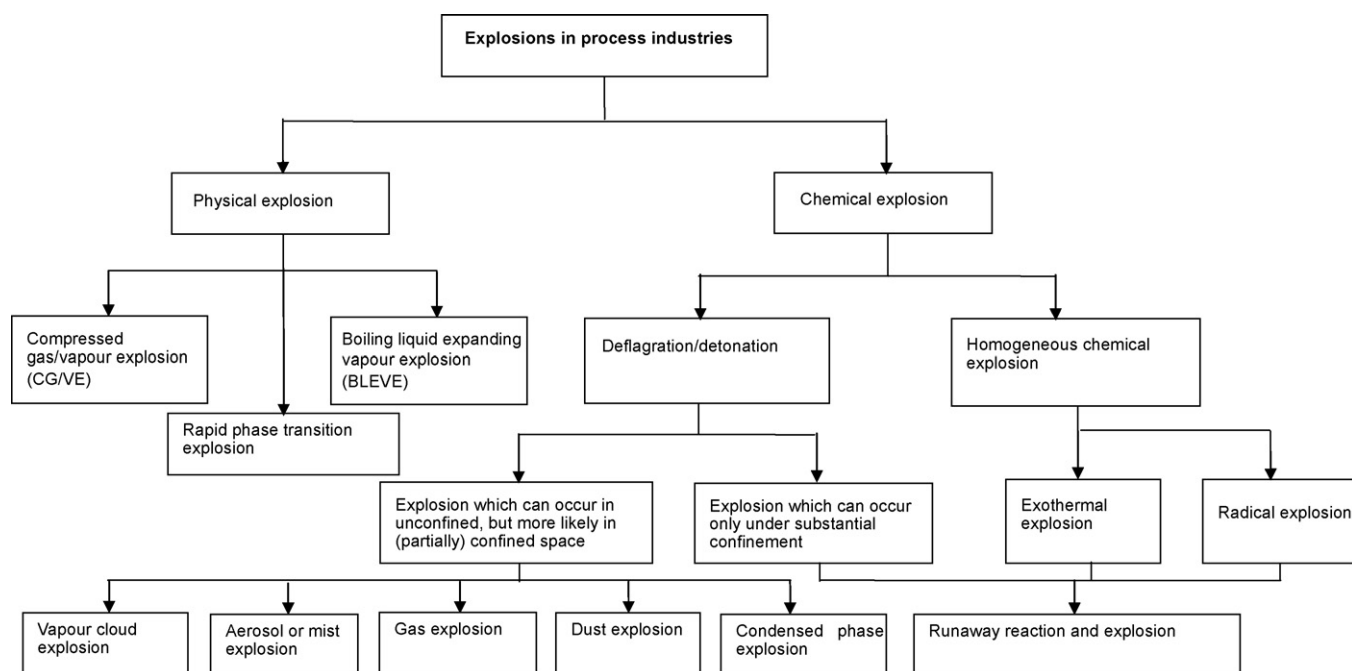
Fig. 3. The proposed scheme for the classification of explosions in chemical process industry.

5. Physical explosion

Before proposing a definition of 'physical explosion' we must emphasize that in all types of explosion much physics is involved. In fact the gas expansion process explained in the previous section is purely physical, but even in an explosion in which the energy is generated in a chemical conversion the mechanism of propagating the reaction is by heat transfer or compression and hence physical.

The term 'physical' in physical explosion refers to the way the energy that enabled the explosion would have been accumulated. It could have been by heating a volatile liquid or a gas in a containment and thus causing pressure build-up. Or mechanically, by simply compressing a gas. The accumulation process may be relatively slower than in the 'chemical explosions' defined in Section 6. A physical explosion occurs when the accumulated energy is suddenly released in a rapid physical change such as the expansion of a compressed gas or the flash vapourization of a superheated liquid by a failure somehow of the containment. After the explosive release a substance may undergo chemical reactions, a flammable substance may start burning due to mixing with air contributing heavily to the overall effect as with the failure of a tank of compressed, liquefied hydrocarbons, but the *cause* of all physical explosions is purely mechanical energy. It may be mentioned that electrical discharge can also cause a shock/blast wave in surrounding air, as with a lightning strike, but this form of physical explosion is not considered here.

Depending on the situations that cause physical explosion such an event may be categorized as follows.

5.1. Compressed gas/vapour explosion (CG/VE)

CG/VE refers to catastrophic rupture of a pressurized gas-filled vessel. The vessel may be filled up entirely with the gas or may contain some liquid. In the latter case we call it CG/VE only if the liquid is not in a superheated state at the instant of vessel failure; in other words when it is at a temperature below its atmospheric pressure boiling point.

A burst of a pressurized vessel in CG/VE can occur for the following reasons:

1. Failure of level control, or of pressure regulating and pressure relief equipment (physical over pressurization).
2. Reduction in vessel wall thickness due to:
   a. corrosion,
   b. erosion,
   c. chemical attack.
3. Reduction in vessel wall strength due to:
   a. overheating,
   b. material defects with subsequent development of fracture,
   c. chemical attack, e.g., stress corrosion cracking, pitting, embrittlement,
   d. fatigue induced weakening of the vessel.
4. Any other mechanical cause (such as a container suffering injury due to accidental fall or a hit).

In situations as in 1, above, failure can normally occur only when the vessel acquires pressure significantly higher than the operating pressure. In other situations failure can occur even at or near the operating pressure of the vessel.

In a situation as in 3a, above, accidental overheating of the vessel may cause some or all of its liquid contents to vapourize, thereby taking the internal pressure beyond the tolerance level of the vessel. This may lead to a variant of CG/VE called rapid phase transition explosion.

5.2. Boiling liquid expanding vapour explosion (BLEVE)

A BLEVE differs from a CG/VE explained above on two counts:

(a) A vessel suffering a BLEVE must contain significant quantities of the substance in a liquid form.
(b) The liquid should be existing at a temperature which is well above the liquid's boiling point at normal (atmospheric) pressure, in other words in a 'superheated' state relative to the normal pressure.

If a vessel containing a superheated liquid under pressure is suddenly depressurized, the liquid suffers instantaneous nucleation and flash vapourization into gas several times larger in volume than the parent liquid [27,29]. The resultant build up of pressure may force the vessel to fail catastrophically, causing a BLEVE. Hence, whereas in CG/VE (described in the preceding section) the bust of energy to generate the explosive pressure wave comes solely from the adiabatic expansion of a gas, in BLEVE the adiabatic vapourization of liquid is the main contributory factor.

For risk analysis distinction is made between a 'hot' and a 'cold' BLEVE, depending on whether the vessel fractures/punctures by mechanical loading or by an external fire. In the latter case the effects can be more severe due to heat input and higher pressure at fracture.

A BLEVE gives rise to the following [4,14,29]:

- Blast wave.
- Flying fragments (missiles).
- Splashing of some of the liquid to form short-lived pools; the pools may be on fire if the liquid is flammable.
- Fire or toxic gas release. If the pressure-liquefied vapour is flammable, as is often the case, the BLEVE leads to a (rising) fireball or at delayed ignition (rarely) to flash fire or vapour cloud explosion. When the material undergoing BLEVE is toxic, as in the case of ammonia or chlorine, adverse impacts include toxic gas dispersion.

5.3. Rapid phase transition explosion (RPT)

Rapid phase transition (RPT) explosion may occur when cryogenic liquids are accidentally exposed to hotter environment, for example liquefied natural gas (LNG) spilled on or in water [29,30]. The precise conditions for the local instability to cause a RPT are still unclear; threshold amounts of ethane and propane in the natural gas are a factor. The effect is relatively weak. The largest blast measured is that of 3.5 kg TNT equivalent. The main effect is producing a large puff of evaporated natural gas temporarily increasing in cloud size.

A variant of RPT which is rare in chemical process industries but more common in metallurgical industries occurs when molten metals or hot oil accidentally come in contact with a much cooler water (or other liquid). This variant, RPT and BLEVE have one aspect in common—in each heat energy is suddenly and abundantly transferred to a liquid which superheats and thereby undergoes instantaneous nucleation. There is a burst of 'boiling liquid and expanding vapour'. The most common, and by far the most destructive, manifestation of this aspect occurs in the form of BLEVEs in vessels containing pressure liquefied gases.

6. Chemical explosion

When the slug of energy needed to generate large quantities of gas within a very short time span, leading to a rate of pressure build-up that is fast enough to cause an explosion even in open space, comes due to a chemical reaction, we may call such an event chemical explosion.

6.1. Homogeneous chemical explosion, deflagration and detonation

The broadest sub-classification of chemical explosion proposed by us is based on where in the material the reactions are taking place at a given time. It can happen in two distinct forms: if it is occurring throughout the mass of material all at once, the phenomenon may be called a *homogeneous chemical explosion*. In case the reaction

occurs only in a propagating reaction zone it can be in two well-defined but very different intensities: *deflagration* and *detonation*. The latter can be made visible as moving flames; the velocity in case of deflagration ranges from very low up to some hundreds of meter per second, while in detonation it is of the order of kilometers per second.

The broad sub-classification is explained further in Section 6.5. Under the second of this broad category – deflagration/detonation – fall chemical explosions which can either occur only under substantial confinement or the ones that can also occur in unconfined space.

6.1.1. Homogeneous chemical explosion

A homogeneous chemical explosion can occur in two ways: sharp rise in temperature due to an exothermal chemical reaction or due to the formation of a net surplus of radicals.

We propose to call them *exothermal explosion* and *radical explosion* respectively, although the former usually is loosely called thermal explosion [1,2,31].

The name *exothermal explosion* hints at the acceleration mechanism in the reactions. To produce hot gas fast, reactions are needed which overall are exothermic. The heat of reaction is partially lost to the surroundings but partially increases the temperature of the reactants and consequently accelerates the reaction. If no heat is lost (adiabatic situation) or the medium is perfectly stirred, the temperature is equal throughout and ideally the reaction rate is also equal throughout. We propose to call this extreme a *homogeneous exothermal explosion*. Another mechanism may also be operative: made possible by branched radical reactions. Reactions propagate often by radicals; hydrogen–oxygen or hydrogen–chlorine reactions are well-known examples. If a reaction occurs in which more radicals are produced than necessary for the reactants to be formed from the original substance, there is 'branching'. This can accelerate the overall reaction even at relatively low temperatures. Peroxide intermediates formed in the reaction of hydrocarbons with oxygen decompose that way. In gases these compounds cause so-called 'cool flames', which are not always harmless. It must be said that the two forms – exothermal and radical explosion – cannot always be sharply distinguished.

6.1.2. Deflagration and detonation

Deflagration literally means 'fast burning'; it consists of a moving exothermic reaction zone sustained by heat flow from hot reaction gases to unreacted material by conduction, convection, and radiation [1,2,29,31]. Propagation can become very slow when unconfined (for example in some ammonium nitrate fertilizer formulations it can be just a few centimeters per hour) to extremely fast; up till hundreds of meters per second. But it is always *subsonic* with respect to the sound velocity in the material.

In a detonation the energy transfer to initiate a reaction in a fresh substance is caused by compression in a shock wave (reactive shock), hence the propagation velocity is *supersonic* [1,2,23,27]. Because of the high velocity of the wave and hence the very short time within which the reactions and the conversion of the substance to a hot expanding gas mass takes place, a shock wave is produced in the ambient air which we perceive as a 'bang'.

The temperature increase by the sudden compression starts the reaction. In condensed substances detonation velocities can, in extreme cases, reach 10 km/s, creating hundreds of megabars in pressure. In gases, on the other hand, the sound velocity is much lower so is their detonation velocity, up to 3 km/s. Due to the lower density of gases the pressures are also lower by factors of ~1000. Whether on the higher side of intensity or lower, due to the high peak pressure detonations are always very destructive.

The high propagation rates in deflagrations occur either under confinement by a mechanism of pressure driven acceleration due

to increased heat transfer and higher reaction rate, or in gases by flame acceleration as a result of turbulence generation in the still unreacted gas in front of the flame. The turbulence increases the burning surface area and 'thickens' the flame. It also, to a certain extent, increases the burning rate relative to the substance. In grained solids with some confinement the hot reaction gases may penetrate into the mass, spreading ignition, and this may very quickly increase the pressure to high levels.

The mechanisms mentioned above may lead to transition between deflagration and detonation (DDT) [2,32,33] which can occur in gases, liquids and solids, leading to catastrophic pressure effects. In the transition stage, the pressure may be temporarily even higher than in a stationary detonation wave. The mechanism of the transition is rather complex but can be explained in rough terms as follows. If due to the acceleration, the deflagration flames reach velocities of hundreds of meters per second, the accompanying compression waves may grow very strong. Either before or just behind the flame front in the local compressed substance, conditions may become such that any perturbation in the reacting mass may be strengthened to a shock wave. It may then suddenly propagate as a detonation wave ('explosion within an explosion').

Deflagrations are often accompanied by flame, detonation always. In both cases reaction products often burn after being mixed with air but this does not contribute to explosion dynamics.

6.2. Fuel and oxidiser mixtures

As explained above many chemical explosions occur in mixtures of an oxidiser and a fuel. This is true for solids, e.g. pyrotechnics; and liquids, e.g. certain types of liquid explosives; but particularly true for mixtures of a fuel and air oxygen as oxidiser. These form the basis for a distinction of explosions used much in practice based on the phase or aggregation state of the fuel:

- Gas and vapour fuelled—gas explosion/vapour cloud explosion.
- (Combustible) dust fuelled—dust explosion.
- Aerosol (in the form of liquid droplets) fuelled—aerosol or mist explosion.

Quite often what is reported as a vapour cloud explosion is either a gas explosion in the open or an aerosol explosion. Most hydrocarbons when released accidentally from a pressure-liquefied or refrigerated condition are initially cold and heavy. They either partly condense by themselves or cause the condensation of the water vapour in the air in which they mix. They can be seen just before the explosion as a white cloud, lying low. A notorious example of an aerosol/vapour cloud explosion is the one that occurred in December 2005 at the Buncefield fuel depot in the U.K. A spill of gasoline from an overflowing tank formed a flammable aerosol which spread over a wide area before it ignited, exploded and set fire to a considerable number of other tanks [5].

In deflagrations and detonations of mixtures of fuel and oxidiser energy release rates and therefore violence of explosion vary with composition. Certain compositions can be found where explosion just does not occur anymore. These compositions form the explosion limits and in between is the explosion range. In case of gas or dust explosion the US terminology uses 'flammability limit' and 'flammable range'; the 'flammability limit' is expressed in terms of mean composition of the fuel–oxidant mixtures in which flame propagation is just possible. In Europe the expressions 'explosion limit' and 'explosion range' are in vogue and the composition which just fails to ignite is declared as limit. Detonation ranges are narrower than deflagration ones. Deflagration near the explosion limit ensues only an upward propagating flame.

6.3. Degree of confinement

Further classification of chemical explosion is proposed as follows:

1. Explosion which occurs in unconfined, partially confined, as well as confined space.
2. Explosion which can occur only with the substance reacting under confinement (since otherwise the reactions are of too low intensity or too slow).

The *first* category is specific to chemical explosion because no physical explosion in chemical process industry (in other words excluding nuclear explosion) is known to occur in unconfined space. Under this category fall the following types of explosions relevant to process industry; these quite often involve mixtures of an oxidiser and a fuel:

(a) Condensed phase explosion (such as the ammonium nitrate explosion in Toulouse, France in 2001; Table 1).
(b) Vapour cloud explosion
(c) Aerosol/mist explosion
(d) Gas explosion
(e) Dust explosion

A condensed phase explosion does not need any confinement. But for the vapour cloud or the aerosol explosions to occur, some degree of congestion or confinement is necessary so also the presence of significantly high quantities of flammable substance. These twin conditions provide sufficient fuel and feedback turbulence to the flame for attaining high enough flame speed leading to a blast. Gas and dust explosions usually take place inside partially confined or vented equipment.

How the physical state of a substance influences the nature of the explosion it undergoes is typified by condensed phase explosions, too. It makes a difference whether a substance is in the form of fine grains or a solid block, whether it is a liquid, a mix of a liquid and a solid, or a liquid and a gas. Usually mixed aggregate states allow physical interactions of shock and flame leading to a more violent reaction than single phase substances. Aggregates may also attain transition from deflagration to detonation more easily. Episodes have occurred in the past when, upon being heated by accidental fires, energetic materials have undergone detonation even in open space.

In the *second* category come runaway reactions mostly of liquids (reactor explosion) and solids (self-igniting exothermic decomposing substances or combustibles reacting with air at elevated temperature). These may occur with or without rapid phase transition causing exothermal explosion, sometimes partially resulting in deflagration. In rare cases the deflagration may transit into detonation. An exothermal explosion in a fuel–oxidiser gas mixture can also occur, at initially elevated pressure. After the explosion of a reactor, the ejected flammable products or reactants can mix with air in the space above the reactor forming a hot cloud which may self-ignite causing a vapour cloud explosion above the reactor.

6.4. Explosion intensity and ease of initiation

As mentioned, the intensity of the phenomena which leads to chemical explosion, may vary considerably. It distinguishes what we may call 'milder' chemical explosions from the more severe ones. It applies in some way to all categories of chemical explosions. Substances that react rapidly and violently (high energy of activation and heat of explosion) produce relatively intense pressures. They are able to propagate the explosive reaction even in strong diverging geometry and hence can be initiated relatively easily by

point source. Usually the required overall energy can be relatively low. Less reactive substances need energetic initiation by either a point source of larger diameter or by initiation over a larger plane area of the substance. In the later case the source itself can also be of lower intensity.

The energy producing reactions in all chemical explosions can be in a pure substance between atoms from the same molecule (*intramolecular*), or in a mixture of different substance components (*intermolecular*). The energy release rate of the latter type is usually lower and hence can determine whether a substance can only deflagrate or also detonate. Slower reaction rate also explains why sometimes absence of confinement can abort an explosion.

In summary three dimensions or facets influence the nature and severity of chemical explosions: the physics of propagation (exothermal explosion, deflagration, detonation), the aggregation state of the fuel–oxidiser mixture (gas, dust, aerosol, or condensed phase) and the presence or absence of confinement. If proper attention is not paid to the existence of all these dimensions and the way in which they influence each other, confusion and misinterpretation occurs leading to flaws in the accident modelling as well as in subsequent control strategies.

6.5. Distinctive features of specific explosion types

The distinctive features of several forms of deflagration/detonation falling under the two categories mentioned in Section 6.3 are presented below under their most common names. Attention is also paid to the processes of explosion initiation.

6.5.1. Vapour cloud explosion (VCE)

When large quantity of flammable vapour or gas is accidentally released into air it may form a vapour cloud. If the release is from a pressure liquefied state, its initial behaviour may be similar to that of a heavy gas even if at normal temperature and pressure the substance may be lighter-than-air. This may be due to its initially low temperature, entrapped liquid droplets (condensed fuel vapour or, in case of high humidity, water mist), and high release density. The resultant vapour cloud is, therefore, likely to hug the ground, at least initially, before slowly rising and moving. In case no immediate ignition resulting in jet flame (torch), (stratified layer) flash fire or rising fire ball occurs the vapour cloud disperses. At sufficiently delayed and strong ignition a vapour cloud explosion (VCE) may take place. Because of strong blast VCEs have the potential to cause heavy damage [17,20–22].

Once flammable material has been accidentally released, for it to lead to a VCE, the following requirements must be met with [2,28]:

(a) The released material must be flammable.
(b) The vapour cloud must mix with air to produce, depending on the fuel's reactivity, a sufficient mass in the flammable/explosive range of the material released.
(c) The environment of the cloud should offer sufficient confinement/congestion for turbulence generation in the flow driven by expanding hot combustion gases to initiate a feed-back flame acceleration process and pressure wave reflections.

Initially the flame ball expands from the place of ignition but the front propagates slowly with respect to the unburned gas, unable to produce a blast. However, while growing, the flame front stretches, starts wrinkling at the surface due to instabilities, and energy release starts to accelerate. Flame surface further increases; in particular passing around obstacles to the flow; further distorting the surface but also generating turbulence in fresh gas pushed ahead; resulting in turbulent flame brush and higher velocities. This feed-back mechanism characterizes VCE and produces its blast.

Analysis of past accidents has revealed [17,27–29] that partial confinement as may occur when the vapour cloud develops in or over, or drifts towards structures such as plant machinery, pipe racks, tanks, buildings, or vegetation all strongly accelerate the flame. Such a rapidly accelerating flame with the hot expanding gas behind it acts like a porous but accelerating piston and generates compression, shock and blast. The high damage potential of such a blast is due to the overpressure and impulse effect of the blast wind on objects. If there were no flame acceleration, the damage would have confined to thermal radiation and direct flame impingement.

A VCE to occur and result in a blast in a totally unconfined space is rare but it can happen with a very strong initiation source such as a detonating high explosive charge.

Following sub-classification of VCE can be done:

a. VCE occurring in unconfined space.
b. VCE occurring in hollow (semi-)confinements (such as empty spaces in a building).
c. VCE occurring in a relatively open space where drag-generating obstructions to the flow of gases ahead of the expanding flame ball are present (congested area).

6.5.2. Aerosol (or mist) explosion

An aerosol explosion is quite similar to a vapour cloud explosion; the difference occurs in the role played by the liquid droplets contained in an aerosol. Their presence enhances the probability of the cloud getting into the flammable range. Secondly once a flame is initiated it generates a blast which in turn can interact with particles ahead of the flame stripping off a micro-mist due to drag. This fine mist can react very intensively when it is reached by the flame. This can make the explosion more violent.

6.5.3. Gas explosion (GE)

'Gas explosion' is a name classically given [34] to explosion which takes place in a container or a conduit that happens to carry a fuel and an oxidiser (both in gas phase) in a mixture ratio within the explosion limits.[1] If the initiation is by a strong shock as from a very energetic spark, a high explosive charge, an exploding wire or a focussed laser locally ionising the air; and if the mixture is sufficiently reactive; an immediate detonation my occur. Otherwise, at least initially, there is deflagration. When the containment is able to sustain the explosion pressure not much is observed outside the containment; at best a sound ensues. Due to pressure oscillations generated by a rising flame instability, this sound can become rather strong.

Additional hazards occur when a gas explosion takes place in a space consisting of chambers inter connected by pipes. An explosion in one of the spaces causes increase in pressure of unburned gas in others. When the flame reaches these spaces the resulting explosion starts at a higher pressure level. This effect keeps propagating, leading to 'pressure piling'. The final pressure is substantially higher than of the initial explosion, with correspondingly high damage potential. Another effect is the flame acceleration that can occur in pipes due to turbulence generated by friction of the flow ahead of the propagating flame. Such acceleration can lead to very violent deflagration propagating with hundreds of meters per second. Over a sufficient run-up distance it can metamorph into a detonation generating much higher pressures. Further enhancement of turbulence, hence flame acceleration, can be caused by pressure

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[1] The difference between GE and VCE is not easy to elucidate. The flame chemistry in both is the same but the physics differs. The term VCE is specifically used for a large cloud in the open, sometimes visible, sometimes not, originating from a spill. GE does not consider source of fuel and can occur in the open only under special situations (e.g. very reactive fuel, high turbulence).

waves which may occur due to flame instabilities or sudden opening of avent. The later may cause the waves to reflect against solid surfaces and repeatedly pass through the flame zone, exacerbating the effect.

A great deal of what has been described above holds true for combustible aerosol–oxidiser mixtures (such as dusts in air and fuel sprays) as well. One fundamental difference is that the behaviour of those mixtures cannot be studied in a stagnant flow field; turbulence to some extent is essential to maintain the aerosol condition. Because of its distinct characteristics, dust explosion is treated below as a category of its own.

6.5.4. Dust explosion (DE)

When combustible, dust-sized particles of a flammable material get (accidentally) suspended in air and the resulting dust cloud catches fire, a dust explosion may result. Ignition may be by a variety of sources such as open flame, mechanical and electrical sparks, friction or other type of heating, such as by an unprotected lamp or even by self-heating of the dust settled in a layer in e.g. a dryer. The reactivity of a dust increases, up to a limit, with the decrease in particle size, increase in surface area to mass ratio, decrease in moisture content, and increase in combustion energy. Explosion indicators are of the same order of magnitude as those of explosive gases, except that the upper explosion limit may be much higher. As in case of a gas explosion, dust explosions generally occur within confined or partially confined space but can do so, albeit rarely, in relatively open spaces as well [6,29].

Therefore dust explosions (DE) can also be sub-classified as:

(a) DE occurring in a confined and vented space such as machinery for diminution, mixing, drying, granulating, separating, filtering, transportation piping, Jacob ladders or storage (silo).
(b) DE occurring in hollow semi-confinements (such as empty spaces in a building, or in corridors as in coal mines and conveyor belts).
(c) DE occurring in unconfined space when the space contains sufficient dust both settled and dispersed in the air and such obstructions to the flow that the velocity of the flame remains sufficiently high to feed itself by whirling up further dust.

An additional hazard is associated with the layers of combustible dust lying around on floors, equipment, etc. It may whirl up when a weak local blast occurs by a starting dust explosion. The explosion then progresses by the whirled up dust and so feeds itself. Also dust explosion flames can accelerate in sufficient confinement and over sufficient run-up distance and such acceleration can eventually lead to detonation. Metal dust explosions are renowned by their violence and high temperatures causing intense heat radiation. Depending on the type of metal and oxygen content in the mixture, self-ignition may also occur. Protection from such eventuality may be ensured by compartmentalization which may restrict the flame from passing on other parts, and by extinguishing, venting, etc. [6,35].

6.5.5. Condensed phase explosion

Certain industrial liquid or solid products of high energy density – also called energetic materials' – on catching fire, can generate pressure waves of energy and speed high enough to cause an explosion even in an unconfined space. But, as with VCE and dust explosion, usually confinement enhances the ferocity and damage potential of condensed phase explosions. Ammonium nitrate, sodium chlorate, organic peroxides are among the industrial chemicals associated with condensed phase explosions. Their reactions are similar but usually less energetic and less complete than of high explosives, propellants and pyrotechnics. Because of the lower reactivity of many of these industrial chemicals an initiation by a point source or a fire at first results in deflagration. Given sufficient mass and confinement this can then turn into a detonation. Due to the presence of impurities/contaminants or moisture some of the condensed phase explosions may be restricted to a deflagration.

In case of substances with low energy density, point initiation must be strong enough to initiate reactions to such an extent that it results in sustained, stable detonation. Initiation over a larger surface area, for example with an explosive pellet, generally results in a stable propagating reaction. Part of the energy in the slow reacting substances, in comparison to high explosives, is released too far behind the shock front to enable sustaining of the detonation wave front. Small grain size, edgy shape, catalysing traces, large porosity, etc., enhance detonability.

Some low-reactive substances only explode when under confinement in a steel vessel or otherwise. There is a run-away reaction following a pre-heating process; it then builds up to a deflagration.

A special but rare form of explosion is *low-velocity-detonation* in which a shock wave generated by a reaction in a substance propagates ahead of the reaction zone in a contact material possessing a higher sound velocity such as steel. Pressure waves radiating back in the substance pre-heat and so a higher propagation rate of the zone occurs than would have without the contact material. Some nitro-alkanes and -aromats are examples.

6.5.6. Runaway reaction (reactor explosion) with or without phase transition

A runaway reaction is a chemical reaction in a gas, liquid or solid material which accelerates out of control as a result of the heat of reaction or decomposition exceeding the cooling capacity of the containing vessel [2,36] or by the multiplying effect of radical reactions. Hence initially it is a form of exothermal or of radical explosion. It may be clarified that radical decomposition mechanisms may often play a role but it need not be the production of net more radicals as in cool flames or in decomposing organic peroxides. Had runaway reactions been occurring throughout the substance in a homogeneous fashion, and everywhere at the same rate, their description would have been relatively simple. In practice, due to physical causes (heat loss, convection) and chemical ones (local concentration gradients, catalysing products) in most cases the situation is far from homogeneous. The pressure increases due to production of heat, formation of non-condensable gases, and/or an increasing vapour pressure of liquid components. In a final stage (cook-off) the substance may deflagrate with a reaction zone starting at a hot spot and propagating through an already reacting substance. In rare cases the process may develop into a detonation. Near the end of the explosive run-away process, the situation is thus often complex and unclear as regards the intensity of the explosion.

This process can only be controlled by a properly dimensioned pressure relief device, like a rupture disc or pressure relief valve. If these devices malfunction or if the reaction is faster than foreseen, the pressure may continue to rise until the vessel fails [1,2,36].

In some cases the contents of the vessel may decompose within milliseconds and the reaction of the entire contents may even be completed before the vessel bursts open [37]. The explosions they cause are more like explosions from high explosives than like pressure vessel bursts.

An exothermic runaway reaction can render the reactants superheated and if the pressure build-up exceeds the tolerance level of the process vessel, the resultant explosion may be similar to a BLEVE [4]. But we would distinguish such explosions from BLEVE on the following counts:

(a) The energy involved in the build up of temperature and pressure came from chemical reactions.

Table 1
Illustrative examples of explosions belonging to the types specified in the proposed classification.

Type of explosion	Event in brief	Reference
Compressed gas/vapour explosion (CG/VE)	1. Natchitoches, Louisiana, 1965: An explosion occurred of a high pressure natural gas pipeline caused by the high-pressure gas, there being no evidence of combustion in the pipeline. The resultant blowout produced a crater 10 ft deep. The subsequent vapour cloud explosion, devastated an area of 13.8 acres, killing 17 persons.	[41]
	2. Worms, Germany, 1988: Carbon dioxide escaping from the relief valve of an excessively pressurized cryogenic storage tank attained critical point and sealed the relief valve by forming dry ice. The resulting blockage of the vent led to an explosion which was so severe that fragments of the tank weighing over 100 kg were hurled upto 500 m.	[42]
Boiling liquid expanding vapour explosion (BLEVE)	1. Feyzin, France, 1966: A 1200 m^3 sphere filled with propane accidentally leaked, caused a pool fire which in turn superheated the tank. It went through a BLEVE. Its flying fragments caused other tanks to suffer BLEVE.	[1,2]
	2. Mexico City, 1984: a flash fire caused by accidental leak of LPG in the San Juan Ixhaautepec refinery and filling station made one of the tanks suffer a BLEVE. The resultant fragments, wrapped in burning propane, precipitated several other BLEVES. The fires spread to nearby housing. About 500 people were killed.	[4]
Vapour cloud explosion	1. Flixborough, UK, 1974: One of the most extensively documented of all vapour cloud explosions occurred when cyclohexane was accidentally released from a ruptured bypass in a reactor train and found a source of ignition. The resulting blast and the fires destroyed not only the cyclohexane plant but several other plants, too.	[1,2]
	2. Ufa, USSR, 1989: A leak in the Trans-Siberian LPG pipeline, which had gone undetected for several hours, formed a vapour cloud which extended five miles in one direction. Two trains, travelling in opposite direction in railway lines passing nearby, provided the spark that led to a massive vapour cloud explosion which killed 462 persons.	[2,42]
Aerosol or mist explosion	1. Phillipsburgh, NJ, USA, 1959: Oil mist in a compressor test facility exploded, killing 6 and injuring 30.	[29]
	2. Sirdal, Norway, 1973: Oil mist explosion in a transformer room killed 3 and injured several others.	[29]
Gas explosion	1. Newham, East London, 1968: A gas explosion on the 18th floor of a 23 storey high-rise pushed out the load bearing side wall of a floor causing a progressive collapse of the entire corner of the block.	[1,2]
	2. Netherlands, 2003: An explosion in a gas-fired furnace at a melamine plant killed 3. The explosion occurred at a start-up after a maintenance operation.	[43]
Dust explosion	1. Harbin, People's Republic of China, 1987: Electrostatic spark in one of the seven linen dust collecting units led to a massive explosion which destroyed all seven units and most of the rest of the plant; killing 58 and injuring 177.	[6]
	2. Kinston, NC, USA: a cloud of polyethylene dust in a pharmaceutical factory exploded, killing 6 and injuring 38.	[6]
Condensed phase explosion	1. Toulouse, France, 2001: A storage facility that held 200–300 tonnes of ammonium nitrate suffered a massive condensed phase explosion that created a 7 m deep crater, killed 29 and injured 2500.	[2]
	2. Ryongchon, North Korea, 2004: Possibly an electric short-circuit triggered a condensed phase explosion in a goods train loaded with ammonium nitrate. The impact of resultant blast covered a radius of ~2 km, generating a 15 m deep crater and destroying 8100 horses. Over 150 persons died and 1300 were injured.	[43]
Radical explosion	1. Gifu, Japan, 1971: A vinyl acetate monomer, which was erroneously stored in a 1 m^3 drum without adding a polymerization inhibitor, went through spontaneous polymerization causing build up of temperature and pressure. Eventually there was an explosion and concomitant fire which caused extensive damage.	[44]
	2. During start-up of a chlorination plant some problems arose and the start-up was terminated after chlorine and an organic material had been fed to the reactor. As no clear-cut purging procedure for this situation had been advised, after handling the problem the start-up was repeated. A short while later the reactor exploded.	[45]
Runaway reaction	1. Stanlow, Cheshire, 1990: A 15 m^3 batch reactor at a Shell plant set to produce 2,4-difluoro-aniline had a runaway reaction leading to an explosion so severe that the vessel body unwrapped into a flat plate. The cover was hurled up 200 m and other missiles reached up to 500 m. The entire plant was devastated and nearby buildings also suffered structural damage.	[2]
	2. Institute, WV, USA, 2008: Runaway reaction created extremely high temperature and pressure in a vessel at a Bayer factory, causing an explosion which demolished process equipment and ruptured pipes and conduits. Two operators were killed and eight suffered from toxic inhalation.	[46]
Rapid phase transition	The phenomenon has been observed in spill experiments with LNG on water such as in the Coyote test series conducted at Lawrence Livermore National Laboratory and Naval Weapons Center at China Lake, USA in 1981.	[47]

(b) The contents were not in the pressure-liquefied form from the outset.

(c) The explosion was not caused by the accidental weakening of the pressure vessel but rather from the excessive pressure generated due to exothermic runaway reactions.

The hot reaction products may also, after mixing with air, self-ignite and cause a VCE outside the reactor.

A great deal of work is continued to be done on the sizing and design of pressure relief devices for reactors prone to runaway reactions with liquid reactants, which in the final stage to explosion form two-phase systems [2,31]. These systems are classified as:

(a) 'gassy' when the gas phase consists of non-condensable reaction products,

(b) 'tempered' if the mixture contains high-volatile components which during the last stages evaporate and therefore cool, and

(c) hybrid systems.

Noteworthy among these include the efforts of the Design Institute for Emergency Relief System, (DIERS), founded in 1976 by AIChE, USA, which undertook a major project on reactor two-phase venting during the mid-1980s. Extensive investigations on the behaviour of different reaction systems, fluid flow through the vent, vapour disengagement in the reaction vessel, etc., were carried out [38,39]. The study identified four factors which influence the overall behaviour of the venting system: (a) reaction regime, (b) vapour disengagement, (c) fluid viscosity, and (d) vent line length.

Vent sizing is based on a number of models developed for the various systems [2,39]. Some companies have integrated DIERS methods with other methods [37]. Guidelines on venting of reactors have also been introduced by others, for example CCPS [40].

7. Gist of the new classification

The gist of the proposed new classification is presented in Fig. 3. Illustrative examples of past accidents, which fit in different categories, are presented in Table 1.

Some of the well-known terms like 'dust explosion' and 'gas explosion' featuring in the proposal classification are not quite precise. Yet they have been retained because the terms have been in vogue since long and are now firmly entrenched in the process safety lexicon. Moreover, unlike some other terms which are used by different authors in different sense to denote a same type of explosion, these terms connotate phenomena of which interpretation is fairly consistent across different users.

Perhaps, in due course, terms like 'dust explosion' – which, to the uninitiated, would imply that it involves exploding dust rather than what it really is, *viz* a combustible dust reacting explosively with the surrounding oxidant – be substituted with more correct and precise terms. Likewise a better name for gas explosion – which otherwise may be similarly misleading to a lay person – may be found. But it has to be an initiative to be taken globally by a consortium of a large number of representative bodies. Till such time it happens the systematization proposed here can be used as a starting point to set that process of a consensus-based systematization in motion. The relative degree of specificity, hopefully achieved by the present attempt, is also bolstered by the fact that the models which predict the causes and effects of explosions as classified now are clearly distinct from each other. Moreover the measures needed to prevent these different types of accidents, or to cushion their impacts if the accidents do occur, are distinct from each other due partly to the different aggregation states and partly to the different degrees of confinement.

There may be situations wherein corrosion may gradually weaken some part of a vessel containing a pressure liquefied gas till, at one point, the vessel suffers a BLEVE. A question may arise whether to call it a chemical explosion or a physical explosion? Likewise, if a vessel weakened at some part on account of creep or fatigue explodes due to a runaway reaction, should it be classified as a physical explosion?

The classification presented by us is based on the source of energy that is involved in an explosion and is independent of the factors which may make a process unit vulnerable to an accident. By this criterion the first of the abovementioned instances will be a physical explosion and the second one a chemical explosion.

Acknowledgements

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