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Protection Systems for Tanks Containing Hazardous Materials Exposed to Fire

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The catastrophic failure of a tank containing a pressure liquefied gas often gives rise to a physical explosion with serious consequences for the possibly exposed people and structures. In fact, the liquid is at a temperature higher than its boiling temperature at atmospheric pressure, and, once released, it will instantaneously vaporize, with the generation of a shock wave.
If the involved chemical is also hazardous (flammable or toxic), additional consequences are also expected (fires or toxic cloud dispersion), so that it is important to prevent the occurrence of this phenomenon as far as possible.
Few studies are available in the literature to analyze the dynamics of this scenario, and, given the complexity of setting up experimental facilities, mainly theoretical approaches have been adopted, though some useful experimental results are also reported. The models proposed over the years allow to calculating the trend of the main parameters involved in the accident, but, in most cases, reference to a bare vessel has been made, while less attention has been devoted to assess the influence of protection systems, such as thermal insulation or pressure relief devices.
In the present paper, a number of reference scenarios have been simulated involving both unprotected and protected systems, and the results have been analyzed and compared, to identify a proper strategy capable of significantly reducing the probability of failure of the tank.

1. Introduction

The instantaneous vaporization of a gas initially stored as a pressurized liquid at a temperature higher than its normal boiling temperature (at ambient pressure) and successively released in the open air, represents one of the most dangerous accidents which can occur in the process industry, and to highlight this it has been given a specific name: Boiling-Liquid Expanding-Vapour Explosion (BLEVE). The rapid expansion of the produced vapour will generate a shock wave which can cause significant damages to the surrounding environment (people, structures, etc.), and in some cases can generate an even more dangerous domino sequence. In particular, when the released material is flammable, its subsequent ignition with the generation of a fireball is also likely; the latter scenario becomes highly likely when the failure of the containment system is caused by the exposure to a strong heat source, like an external fire. Actually, different causes may lead to the failure of the tank: chemical corrosion of the vessel material, mechanical or weld defects, impacts by external objects, etc. However, in practice this accident is frequently associated with the exposure of the vessel to a strong external heat source, such as an external fire, and consequently a number of studies have been produced over the years to investigate the dynamics of this accident.
A detailed knowledge of the phenomena occurring before the failure of the vessel would actually allow to better predicting the evolution of a given accidental scenario and, even more important, to avoid the occurrence of the conditions which might lead to that failure.
During the 1970s and 1980s a number of experimental works were published about the behaviour of vessels containing pressure liquefied gases (mainly propane) exposed to an external fire (Anderson et al., 1974; Aydemir et al., 1988; Droste and Shoen, 1988; Moodie et al., 1988). Additional studies have been published more recently addressing further issues such as the scale effects on the response of the tank (Birk, 1995), the

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effect of thermal stratification on the consequences of the BLEVE (Birk and Cunningham, 1996), the effect of localized partial engulfment, in contrast with a full engulfment (Birk et al., 2006), the extent of thermal stratification as a function of the LPG level inside the tank and of the received heat flux (Lin et al., 2010); in the latter case, it is worth noting, however, that much lower heat flux values were adopted (4 to 10 kW/m^2) compared to the values more commonly encountered in real accidents (several tens of kW/m^2).
Unfortunately, though their number is slowly increasing and they represent a fundamental way to investigate the problem, the experimental results reported in the literature still need to be integrated with alternative approaches. In fact, given the complexity and the costs of the experimental tests, which necessarily limit their number, they not always allow to deriving clear and thorough conclusions about the mechanisms involved: in some cases, the results are in contrast with each other, in other cases the tests do not cover a sufficiently large range of variability of the involved parameters, and so on. Therefore, the theoretical analysis of this accident scenario represents a necessary step and several analyses have been published so far. In some cases they are simple models requiring very limited calculation burden and providing the time dependency of some of the main characteristic parameters, such as the average liquid and vapour temperatures, the internal pressure, the trend of the pressure relief valve release (when present), and of the residual liquid inside the tank, and so on (Hadjisophocleous et al., 1990; Chen and Lin, 1999; Salzano et al., 2003; Gong et al., 2004; Bubbico and Mazzarotta, 2018). In other cases these are much more accurate, but time-consuming, models usually based on Computational Fluid Dynamics (CFD) (D'Aulisa et al., 2014; Landucci et al., 2016).
Independently of the adopted approach, whether experimental or theoretical, most of the tests reported in the above analyses adopted a bare tank, with no protection systems, except for, but not always, a pressure relief valve. However, given the possibility of delaying, or hopefully avoiding, the catastrophic failure of the tank, attention has also been sometimes devoted to other possible protection/mitigation methods: Townsend et al. (1974) (who focused on a rail tank car) and Droste and Shoen (1988), compared the behaviour of uninsulated and thermally protected propane tanks; Shoen and Droste (1988) investigated the use of water spray systems to mitigate the effect of external fires on LPG tanks; more recently, Shebeko et al. (1996) analyzed the influence of relief valves from a theoretical point of view, while further experimental data have been produced and compared with either simplified (Shebeko et al., 2000) or CFD (Landucci et al., 2009) theoretical models.
In the present paper, the transient behaviour of a propane tank exposed to an external pool fire under different configurations has been studied using a simplified lumped-parameters approach (SuperChems Expert v.6.20 by ioMosaic, USA). It is recognized in the literature that for a range of conditions and purposes, simplified models are adequate and no significant improvement is obtained by using more time consuming methods (Beynon et al., 1988; Hadjisophocleous et al., 1990; Lin et al., 2010), therefore, since the focus here was on the assessment of the protection efficacy of the mitigation systems rather than on a detailed representation of a single scenario, this approach has been deemed here adequate.
The model has been first validated against literature data, both for unprotected and protected tank configurations, and then applied to a specific study case. The time evolution of the main parameters obtained by adopting some protective measures (a pressure safety valve and a thermal insulation coating) have been compared with those relative to a completely unprotected tank. The differences in the tank response were remarkable and the efficacy of the protective systems, in particular for the thermal insulation, has been widely demonstrated. However, for the sake of completeness and accuracy, it must be stressed that for a detailed analysis of a particular case or for cases where a simplified model is not applicable, a more accurate approach (e.g. CFD) is recommended.

2. Model validation

Before being applied to the study case, the model has been validated (Biggi, 2011) against literature experimental data, and only a few representative comparisons are reported here.

2.1 Partially protected vessel

In Table 1, the calculated values of the time for pressure relief valve (PRV) first opening and of the tank time to failure (ttf) are compared with the data reported by Droste and Schoen (1988). They were derived for propane tanks of 4.85 m^3 (4.3 m length and 1.25 m diameter), 50 % full, equipped with a 1" PRV, set at 15.6 bar, and exposed to an external pool fire, but with no other protection means. Some conditions (initial conditions, tank engulfment, PRV operation) slightly changed from test to test and this was as far as possible taken into consideration in the simulations (see Table 1). Despite an uncertainty about the actual heat flux received during the experimentation (the tank was not always actually fully engulfed), the comparison is quite good, with a maximum error of 15 %.

Table 1: Comparison between experimental (Droste and Schoen, 1988) and calculated values for an unprotected (no thermal coating) vessel

Test no.	Initial tank temperature [°C]	Initial tank pressure [bar]	PRV opening pressure [bar]	Experimental t_{PRV} [s]	Calculated t_{PRV} [s]	Experimental ttf [s]	Calculated ttf [s]
1	10	5.5	16.4	340	336	720	749
2	37	13.5	17.3	100	97	440	508
3	26	9.8	16.0	150	172	540	586

Of course, up until the first opening of the pressure relief valve, such a tank behaves like a completely unprotected tank.

2.2 Protected vessel

Droste and Schoen (1988) also carried out two additional runs with the same tank as shown above, but covered with a layer of mineral wool in order to check the possibility of extending the capability of the tank to withstand the thermal load up to 90 minutes. With an initial tank pressure of 9 bar and a fill level of 20%, and adopting a coating thickness of 100 mm, the PRV first opened after 53 minutes, and the tank pressure never exceeded 15 bar for the whole test duration. The comparison with the simulation is reported in Table 2, with an assumed input heat flux of 100 kW/m^2 and an average thermal conductivity for mineral wool of 0.0875 W/mK:

Table 2: Comparison between experimental (Droste and Schoen, 1988) and calculated values for a thermally insulated vessel

Initial tank fill level [°C]	Initial tank pressure [bar]	PRV opening pressure [bar]	Experimental t_{PRV} [s]	Calculated t_{PRV} [s]
	9	14.8	3180	3182

Further comparisons have been carried out against additional experimental data (Townsend et al., 1974; Moodie et al., 1988) but they are not shown here for brevity reasons.

3. Results and discussion

In order to assess the efficiency of possible protection systems on a vessel containing propane, of size comparable with those actually used for road transportation, the model has been applied under the following different conditions:

1. a bare vessel with no protection systems (unprotected);
2. a vessel provided with a pressure relief valve;
3. a vessel provided with thermal insulation and pressure relief valve (fully protected).

In all cases the vessel volume was 56 m^3 (2.3 m diameter, 13.5 m length and wall thickness of 12.7 mm) with 50% fill level. It was assumed to be fully engulfed in a hydrocarbon pool fire generating an average heat flux of 130 kW/m^2 and the initial temperature of the propane was 10 °C, with a corresponding initial pressure of 5.5 bar (P_s@10 °C).

3.1 Unprotected vessel

As expected, in the case of an unprotected vessel, both the internal pressure and temperature will quickly rise with time, with the failure of the vessel expected to occur in less than 10 minutes from the beginning of the exposure to the fire. The pressure increase is represented in Figure 1, while the final temperature and pressure are reported in Table 3, along with the results relative to the other conditions simulated and other significant data (including the initial conditions).

3.2 Vessel provided with PRV

The second vessel configuration which has been investigated, assumed a tank provided with a pressure relief valve operating in two-phase (liquid-vapour) service: the discharge section was 4.12 10^{-3} m^2, the discharge coefficient was assumed 0.975 and the set pressure 16 bar (API standard). As can be seen from Figure 1, the relief through the PRV allowed to limit the internal pressure increase up to a maximum of about 25 bar, with the PRV opening for the first time after about 5 minutes from the beginning of the fire exposure (Table 3). The

release through the valve also caused a continuous decrease of propane mass within the tank (data not shown), so that after about 10 minutes from the start (634 s), no liquid remained in the vessel; this is also represented in Figure 1 by the slope change in the pressure profile, when a marked and continuous decrease in the internal pressure starts.
Due to the additional exposure to the fire, the tank was estimated to fail after about 15 minutes of the simulation time.

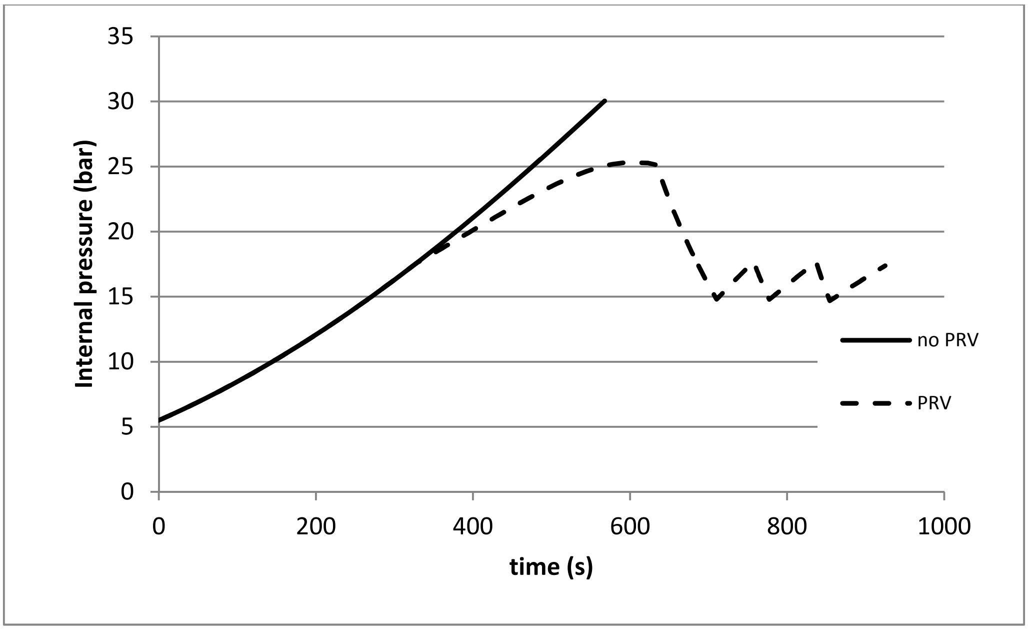

Figure 1: Internal pressure trend for an unprotected vessel and for the same vessel provided with a PRV.

Table 3: Initial conditions and main results for the three simulated vessel configurations: unprotected, PRV-provided, and vessel with both PRV and thermal insulation ("fully protected").

Initial conditions and results	Unprotected	PRV	Full protection
Propane initial pressure, (bar)	5.5	5.5	5.5
Heat flux, (kW/m^2)	130	130	130
Heat transfer coefficient for thermal insulation, (W/m^2K)	-	-	2.67
Simulation time, (min)	110	110	110
PRV first opening time t_{PRV}, (s)	-	329	-
Time to failure, (s)	568	925	-
Propane final pressure, (bar)	30.04	17.38	14.08
Propane final temperature, (K)	353.30	474.35	317.42
Final fill level, (%)	62	-	53.97

It is clear that the adoption of the PRV leads to a number of advantages:

- the vessel is able to withstand the thermal load for a longer time (more than 15 minutes, versus 10 minutes in the case of an unprotected vessel);
- the vessel pressure at the time of the failure is much lower than in the case of an unprotected tank. This will correspond to a lower explosion energy during failure;
- the lack of liquid phase at the time of failure also significantly reduces the amount of energy available after the failure, both for the BLEVE (i.e. for the physical explosion of the released liquid) (Birk, 1995) and for a possible fireball following the ignition of the released material.

On the other hand, it must be observed that, even though the reduced amount of material present in the tank at the moment of the failure will generate more limited consequences during or after the catastrophic release, that amount has been previously released in the environment via the PRV, so that it can be involved in some other dangerous events such as a jet fire (in case of an immediate ignition), a flash fire or, under particular conditions, a vapor cloud explosion (the two latter events occurring in case of a delayed ignition). Therefore, for the sake of completeness, it must be observed that the probability of occurrence of the various dangerous events should also be taken into consideration when evaluating the suitability of protection systems.

3.3 Vessel provided with PRV and insulation

Besides the PRV already adopted in the previous configuration, in this case a thermal insulation composed of 10 mm of an intumescent coating with 0.066 W/mK thermal conductivity and an expansion factor of 2.5 was considered. It was assumed that the final thickness of 25 mm was reached instantaneously at the beginning of the fire exposure. Given the specific geometrical configuration, an overall heat transfer coefficient of 2.67 W/m^2K was calculated, and the simulation time was set at 110 min as in all other cases. With reference to this latter parameter, it is worth noting that the average response time for Italian firefighters is about 15 minutes, so that, if the tank were able to withstand for the assumed simulation time interval, there would be enough time for emergency responders to efficiently carry out all the emergency activities such as pool fire fighting, population assistance, etc. In conclusion, a duration of 110 minutes can be considered with confidence a conservative approach.

All other parameters relative to the simulated scenario, as well as the results of the calculations, are reported in Table 3.

As can be seen from Figure 2, due to the reduced heat input to the tank, the internal pressure of the vessel continuously, but slowly, increases with time, reaching a value of about 14 bar at the end of the simulation time, i.e. still below the set pressure of the valve, which therefore never activates during the accident. It is thus apparent the remarkably high efficiency of the thermal coating in preventing the onset of dangerous conditions, compared to both the vessel with PRV only and, more obviously, with the unprotected one.

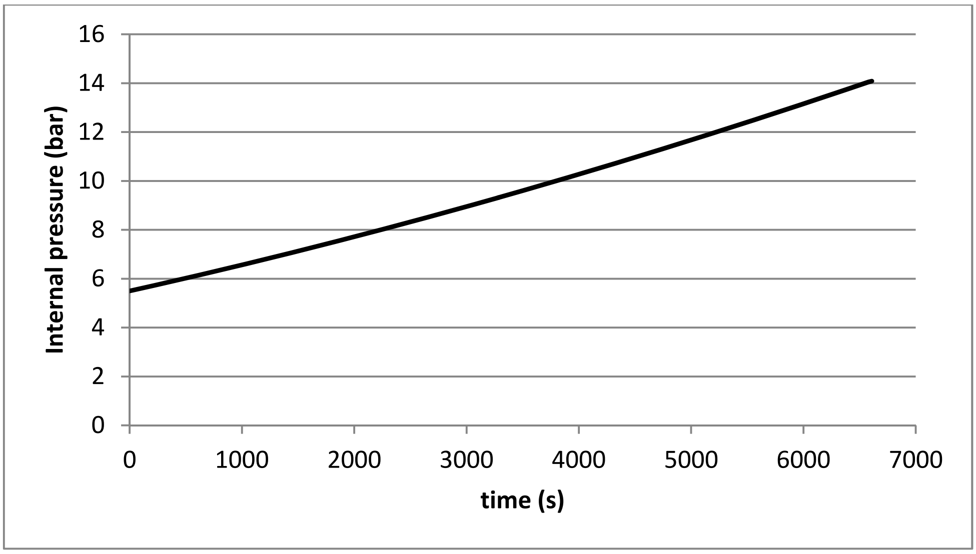

Figure 2: Internal pressure trend for a vessel provided with PRV and protected with thermal coating.

4. Conclusions

In the present paper the behaviour of a tank containing propane and exposed to an external fire has been investigated under different configurations: without any type of protection, with a pressure relief valve, and with both a fire-proof insulation and a PRV. Even though with a simplified approach, it was demonstrated that the adoption of protection systems can significantly delay the onset of dangerous conditions or the complete failure of the tank. In particular, the use of a proper thickness of insulating material can markedly reduce the heat input rate with respect to a completely unprotected vessel and thus allow the vessel to withstand the action of the fire for a much longer time with a much slower increase of the internal pressure.

Of course, by increasing the coating thickness it is possible to further reduce the heat flow into the vessel and consequently the pressure increase, until possibly making the use of a PRV unnecessary; this might be a further significant improvement, since the release through the valve, though it allows to keep the internal pressure lower, might give rise to other hazards in the environment, associated with the air dispersion of a flammable gas cloud.

At the moment, the regulations in force concerning the transportation of hazardous materials do not impose the adoption of specific measures. In this regard, it is believed that the presented results might prompt further attention to the problem, since it was shown that the thermal response of a hazardous materials tank exposed to a fire can be significantly improved, extending its resistance up to a couple of hours, and thus increasing the personal safety of the emergency responders and allowing them to operate in a much more efficient way.

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