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Rigorous Simulation of LPG Releases from Accidental Leaks

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The accidental release of LPG from trucks or other containers is a dangerous event due to the subsequent dispersion followed by possible fires and explosions. Unfortunately this scenario is that of the accident occurred at the Viareggio railway station on the night of June, 29 2009, where the released LPG caused a large number of fatalities.Some simulations of the event, as proposed in published papers, assume a liquid release for the calculation of the discharge time.
Since the LPG is at saturated conditions, it is subject to a flash during discharge as soon as the pressure is lowered; so the real event is more complexas the LPG discharge moves from mixed phase to vapor phase.This article presents rigorous simulations of the event focusing on the discharge time period required to empty the damaged vessel.The simulation uses 'state of the art' equations of state to model the thermodynamic behaviour of the fluid during the release. Vapor generation due to depressurization and related temperature effects are fully modelled.

1. Introduction

The accidental release of LPG from trucks or other containers is a dangerous event due to the subsequent dispersion followed by fires and explosions. These effects are favoured by the large flammability range of this fluid. The release of LPG can be followed by pool boiling fires, cloud explosion and eventually BLEVE explosions.Unfortunately a part of this scenario is that of the accident occurred at the Viareggio on June, 2009, where the released LPG caused a large number of fatalities.
For the simulation of events following the release of LPG, the instantaneous discharge flowrate and the total time required to empty the vessel is obviously a key parameter.Some simulations of the event, as proposed in published papers, assume a liquid release for the calculation of the discharge time. This approach is quite simplified and with this hypothesis a very short discharge time interval is calculated.
This article focus on the simulation of the LPG discharge with the objective of the rigorous evaluation, from a thermodynamic point of view, of the discharge time required to empty the damaged vessel. All the possible following events are not considered and are not simulated in this article.The simulation uses 'state of the art' equations of state to model the thermodynamic behavior of the fluid during the discharge. Since the initial vessel content is LPG at saturated conditions, the fluid will flash as soon as the pressure is lowered, so the vapor generation and related temperature and pressure effects are fully modelled. Flow discharge is critical and due to the two-phases the fluid velocity is lower than experienced for either gas or liquid as separate phase.The discharge of the LPG caused by leaks of its container is not different from that caused by a pressure relief system (pressure safety valve or safety disk).Fast depressurization of vessels, by means of fluid discharge to the blow-down system or atmosphere, is a common way of reducing the consequences associated with pressure increases.Calculation has been performed using rigorous thermodynamic models from the traditional

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cubic equations of state SRK (Soave, 1972) or PR (Peng and Robinson, 1976) for vapor-liquid equilibriaand the LK (Lee and Kesler, 1975) model for enthalpy, entropy and density calculations.

2. Problem Definition

Basic data for this study are taken from the work developed by Brambilla et al.(2010), that analyses in detail the Viareggio incident. In this paper the LPG carrier was considered a horizontal cylinder 15.95 m long with a diameter of 3.04 m. The total LPG content was assumed to be 45,000 kg at 15 bar. The leak caused by the incident was assumed to have a section of 100 cm^2 located at the bottom part of the cylindrical vessel; a discharge coefficient C_d of 0.6 was used.Due to the leak position it is assumed that the release was liquid and its mass flowrate was calculated using the following relation.

$$\frac{dm}{dt} = \rho A C_d \sqrt{(P - P_a)\rho + gh} \tag{1}$$

In this equation, ρ is the fluid density, A the leak surface, $C_d$the discharge coefficient, P the vessel internal pressure, $P_a$the atmospheric pressure, while the product gh represents the hydrostatic pressure due to liquid level. This approach assumes that in the discharging process the LPG remains in a liquid state, and this simplified approach is justified in the economy of the Brambilla's approach, where the main interested was the effects of the LPG dispersion in the neighborhood and the subsequent fire effects from pool fire. On the basis of this approach, the discharge of 45,000kg of LPG is completed in about 3 min 13 s (193 s) followed by the emission of the remaining gas contained in the vessel.From the thermodynamic point of view this approach is to be considered strongly simplified. One can observe that due to the sudden pressure decrease from the tank through the hole the saturated LPG will immediately reach the bubble point and a partial evaporation should be expected.The effect of a critical discharge due to the immediate formation of gas bubble producing a two-phase discharge through the hole is the most important effect that contribute to a lower discharge flux.In the following paragraphs, we will not consider any more the Viareggio incident scenario and present a rigorous dynamic simulation of the discharge of GPL from a leaked horizontal vessel of the same size and with the same content.A very different scenario would have occurred if the hole is located on the upper part of the vessel. In this case the discharged mass would be mainly vapor and the discharge time sensibly higher.

3. Homogeneous Two-Phase models and Critical Flow Calculations

The discharge of fluid from a leak is equivalent to the relief of fluid from a safety disk installed to provide protection from overpressure phenomena.When a compressible fluid like a gas or a vapor is expanded across a nozzle, the velocity increases as the pressure of the fluid decreases to reach the down-stream pressure. For a given fluid and a set of upstream conditions (T_0 and P_0) the mass flowrate increases until a limit speed value is reached. It can be shown that this limit velocity corresponds to the velocity of the sound at the point. The flowrate determined by this limit velocity is the 'critical flowrate' and the ratio of the pressure at the nozzle exit at sonic velocity P_{cf} to the inlet pressure P_0 is the critical pressure ratio.It should be mentioned that for a gas, when ideal behaviour is assumed, the critical flow pressure ratio $R_{cp}$is calculated as:

$$R_{cp} = \left[\frac{2}{k+1}\right]^{\frac{k}{k-1}} \tag{2}$$

where k is the ratio of specific heats. This value which is near 0.5 represents the separation between the critical and subcritical flow and is often used as a 'rule of thumb'.When two phase flow is considered various models can be developed.An American Petroleum Institutestandard procedure RP 520 (API, 2000) proposes the application of a calculation modelbased on the 'Omega method' that was

originally proposed by Leung (1995).The method may be used for sizing pressure relief valves for either flashing or non-flashing flow.
To avoid limitations related to the API and Omega methods, a more general algorithm for the calculation of the maximum allowable flowrate discharged through an orifice for a given upstream conditions can be developed. This method (Raimondi, 2007) is fundamentally based on the rigorous evaluation of the sonic velocity: the limit critical pressure is calculated by finding the pressure at which the fluid velocity takes a value equal to the local sonic velocity.It will be referenced as **"Flowmx method"** in the following chapters.
Inlet conditions defined by fluid pressure $\mathbf{P_0}$, temperature $\mathbf{T_0}$, total composition **z**, molecular weight $\mathbf{M_w}$, enthalpy$\mathbf{H_0(T_0,P_0,z)}$, entropy $\mathbf{S_0(T_0,P_0,z)}$and by initial fluid velocity$\mathbf{v_0}$.The flowing fluid is characterized by its velocity**v**., enthalpy**H(T,P,z)**, entropy **S(T,P,z)** and by the local sonic velocity**c=c(T,P,z**). The critical flow condition is therefore defined by the following system of equations written for a unit mass of fluid:

$$H_o(P_0,T_0,\mathbf{z})/M_w = H(P,T,\mathbf{z})/M_w + v^2/2 \tag{3}$$

$$S_o(P_0,T_0,\mathbf{z}) = S(P,T,\mathbf{z}) \tag{4}$$

$$v \le c(P,T,\mathbf{z}) \tag{5}$$

Equation (5) sets the limit of the fluid velocity as lower or equal to the sonic velocity defined by:

$$c = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} \tag{6}$$

The sonic velocity is calculated using the same equations of state that are applied for the calculation of thermodynamic properties.

4. Problem Simulation

We have simulated the LPG discharge by applying the methods described in the previous chapter 3. Calculations have been performed using a process simulator XPSIM (2011), developed by the author. Two different scenarios are analyzed. The first considers a hole in the bottom part of the vessel whereas the second considers the same hole located on the top of the vessel.Obviously in the first case the relief will be preferably liquid followed by vapor relief when all the liquid part will be completely discharged. In the second case the fluid is discharged as vapor phase.The LPG composition used throughout the simulation is reported in Table 1.

Table 1: LPG composition

Component	Molar Composition, %
Ethane	2.25
Propane	32.70
n-Butane	64.21
n-Pentane	0.84

To fully understand the following diagrams it is important to realize the initial thermodynamic conditions of the fluid. Since it is liquid and does not entirely fill the vessel, the overhead empty part will be fill by vapor in equilibrium and its pressure is a unique function of the temperature. This relation is presented on Figure. 1.From this figure one can easily realize that LPG at a pressure of 15 bar has a temperature slightly over 70 °C. We can first compare the initial difference for the flowrate between a liquid, or more exactly, sub-cooled liquid discharge with respect to a saturated liquid discharge. The following Table 2

shows the results of the calculated flow rate for a sub-cooled LPG (case 1) and for a saturated LPG (case 2 and 3) from a leak of 100 m^2 with a $C_d$value of 0.6.
Cases 2 and 3 differ in the method used: case 2 is calculated using the 'Flowmx method' while case 3 is simulated according to the Omega method. What can be remarked immediately is that for saturated LPG the discharge flow rate is about one third of the value calculated when a liquid discharge is assumed.The first simulation is developed by assuming a hole located in the bottom part of the vessel, so that the flashing liquid phase is discharged first. Results for this scenario are summarized by the following Figures 2 and 3. They show the change of main process (pressure, temperature, mass content and relief flowrate) with respect to time.

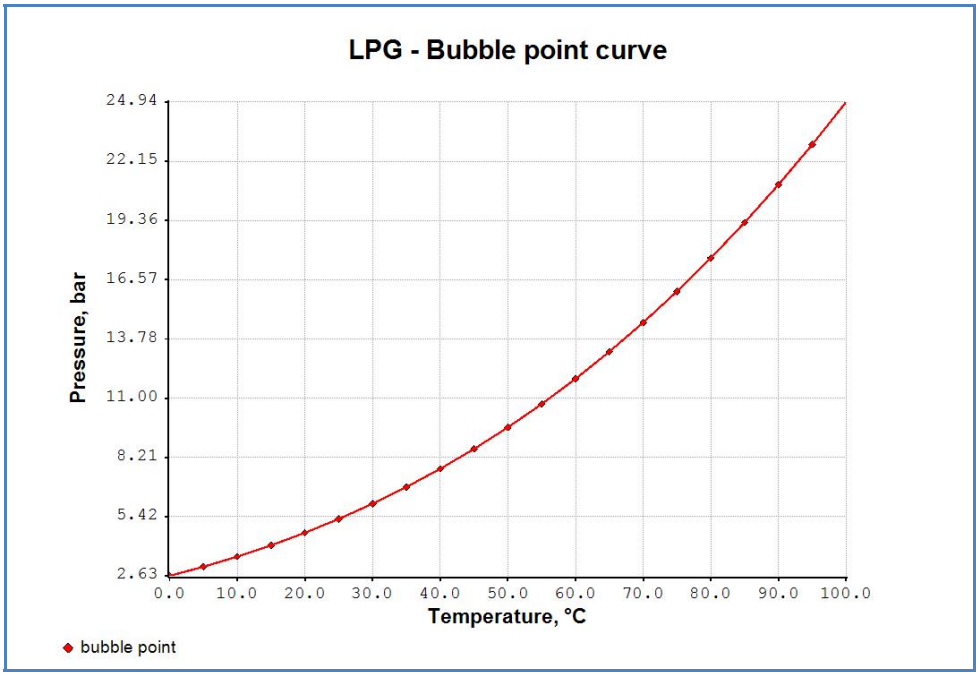

Figure 1: bubble point pressure with respect to temperature of the LPG fluid defined by Table 1.

Table 2: Initial relief conditions

Case	Relief temperature, °C	Critical vapor fraction	Critical flow pressure, bar	Sonic speed, m/s	Fluid velocity, m/s	Fluid flowrate, kg/h
1	30.0	0.000	5.985	670.7	58.4	673,507
2	71.4	0.116	11.108	52.1	54.8	191,034
3	71.4	0.091	11.942	46.6	28.1	199,036

The simulation shows that the liquid is completely discharged in about 15 min, with a discharge flowrate decreasing from the initial value of 190,000 kg/h to about 120,000 kg/h. When the liquid is completely discharged the following gas relief rate drops to about 70,000 kg/h and the internal pressure reaches the atmospheric value in about 21 min.
In the case of a leak located on the top of the vessel the discharge behaviour would be quite different.Though the critical sonic speed would be higher, the relief flowrate would be significantly lower due to the lower vapor density.One diagram related to this scenario is presented in the following Figure 4.

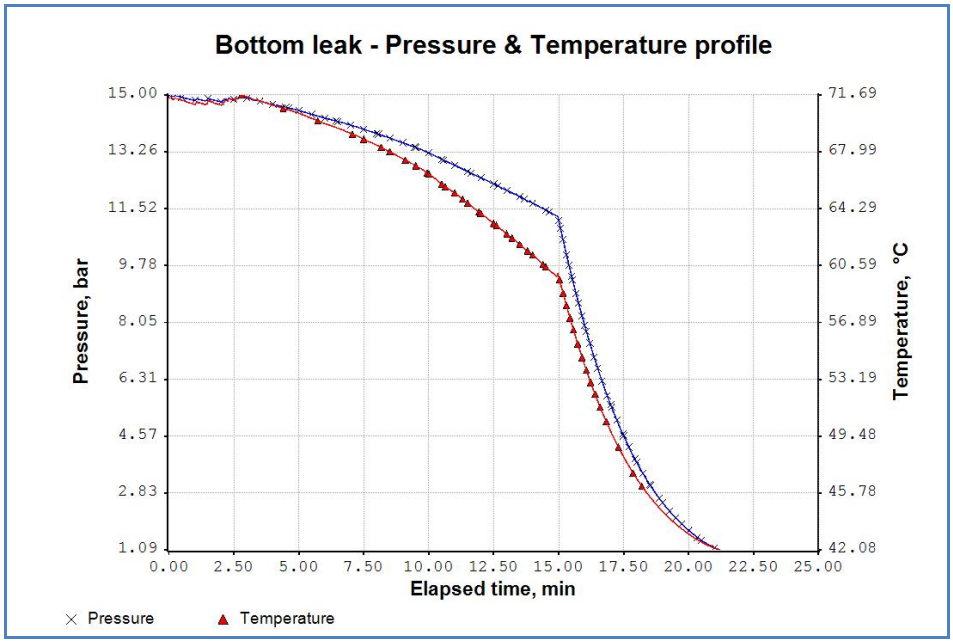

Figure 2: bottom leak case. Temperature and pressure profile vs time.

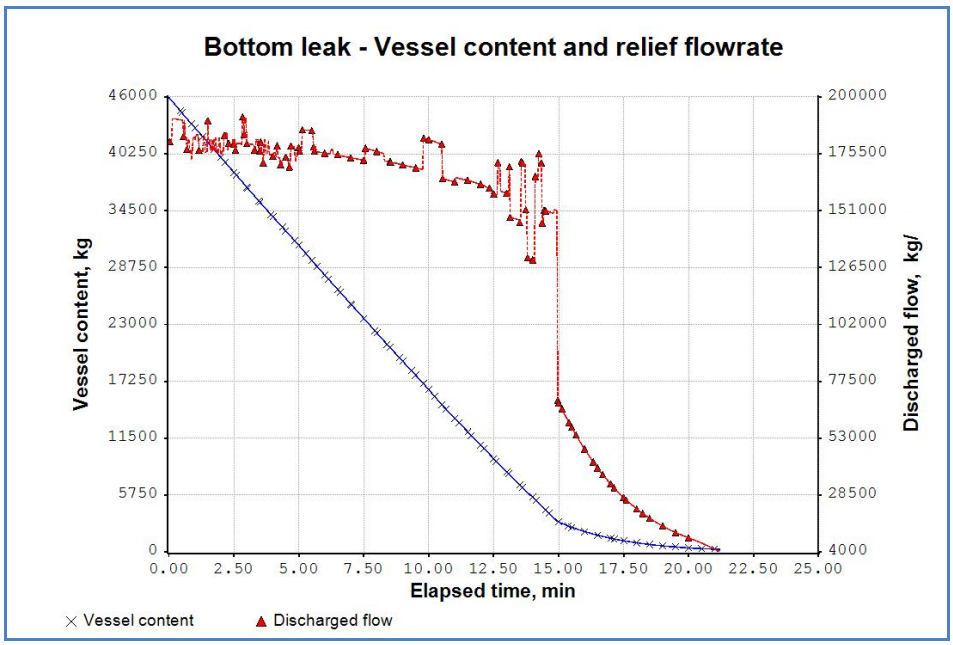

Figure 3: bottom leak case. Vessel mass content and relief flowrate as function of time.

5. Results and Conclusion

Simulations presented in the previous chapter clarify the effect of a two-phase flow depressurization with respect to a single phase either vapour or liquid. For a leak located on the bottom part of the vessel, a rigorous thermodynamic simulation predicts a larger depressurization time with respect of the assumption of a liquid release with no vapor formation. With respect to a depressurization time of 3 min 13 s calculated for a sub-cooled liquid, the calculated discharge time for a flashing LPG is 15 min and

the total discharge time takes about 21 min. For comparison, the case of a leak of the same size located on the vessel top is also simulated. This scenario would have produced very different consequences for two main effects: a) a gas relief of lower flowrate; b) a significant part of the LPG, about one fourth of the initial 45,000 kg, is still in the vessel when the atmospheric pressure is reached.

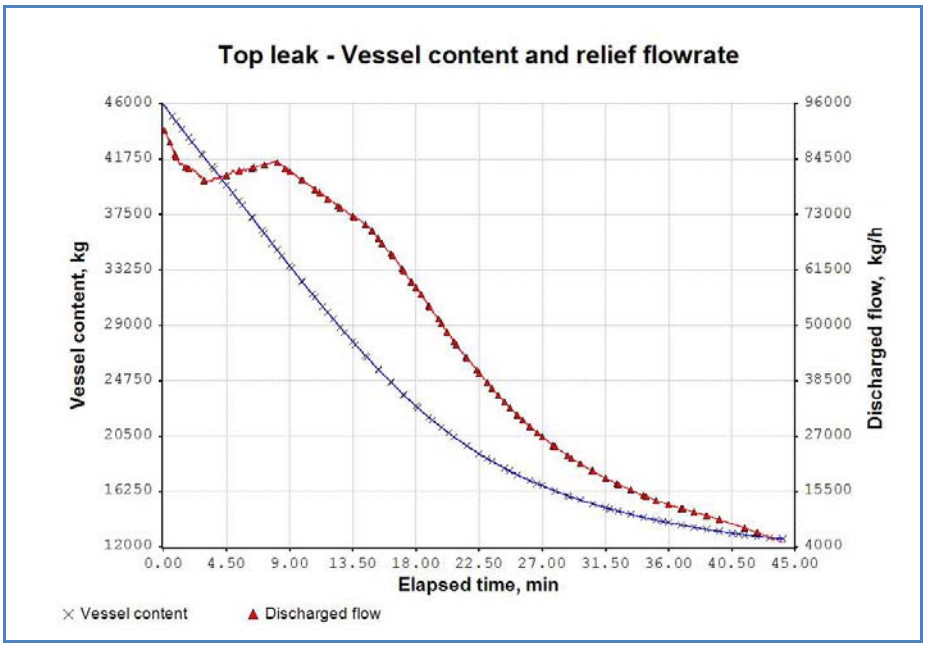

Figure 4: top leak case. Vessel mass content and discharge flowrate as function of time.

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