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## GENERAL RESEARCH

## Hazard of Pressurized Tanks Involved in Fires

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Tanks devoted to the storage and transportation of liquefied petroleum gases (LPGs) are exposed to serious hazards when involved in a fire. Under particular conditions, the boiling liquid expanding vapor explosion (BLEVE) can occur with catastrophic consequences. In the present paper, a mathematical model developed to evaluate the LPG tank behavior for different fire scenarios is presented. Major hazards have been identified distinguishing, in order of gravity, among jet release, catastrophic loss of containment, i.e., the failure of the tank followed by rapid evaporation of the superheated liquid without the development of blast waves, and BLEVE. The effects of accidental cracks, of the presence of a pressure safety valve, and of an insulating layer have been investigated as well. Eventually, the severity of the fireball, of the blast wave, or of the fragments produced by the BLEVE has been assessed as a function of both the scenario and the thermal condition of the containment at the moment of failure.

## Introduction

The storage and transportation of liquefied petroleum gases (LPGs) are potential sources of serious hazards. Indeed, several accidents involving LPG tanks are reported in the literature.<sup>1</sup> Those resulting in the boiling liquid expanding vapor explosion (BLEVE), followed by the “fireball”, are of primary concern because of the catastrophic damages produced. The observed BLEVE phenomena mainly occurred as a consequence of a strong external heat load deriving from fires, which involve LPG railcars, tank trucks, or fixed storage tanks. In the presence of a fire impinging on the tank shell, the evaporation of the liquid leads to a pressure increase inside the tank; in addition, the tank metal wall undergoes a degradation of mechanical properties due to thermal weakening, which mainly occurs in the portion of the tank shell in contact with the vapor. Indeed, because of the relatively high heat-transfer coefficient in the liquid phase, the wet wall temperature is close to the liquid temperature, whereas the vapor does not cool the wall effectively. In this condition a fissure can be generated,<sup>2</sup> which can either stop, giving rise to a jet release (JR), or grow, thus producing the tank catastrophic rupture. The crack propagation depends on both wall mechanical conditions and the energetic content of the tank loading.<sup>3</sup>

The sudden release of the tank content in the environment generates an explosive effect due to the vapor expansion and liquid flashing: the tank rupture is then

followed by a blast wave and by the formation of fragments, which can be propelled over significant distances.<sup>2</sup>

Different interpretations of the BLEVE phenomenon have been proposed in the literature.<sup>4</sup> The most accepted relates the BLEVE to the overcoming of the liquid superheat limit  $T_{sl}$ , i.e., the temperature corresponding to the setup of homogeneous nucleation.<sup>5</sup> Specifically, the explosive flashing of the liquid occurs only when the liquid temperature at the time of failure exceeds  $T_{sl}$ . On the contrary, Birk and Cunningham<sup>6</sup> reported the BLEVE of liquefied propane tanks exposed to fire even for a liquid temperature of about 293 K, i.e., well below the propane superheat limit of 326 K. However, in this paper we have defined such an accident as catastrophic loss of containment (CLOC):<sup>7</sup> the tank is often flattened on the ground, the flashing of liquid is slow, and the blast wave is usually weak or of negligible strength.<sup>8</sup> In any case, the rapid release of the LPG in the environment is followed by a fireball, whose consequences are very destructive.

Knowledge of the conditions that may generate the described phenomenon is of crucial importance in order to prevent disasters. In this context, the development of reliable and simple models able to predict the evolution of the system is very useful.<sup>9</sup>

In the present work, a mathematical model, developed for the analysis of LPG tank behavior when exposed to different fire conditions such as fully engulfing fire, pool fire, and jet fire, is proposed. Different hazards associated with each fire scenario were identified by distinguishing, in order of gravity, among JR, CLOC, and BLEVE. The effects of an accidental crack—or equivalently a “nonpropagating fissure”—on the tank shell, of an insulation shell, and of a safety valve were investigated as well.

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## The Model

Several models, reported in the literature, are focused on the description of the behavior of pressure-liquefied gases contained in a tank when the latter is exposed to a fire.<sup>9–15</sup> These models generally refer to closed cylindrical tanks, protected by a pressure relief valve (PRV) and exposed to either a pool or torch fire. They provide temperature and pressure histories inside the tank and, in some cases, the temperature profiles within different tank zones (liquid phase, vapor phase, and tank wall) are calculated to take into account temperature stratification phenomena.<sup>16,17</sup>

The lumped parameters type model, described in the present paper, aims to investigate the behavior of a LPG tank exposed to fire. The tank is divided into four main parts: liquid phase, vapor phase, dry wall, and wet wall. The basic model assumptions are as follows:

(a) The liquid and vapor phases are well mixed; the liquid temperature stratification is considered to be negligible. This assumption is certainly acceptable for a tank diameter greater than 2 m.<sup>16</sup>

(b) The liquid phase is assumed to be at saturation conditions, whereas the vapor phase is superheated.

(c) Wet and dry walls have uniform temperature along the thickness (metal conductivity is large enough to neglect the thermal gradient).

(d) A single-phase flow (either liquid or vapor) sets up when a leak is produced on the tank shell.

(e) In the case of elliptical heads, an equivalent cylindrical tank with the same total volume and diameter, thus increasing the length, has been considered.

Three different external fire scenarios are specified: fully engulfing fire, pool fire, and jet fire either on the vapor phase or on the liquid phase. Fully engulfing fire conditions occur in the presence of a fire on installations adjacent to the tank or when an accidental leak is produced on the tank wall located in partially confined environments, like road and rail tunnels; the hot combustion products are not able to expand in the surrounding environment because of the confinement, thus producing a strong heat loading on the tank wall.<sup>18</sup>

Generally, pool fire scenarios originate from the formation of a leak in the lower part of the tank shell<sup>1</sup> or from an adjacent tank.<sup>4</sup>

Finally, jet-fire scenarios apply when a hole is produced on the vapor side wall and the vapor exiting from the tank ignites, heating the tank itself or impinging on an adjacent tank.

For all of the above-mentioned fire scenarios, the heat transfer from the external fire to the tank occurs by radiation and convection. These mechanisms are included in the model by means of two lumped parameters such as the mean fire temperature ( $T_f$ ), representing the asymptotic temperature of the flame once the fire is fully developed (i.e., neglecting the fire establishing phase), and the mean external air temperature ( $T_e$ ), which is the average temperature of the hot burned gases in the surrounding atmosphere. Both temperatures are considered to be constant.

The thermal flux radiated from the external fire to the tank,  $q_{r,e}$ , is expressed by considering the flame as a blackbody emitter and the metal walls as gray bodies characterized by an emissivity  $\epsilon$ :

$$q_{r,e} = \sigma \epsilon F_v (T_f^4 - T_w^4) \quad (1)$$

where  $\sigma$  is the Boltzmann constant,  $T_w$  is the time

changing wall temperature, and  $F_v$  is the view factor, which is assumed to be 1 for fully engulfing fire. As far as a pool fire is concerned,  $F_v$  is 1 for the wet wall, whereas a mean value of 0.30 was assumed for the dry wall.<sup>19</sup>

In the case of a jet fire following a leak on the dry wall, the torch was modeled as a vertical gaseous diffusion flame of conical shape, with an angle of 20° and a flare length  $L$ , given by<sup>20</sup>

$$\frac{L}{D} = \frac{5.3\beta}{C_{st}\alpha} \sqrt{C_{st} + (1 - C_{st}) \frac{M_{air}}{M_{fuel}}} \quad (2)$$

where  $D$  is the diameter of the leak,  $C_{st}$  is the stoichiometric concentration of the fuel–air mixture,  $M_{air}$  and  $M_{fuel}$  are the molecular weights of air and fuel, respectively, and  $\alpha$  and  $\beta$  are two constants, which depend on the fuel type ( $\alpha = 0.97$  and  $\beta = 7.6$  for propane). The view factor for the dry wall was evaluated by adopting the Craven model:<sup>4</sup>

$$F_v = \frac{zR}{\pi} \left( \frac{1}{\frac{L^2}{2} + z^2} - \frac{1}{L^2 + z^2} \right) \quad (3)$$

where  $z$  is the distance of the target from the jet axis and  $R$  is the jet radius at the cone tip. As  $z$  increases,  $F_v$  passes through a maximum. In the present model, the leak was assumed to occur at the dry wall center and  $z$  was set to one-fourth of the tank length.

The thermal flux transferred by convection from the hot combustion products to the tank wall  $q_{c,e}$  is expressed as

$$q_{c,e} = h_{c,e} (T_e - T_w) \quad (4)$$

where  $h_{c,e}$  is the heat-transfer coefficient calculated through the relationship<sup>21</sup>

$$Nu = a(Gr \times Pr)^b \quad (5)$$

where  $Nu$ ,  $Gr$ , and  $Pr$  are the Nusselt, Grashof, and Prandtl numbers, respectively, and  $a$  and  $b$  are appropriate constants depending on the system geometry.

Heat is transferred from the walls to the vapor and liquid phases by convection and radiation. The transient equations of energy balance for the liquid and vapor phases are respectively

$$\left[ mc_v \frac{dT}{dt} + \frac{dm}{dt} \Delta H_{ev} \right]_l = [h_{c,l} A (T_w^l - T) + h_{r,w} A^l (T_w^v - T)]_l + h_{c,l-v} A^l \Delta T \quad (6)$$

$$\left[ mc_v \frac{dT}{dt} \right]_v - \frac{dm_l}{dt} (\Delta H_{sh} - RT_l) = [(h_{c,i} + h_{r,i}) A (T_w^v - T) - SRT]_v - h_{c,l-v} A^l \Delta T \quad (7)$$

where  $m$ ,  $c_v$ , and  $T$  are the mass, specific heat, and temperature of the phase,  $T_w^v$  and  $T_w^l$  are the temperatures of the dry and wet walls,  $\Delta H_{ev}$  and  $\Delta H_{sh}$  are the liquid heat of evaporation and the superheating heat of the vapor,  $A$  is the surface of the walls enclosing liquid or vapor,  $h_{r,w}$  is the coefficient expressing the radiative heat transfer from the dry wall to the liquid, and finally  $h_{c,i}$  and  $h_{r,i}$  are the internal convective and radiative heat-transfer coefficients, respectively. The term  $S$

represents the released mass flow rate in the case of vapor spilling due to an accidental leak. If the latter is generated on the wet wall, eqs 6 and 7 are modified to take into account the energy loss due to the liquid spilling. The released mass flow rate has been computed according to the orifice model, for a liquid as well as a vapor spill.<sup>22</sup> The term  $h_{c,l-v}A^1\Delta T$  expresses the heat transfer by convection at the liquid–vapor interface, where  $h_{c,l-v}$  is the transfer coefficient,  $A^1$  is the interface area, and  $\Delta T$  is the difference between the vapor and liquid temperature.

Special care was devoted to the modeling of the heat transfer by convection from the wet wall to the liquid phase. The pool boiling theory was introduced to discriminate between two possible mechanisms: heterogeneous vapor nucleation and vapor film generation in the liquid layer adjacent to the wet wall, with the latter occurring when proper superheating conditions are reached.<sup>21</sup>

Vapor and liquid masses change with time as a result of both liquid evaporation and spilling through an accidental leak. They were computed by the following mass balances:

$$\frac{dm_t}{dt} = -S \quad (8)$$

$$\frac{dm_l}{dt} = -Sx + m_t \frac{dx}{dt} - E \quad (9)$$

$$m_v = m_t - m_l \quad (10)$$

where  $m_t$  is the total mass contained in the tank and  $x$  is the liquid mass fraction at equilibrium, which depends on both  $m_t$  and liquid temperature. The term  $E$  represents an additional contribution to liquid evaporation deriving from the depressurization phase ensuing the leak formation on the tank shell. In this case, the fluid spill causes a pressure drop inside the tank that drives the liquid–vapor system to nonequilibrium conditions. This sets up a further driving force for evaporation.<sup>17</sup>

$$E = KA^1(P_{\text{sat}} - P) \quad (11)$$

where  $P_{\text{sat}}$  is the liquid–vapor pressure,  $P$  is the internal pressure, and  $K$  is the mass-transfer coefficient at the liquid–vapor interface evaluated by a balance between the vapor–liquid convective heat-transfer coefficient  $h_{c,l-v}$  and the latent heat associated with the liquid to vapor convective mass transfer.

Dry and wet wall temperatures were obtained from eq 12, expressing the energy balance for the tank walls:

$$\left[ m_w c_{p,w} \frac{dT_w}{dt} \right]_j = [h_{c,e}A(T_e - T_w) + q_{r,e}A - h_{c,i}A(T_w - T)]_j \quad (12)$$

where  $j$  refers to the liquid or vapor phase,  $m_w$  and  $c_{p,w}$  are the mass and specific heat of the dry or wet wall, and  $q_{r,e}$  is expressed through eq 1 specified for the considered fire scenario. In the case of the dry wall, an additional term  $Q_{r,i}$  has to be included in eq 12:

$$Q_{r,i} = -[h_{r,w}A^1(T_w - T)]_l - [h_{r,i}A(T_w - T)]_v \quad (13)$$

which takes into account the heat lost by the dry wall by radiation to both liquid and vapor phases.

As pointed out previously, generally, the dry wall temperature markedly influences the failure sequence. Tank failure was assumed to occur when the internal pressure equals the tank burst pressure,  $P_{\text{burst}}$ , which was calculated from the ultimate strength of the carbon steel:<sup>6</sup>

$$P_{\text{burst}} = 2\sigma_u(W/D_t) \quad (14)$$

with  $W$  being the wall thickness,  $D_t$  the tank diameter, and  $\sigma_u$  the ultimate strength, evaluated as a function of the dry wall temperature according to Birk.<sup>2</sup>

Thermal insulation by means of rock wool was also considered. In this case, the set of equations has been modified: the profile of the temperature within the width of the insulation was obtained by the equation

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = \frac{1}{\xi} \frac{\partial T}{\partial t} \quad (15)$$

where  $r$  is the tank radius and  $\xi$  is the thermal diffusivity of the rock wool. The equation was solved with the following boundary conditions:

$$\left[ k_{rw} \frac{\partial T}{\partial r} \right]_{j,\text{external}} = [h_{c,e}(T_e - T) + q_{r,e}]_j \quad (16)$$

$$\left[ k_{rw} \frac{\partial T}{\partial r} \right]_{j,\text{steel}/rw} = [q_k]_j \quad (17)$$

where  $k_{rw}$  is the thermal conductivity of the rock wool and the term  $q_k$  is the conductive thermal flux between the insulating layer and the steel wall either on the vapor section or on the liquid section. The wall equation becomes

$$\left[ m_w c_{p,w} \frac{dT_w}{dt} \right]_j = [q_k - h_{c,i}A(T_w - T)]_j \quad (18)$$

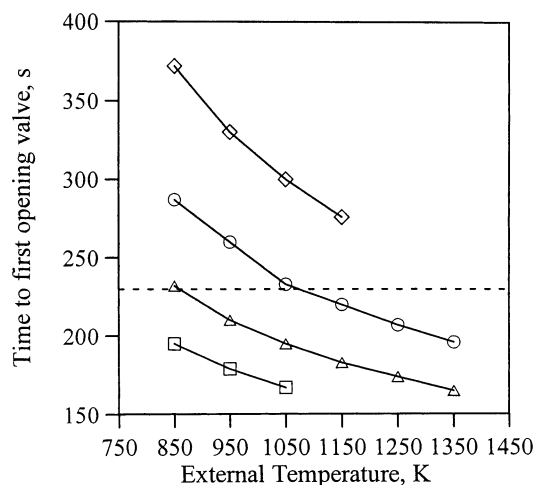
The radiative and convective heat-transfer coefficients were calculated by using empirical correlations available in the literature.<sup>21,23</sup> All of the fluid properties were computed by taking into account the dependence on the temperature.<sup>21,23</sup>

Equations 6–12 were solved by using a Runge–Kutta method (IV order). In the case of the insulation, the set of equations related to the rock wool layer was solved by using a finite-difference technique; an implicit method was used to solve the set of equations expressed by the finite-difference formulas for the second-order derivatives.<sup>24</sup>

## Model Sensitivity

A first set of simulations was devoted to analyzing the sensitivity of the results to the model parameters. These are represented by the external ambient temperature  $T_e$  and by the flame temperature  $T_f$  to be used for convective and radiative heat-transfer calculations, respectively. To achieve the best parameter configuration, the simulations were compared with experimental results available in the literature and referred to LPG tanks engulfed in fires.<sup>25–27</sup> The results showed rather high model sensitivity to both parameters. As an example, Figure 1 reports the time of safety valve first opening as a function of  $T_e$  and  $T_f$  for a LPG tank with





**Figure 1.** Time of the safety valve first opening for a LPG tank of 1 ton, 80% filled, as a function of  $T_e$ , at various  $T_i$ :  $\diamond$ , 1200 K;  $\circ$ , 1400 K;  $\triangle$ , 1600 K;  $\square$ , 1800 K. The dashed line represents the experimental value.<sup>26</sup>

a capacity of 1 ton and a filling degree of 80%; the pressure safety valve (PSV) is set to the pressure of 15.2 bar. The agreement with the experimental data is obtained for values of  $T_e = 1050$  K and  $T_i = 1400$  K. These values correspond to the average value of the flame temperature as measured in the experiments,<sup>26</sup> which ranges between 1000 and 1300 K. Besides, the use of these temperatures results in an average heat flux to the tank of about 80 kW/m<sup>2</sup>, which is also in agreement with the experiments. These values were found to be suitable to reproduce the behavior of LPG tanks of other experimental runs<sup>2,26,27</sup> and have been adopted for all of the following numerical simulations.

As an example of the calculated results, Figure 2a reports the vapor pressure histories for a small tank (volume = 0.5 m<sup>3</sup>; fill level = 40%) and a larger tank (volume = 10.0 m<sup>3</sup>; fill level = 58%). As referred by Moodie et al.,<sup>25,26</sup> an initial delay of about 1 min is present in all of the experimental runs considered here, because of ignition of the pool of kerosene. This time has been added to the calculated histories and has been regarded as negligible in the following, aiming at a comparison of different fire scenarios. Figure 2b reports

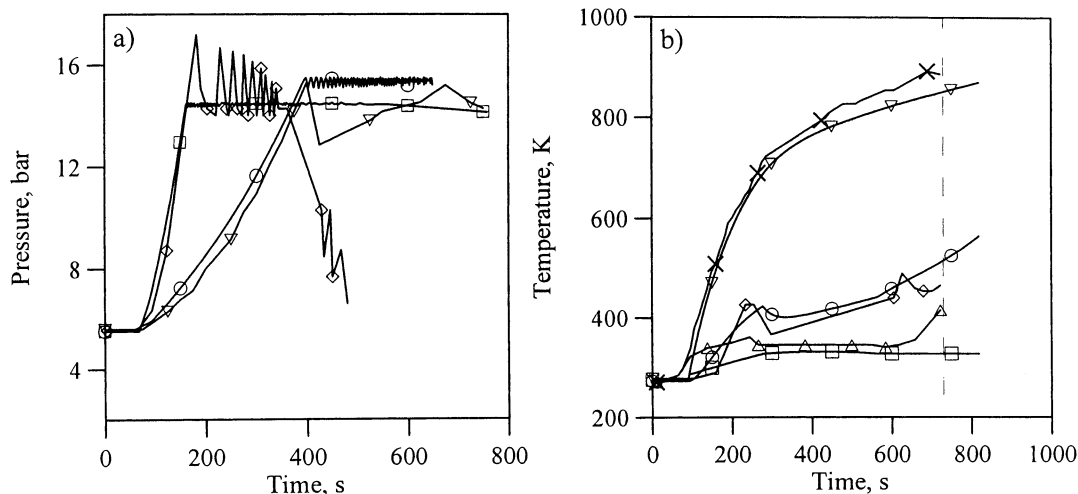
the vapor and liquid temperatures and the corresponding wall temperatures for a 2.5 m<sup>3</sup> tank, 40% filled by propane.

Here it is worth noting that the time of the first opening of the safety valve is reproduced within a maximum error of about 10%, which has to be considered acceptable if taking into account the complex phenomena either external (the fire) or internal to the tank. Also, the increase of pressures and the trend of the temperatures of walls and tank contents are well reproduced.

Deviations from the experimental behavior, specifically for the vapor pressure after the first opening, are mainly due to improper safety valve action, which is unpredictable, and to the two-phase flow through the relief area, especially when very high fill levels are considered.

With reference to the vessel failure, many factors influence the failure time: mechanical characteristics of the tanks (welding, corrosion, type of carbon steel, etc.), thickness of the walls, composition of LPGs, the specific fire scenario with its dependence on environmental temperature and wind, insulation, tank location, type, and effectiveness of the safety valve. These data are not reported accurately in the literature and are often unquantifiable. Moreover, the experiments are often conducted by trying to avoid very dangerous scenarios which can derive from the BLEVE of tanks. Hence, the quenching of the tank and/or the extinguishing of the fire is often operated when dry wall temperatures are very high.

Birk<sup>2</sup> reports the approximate time to failure of tanks exposed to different levels of fire impingement by varying the tank diameter. This time increases approximately linearly on a log-log scale diagram with the diameter and with the decreasing of the vapor section of the tank wall impinged by fire. This trend is confirmed for all of the test cases reported in this work (see the next chapter). For the specific test cases previously reported for validation, the calculated time to failure is about 12 min for both vessels with diameters of 1.0 and 2.0 m. This time is not far from the values ranging between 8 and 12 min as given by Birk. For the smallest vessel, the failure is reached about 3 min before, because of the anomalous mechanical re-



**Figure 2.** Propane tanks exposed to fully engulfing fires.<sup>25,26</sup> (a) Vapor pressure; volume = 0.5 m<sup>3</sup>; 40% filled:  $\diamond$ , exptl;  $\circ$ , calcd; volume = 10.0 m<sup>3</sup>, 58% filled:  $\nabla$ , exptl;  $\square$ , calcd. (b) Temperature; volume = 2.5 m<sup>3</sup>, 40% filled. Vapor phase:  $\diamond$ , exptl;  $\circ$ , calcd. Liquid phase:  $\triangle$ , exptl;  $\square$ , calcd. Vapor wall:  $\times$ , exptl;  $\nabla$ , calcd. The dashed line refers to quenching of the tank by water to avoid dangerous failure.

**Table 1. Tank Characteristics Used in the Numerical Simulation**

diameter (m)	2.05
length (m)	3.60
volume (m <sup>3</sup> )	10.00
shell thickness (mm)	6.00–8.00
filling percentage (%)	50.00
PSV set pressure (if installed) (bar)	14.00
PSV section (if installed) (cm <sup>2</sup> )	10.00
rock wool thickness (if present) (mm)	50.00

**Table 2. Summary of Model Outcomes for the Full Engulfing Fire<sup>a</sup>**

	time to failure (s)	$T_l^{\max}$ (K)	$T_w^{\max}$ (K)	$T_v^{\max}$ (K)	$T_w^{v,\max}$ (K)	$P_{\text{burst}}$ (bar)
Propane ( $T_{\text{sl}} = 326$ K)						
no leak	244	321	332	431	728	16.4
5 cm <sup>2</sup>	294	315	326	401	759	14.2
10 cm <sup>2</sup>	372	305	319	388	799	11.4
20 cm <sup>2</sup>	JR					
PSV	282	317	329	380	747	15.1
LPG, $x_{\text{prop}} = 0.50$ ( $T_{\text{sl}} \approx 360$ K)						
no leak	292	329	340	459	772	13.3
5 cm <sup>2</sup>	360	325	337	423	802	11.2
10 cm <sup>2</sup>	458	319	332	410	837	8.9
20 cm <sup>2</sup>	JR					
PSV	292	329	340	459	772	13.3
Butane ( $T_{\text{sl}} = 403$ K)						
no leak	390	347	359	504	839	8.8
5 cm <sup>2</sup>	438	344	357	456	848	8.29
10 cm <sup>2</sup>	497	340	353	430	860	7.54
20 cm <sup>2</sup>	JR					
PSV	390	346	359	504	839	8.8

<sup>a</sup> Tank shell of 6 mm. JR = jet release.

sponse of the safety valve. In the following, it should be clear that times to failure are only given as order of magnitude, aiming essentially at a comparison between different fire scenarios, and that attention should be given if any mitigation response has to be designed.

## Simulation Results

A typical LPG tank, whose characteristics are reported in Table 1, has been considered in the following simulations. The numerical tests were carried out by considering propane, butane, and a mixture of 50% of both gases, to simulate the LPG behavior. Particular emphasis has been placed on the effect of cracks produced either on the dry wall or on the wet wall. These leaks were assumed either to be present at the start of calculation, thus simulating cracks generated as a direct consequence of tank collisions, or to be formed after different fire exposure times because of the dry wall thermal degradation or as a result of external causes.

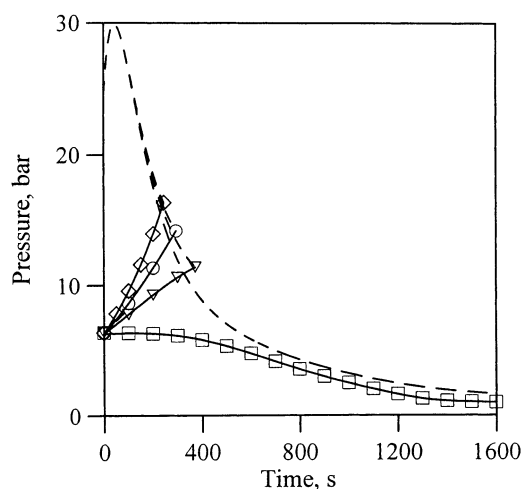
The presence of a PSV with an opening pressure of 14 bar and a section of 10 cm<sup>2</sup> was also considered. The choice of the PRV has been dictated by API RP 520,<sup>28</sup> API RP 521,<sup>29</sup> and ASME "Boiler and Pressure Vessel Codes",<sup>30</sup> having used a conservative approach for a bare (noninsulated) vessel totally engulfed in fire.

**Fully Engulfing Fire.** Tables 2 and 3 summarize the numerical results obtained for the tanks with a shell thickness of respectively 6 and 8 mm, completely engulfed in fire, in the case of a tank: (a) without insulation and no PSV; (b) with a crack on the dry wall with a section ranging from 5 to 20 cm<sup>2</sup>, no insulation, and no PSV; (c) with a PSV and no insulation. Results are reported in terms of vapor and liquid temperatures,

**Table 3. Summary of Model Outcomes for the Full Engulfing Fire<sup>a</sup>**

	time to failure (s)	$T_l^{\max}$ (K)	$T_w^{\max}$ (K)	$T_v^{\max}$ (K)	$T_w^{v,\max}$ (K)	$P_{\text{burst}}$ (bar)
Propane ( $T_{\text{sl}} = 326$ K)						
no leak	338	335	344	445	727	22.0
5 cm <sup>2</sup>	442	326	336	415	766	18.2
10 cm <sup>2</sup>	JR					
20 cm <sup>2</sup>	JR					
PSV	684	314	326	423	813	14.0
LPG, $x_{\text{prop}} = 0.50$ ( $T_{\text{sl}} \approx 360$ K)						
no leak	401	345	354	470	767	18.2
5 cm <sup>2</sup>	557	341	351	440	808	14.4
10 cm <sup>2</sup>	JR					
20 cm <sup>2</sup>	JR					
PSV	650	344	354	443	813	14.0
Butane ( $T_{\text{sl}} = 403$ K)						
no leak	515	365	375	514	824	13.0
5 cm <sup>2</sup>	617	362	372	465	834	12.2
10 cm <sup>2</sup>	854	356	367	455	853	10.7
20 cm <sup>2</sup>	JR					
PSV	515	365	375	514	824	13.02

<sup>a</sup> Tank shell of 8 mm. JR = jet release.

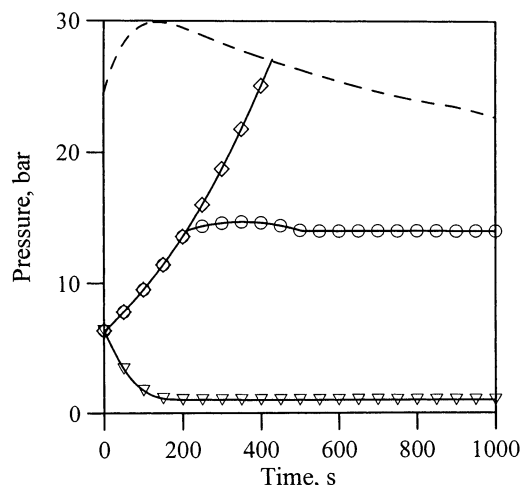


**Figure 3.** Pressure histories for the propane tank exposed to fully engulfing fire conditions, ranging from 5 to 20 cm<sup>2</sup>: dashed line, burst pressure;  $\diamond$ , closed vessel. Crack area with a section as follows:  $\circ$ , 5 cm<sup>2</sup>;  $\nabla$ , 10 cm<sup>2</sup>;  $\square$ , 20 cm<sup>2</sup>.

tank wall temperatures, and burst pressure once failure conditions are reached. The time to failure is indicated as well. JR corresponds to a loss of containment without the failure of the tank.

The time to tank rupture was calculated from the intersection of the internal pressure time history with the burst pressure curve. As expected, because of the increase in the discharge flow rate, the larger the leak, the longer the time to tank rupture. In addition, failure conditions are not achieved for a crack area of 20 cm<sup>2</sup>. This is also clear from Figure 3, which shows the model results for pure propane in terms of internal pressure and burst pressure history: a hole section of 20 cm<sup>2</sup> produces a pressure decrease inside the tank due to a large JR up to the complete tank emptying.

By inspection of Tables 2 and 3, it appears that LPG behavior lies between those pertaining to pure propane and pure butane. Moreover, the liquid temperature is always close to the wet wall temperature, reflecting the high heat-transfer rate produced by the rapid setup of the nucleate boiling regime, in agreement with the reports of other investigators.<sup>26,27</sup> Results also suggest that the risk of BLEVE does exist only as far as propane



**Figure 4.** Pressure histories for the propane tank exposed to a pool fire: dashed line, burst pressure;  $\diamond$ , closed vessel;  $\circ$ , closed vessel with a PSV;  $\nabla$ , crack on the wet wall with a 5 cm<sup>2</sup> section.

is concerned, and the tank shell with a thickness of 8 mm is considered. Indeed, in these cases the liquid temperature at failure conditions exceeds the superheat limit value, whereas in the other cases, the tank failure leads to a CLOC.

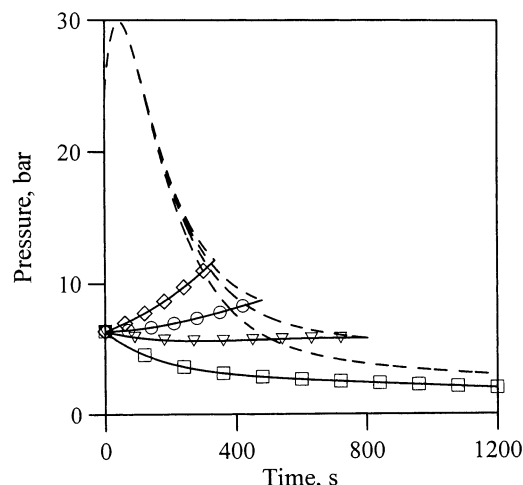
The results of numerical simulation using a 50-mm-thick layer of rock wool as thermal insulation, in the presence of the safety valve set at 14 bar, show that the failure of the tank is reached after about 55 min ( $T_l = 314$  K) with a total mass contained in the vessel of about 350 kg and the first opening of the PSV is after about 17 min, in the case of propane.

In the case of butane, the failure is reached after the total vaporization of the liquid. In the case of a LPG of 50% butane, the failure is reached after about 1 h but the liquid temperature is lower than the superheat limit.

This behavior is comparable to the experimental behavior reported in the literature<sup>31</sup> and can be considered "conservative", in terms of the time of failure, with respect to all of the possible fire scenarios, unless the loss of insulating properties of rock wool at high temperature is considered. This could occur in the case where an external jet fire impinges directly on the shell. This effect will be subject of future analysis.

**Pool Fire.** Two different scenarios leading to a pool fire have been analyzed: a stand-alone tank with a leak on the wet wall and a tank engulfed in a pool fire originating from the spill of any flammable material from an adjacent tank (closed vessel). The latter occurs, for instance, when rail tanks transporting LPG are involved in a derailment.<sup>1</sup> Figure 4 reports the results in terms of pressure buildup and burst pressure for pure propane.

In the case of a leak on the tank wet wall, the calculation results suggest that the tank does not reach the failure conditions even for the relatively small crack of 5 cm<sup>2</sup> because of the depressurization induced by the liquid outflow with consequent liquid evaporation, which cools the liquid phase. The strong liquid cooling generates a large temperature difference between the liquid phase and the wet wall and a transition to the film boiling regime is observed. This causes a rapid decrease of the heat-transfer coefficient and, hence, an increase in the wet wall temperature, which reaches large values (about 630 K).<sup>4,21</sup>



**Figure 5.** Pressure histories for the propane tank exposed to a jet fire in a confined environment, i.e., completely engulfing the dry wall of the tank (scenarios b and c): dashed line, burst pressure;  $\diamond$ , closed vessel, external jet fire. Jet fire generated by a crack in the dry wall of the tank with a section as follows:  $\circ$ , 5 cm<sup>2</sup>;  $\nabla$ , 10 cm<sup>2</sup>;  $\square$ , 20 cm<sup>2</sup>.

For the closed vessel (the "external" pool fire), the burst pressure is rapidly reached after about 455 s. The time to failure ( $t_f$ ) is longer with respect to fully engulfing fire conditions, and so the liquid temperature (348 K at failure time) reaches the BLEVE threshold.

The presence of the PSV markedly increases  $t_f$  to 2382 s. In this case, the corresponding  $T_l$  is 316 K, thus avoiding the occurrence of BLEVE.

Increasing the thickness to 8 mm does not lead to significant behavior differences, with the liquid temperature being 364 K (BLEVE occurrence) at the failure time of 609 s in the case of a closed vessel and 318 K (CLOC occurrence) at the failure time of 3211 s with the presence of a PSV.

When butane is considered,  $t_f$  is about 819 s and  $T_l$  is 401 K, so that in this case, the BLEVE conditions are approached but not reached. The installation of the PSV allows the CLOC scenario after 2687 s, with  $T_l = 371$  K. When the wall thickness is increased,  $t_f$  increases to 988 s and  $T_l$  overcomes the superheat temperature, whereas the behavior with the PSV does not change ( $t_f = 3553$  s;  $T_l = 374$  K).

**Jet Fire.** Numerical simulations were carried out in order to analyze the tank behavior when exposed to a jet fire on the dry wall. Different fire scenarios were considered: (a) a free jet fire impinging on the dry wall, derived from a crack in the tank shell itself, a scenario which typically takes place in open environments and in the transportation of flammable liquids; (b) a free jet fire, which completely engulfs the dry wall, because of a crack in the tank shell itself in a confined or obstructed environment (rail and road tunnels or industrial plants); (c) a free jet fire which engulfs half of the surface of the dry wall as a result of an external jet fire produced by an adjacent tank. It is worth noting that a free jet impinging on the wet wall side can be addressed to the pool fire scenario.

The results obtained for pure propane indicate that free jets (scenario a) are not able to produce a strong heat load on the tank, which pressurizes very slowly without reaching failure conditions, thus slowly emptying. On the contrary, when the jet fire completely engulfs the dry wall of the tank shell (scenario b), as in Figure 5), the complete emptying of the tank for a



greater crack area (20 cm<sup>2</sup>) can be observed, whereas a rapid pressure increase is observed for smaller sections: the failure conditions are achieved in rather short times, but the calculated  $T_l$  values are sufficiently low (300 K), with the nucleate boiling mechanism being controlling, to produce a CLOC rather than a BLEVE.

In the case of an external jet fire impinging on the vapor section of the closed vessel, numerical simulations show that the vessel crashes after 636 s, with a liquid temperature higher than that for the BLEVE threshold ( $T_l = 326$  K). Increasing the wall thickness to 8 mm gives rise to a failure after 891 s, but still BLEVE conditions are reached because  $T_l$  is 343 K. The presence of the PSV avoids the occurrence of BLEVE for both values of wall thickness because tank failure is reached after 1985 s with  $T_l$  of 314 K (6 mm) and after 2715 s with  $T_l$  of 314 K (8 mm).

If the jet fire completely engulfs the dry section of the tank shell (scenario c), as in Figure 5, failure rapidly occurs after 335 s but the occurrence of BLEVE is avoided ( $T_l = 307$  K). The presence of the PSV and the increase of the shell thickness do not affect significantly the time of failure and the final liquid temperature.

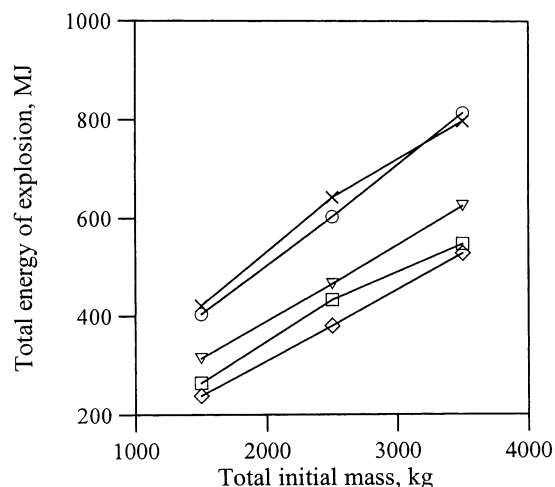
The results obtained for pure butane in the case of free jet (scenario a) are similar to those obtained for the pure propane. Indeed, this scenario is not able to produce a strong increase of the liquid temperature; thus, the vessel slowly empties. When the vessel dry wall is completely engulfed by a jet fire in a confined environment, the numerical results showed that vessel failure is avoided for a crack section greater than 20 cm<sup>2</sup>. However, if the crack section is smaller, the relatively fast pressure increase gives way to a CLOC rather than a BLEVE because the liquid temperature is sufficiently low ( $T_l = 330$  K).

Finally, in the case of an external jet fire impinging on the vapor section of the closed vessel containing pure butane, numerical simulations show that the occurrence of BLEVE is not possible either for a fire engulfing half of the vapor surface of the vessel or in the case of full engulfment (confined environment). In the first case,  $t_f$  is reached after 1129 s ( $T_l = 368$  K), whereas in the latter, the vessel crashes after 583 s ( $T_l = 329$  K). The results are similar if a PSV is present. When increasing the shell thickness to 8 mm,  $t_f$  is 1471 s ( $T_l = 390$  K) for an open external jet. The introduction of a PSV allows a rise of  $t_f$  up to 3140 s ( $T_l = 369$  K). For the confined environment,  $t_f$  is 797 s ( $T_l = 345$  K), thus still avoiding the BLEVE conditions, and similar results are obtained when the PSV is installed.

### Hazard of BLEVE of a LPG Vessel

The hazard of vessel containing pressurized, flammable substances can be essentially related to three catastrophic phenomena which can severely produce damages to the surroundings of the vessel itself, either mobile or fixed: a blast wave produced by the BLEVE of the substance contained in the vessel, the combustion of the fuel in the atmosphere after the failure of the vessel, and its mixing with air (fireball) and the fragments produced by the explosion of the shell, if any.

Actually, aiming at evaluating the risk of LPG storage, even the time prior to the loss of containment (the vessel failure), is important because the evacuation and the intervention of safety personnel can only be effective if the predictable time is consistently long.



**Figure 6.** Total energy of the explosion for propane and butane vessels without PSV or a leak, subjected to fire, in the case of BLEVE: ( $\diamond$ ) full engulfment,  $W = 8$  mm, propane; ( $\circ$ ) pool fire,  $W = 8$  mm, propane; ( $\nabla$ ) pool fire,  $W = 6$  mm, propane; ( $\times$ ) pool fire,  $W = 8$  mm, butane; ( $\square$ ) external jet fire,  $W = 8$  mm, propane.

With reference to the possibility of BLEVE, numerical results have shown that for our own tank volume the presence of a PSV with a section of at least 10 cm<sup>2</sup> eliminates the occurrence of BLEVE, for any considered fire scenario; however, the occurrence of CLOC (and subsequent fireball) is never avoided by the presence of the valve.

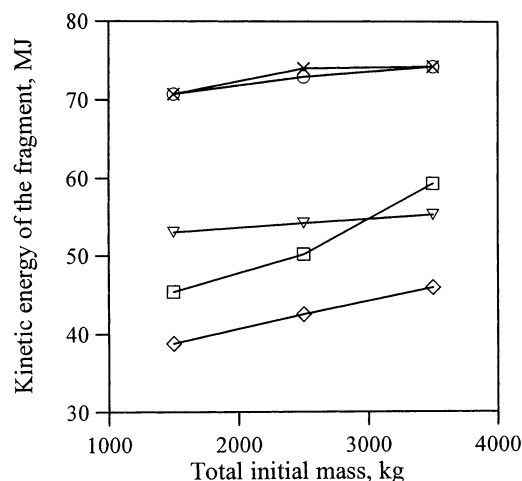
When completely closed vessels, in the absence of PSV, are considered, sensibly short times to failure are obtained, thus excluding the possibility of any intervention, and BLEVE conditions are reached in the case of a propane vessel subjected to a pool fire, an "external" jet fire impinging on the dry wall, and a fully engulfing fire with a shell thickness of 8 mm; in the case of butane, BLEVE is only reached in the case of a pool fire with a shell thickness of 8 mm. Increasing the thickness of the shell from 6 to 8 mm influences the time to failure by about 30–40% in most cases. As expected, the comparison between propane and butane shows that the time to failure of the vessel, resulting in either a CLOC or a BLEVE, is almost doubled in the case of butane.

The description of the propagation of the blast wave in the space, characterized by a peak overpressure and an impulse, can be obtained by TNT methods once the total energy of the explosion at the moment of failure is known, calculated by means of the internal energy of liquid and vapor phases.<sup>8</sup> The numerical results obtained for different scenarios all leading to a BLEVE are reported in Figure 6, for propane and butane vessels. In light of comparison, the total energies calculated for different degrees of filling (25%, 50%, and 75%) are also reported. Results clearly show that pool fire scenarios are the most hazardous because the energy freed after failure is almost double that of other scenarios.

The diameter of the fireball is dependent on the total mass contained in the vessel at the moment of failure, through the equation of Roberts.<sup>8</sup> When CLOC or BLEVE is reached, the diameter ranges between 60 and 75 m, regardless of the shell thickness, the type of substance, or the presence of PSV, unless thermal insulation is considered and with the exception of a pool fire on a PSV-equipped vessel, with the diameter being about 40 m in this case.

Evaluating the fragment formation behavior and the total distance run by the fragments is not a straight





**Figure 7.** Kinetic energy of the fragment for propane and butane vessels without PSV or a leak, subjected to fire: (◇) full engulfment,  $W = 8$  mm, propane; (○) pool fire,  $W = 8$  mm, propane; (▽) pool fire,  $W = 6$  mm, propane; (×) pool fire,  $W = 8$  mm, butane; (□) external jet fire,  $W = 8$  mm, propane.

task. A very simple approach uses the kinetic energy of the fragment itself,<sup>4</sup> but other considerations regarding the welding points of the tank vessel should be done. However, some indications can be given if kinetic energy is considered. As expected, the results (Figure 7) depend mainly on the vessel wall thickness, but again, as for BLEVE, the hazard of a pool fire is evident.

## Conclusions

A mathematical model was developed in order to predict the behavior of LPG tanks exposed to different fire scenarios. The developed code can be easily extended to other substances with comparable characteristics.

Numerical results have shown that the probability of occurrence of BLEVE is relatively small because particular fire conditions are necessary. However, the CLOC can be considered to be as dangerous as BLEVE because the fireball phenomenon and the formation of fragments may damage humans and things even far from the location of the tank.

The use of effective PSVs and/or insulation is strongly recommended even on road tanks because the times of failure are generally strongly increased and BLEVE conditions are never reached.

Future analysis should be carried out in order to evaluate the effect of the two-phase flow through the PSV and the loss of physical characteristics of the insulator as a result of high temperature.

## Nomenclature

$a$  = constant in eq 5  
 $A$  = heat exchange surface ( $\text{m}^2$ )  
 $b$  = constant in eq 5  
 $C_{\text{st}}$  = stoichiometric concentration ( $\text{kg m}^{-3}$ )  
 $c_p$  = specific heat at constant pressure ( $\text{kcal K}^{-1} \text{kg}^{-1}$ )  
 $c_v$  = specific heat at constant volume ( $\text{kcal K}^{-1} \text{kg}^{-1}$ )  
 $D$  = diameter (m)  
 $D_t$  = tank diameter (m)  
 $E$  = Evaporation rate ( $\text{kg s}^{-1}$ )  
 $F_v$  = view factor  
 $Gr$  = Grashof number  
 $h$  = heat-transfer coefficient ( $\text{kcal m}^{-2} \text{K}^{-1} \text{s}^{-1}$ )  
 $k_{\text{rw}}$  = thermal conductivity of the rock wool ( $\text{kcal m}^{-1} \text{K}^{-1} \text{s}^{-1}$ )

$K$  = mass-transfer coefficient ( $\text{kg m}^{-2} \text{bar}^{-1} \text{s}^{-1}$ )

$L$  = flare length (m)

$m$  = mass (kg)

$M_{\text{air}}$  = molecular weight of air ( $\text{g mol}^{-1}$ )

$M_{\text{fuel}}$  = molecular weight of fuel ( $\text{g mol}^{-1}$ )

$Nu$  = Nusselt number

$P$  = internal pressure (bar)

$P_{\text{burst}}$  = burst pressure (bar)

$Pr$  = Prandtl number

$P_{\text{sat}}$  = vapor pressure (bar)

$q$  = thermal flux ( $\text{kcal m}^{-2} \text{s}^{-1}$ )

$Q$  = thermal power ( $\text{kcal s}^{-1}$ )

$r$  = tank radius (m)

$R$  = jet radius (m)

$S$  = mass flow rate ( $\text{kg s}^{-1}$ )

$t$  = time (s)

$t_f$  = failure time (s)

$T$  = temperature (K)

$T_{\text{sl}}$  = liquid superheat limit (K)

$W$  = wall thickness (m)

$x$  = liquid mass fraction

$z$  = distance of the target from the jet axis (m)

$\Delta H_{\text{ev}}$  = liquid heat of evaporation ( $\text{kcal kg}^{-1}$ )

$\Delta H_{\text{sh}}$  = superheating heat of the vapor ( $\text{kcal kg}^{-1}$ )

## Greek Symbols

$\alpha$  = coefficient in eq 2

$\beta$  = coefficient in eq 2

$\epsilon$  = emissivity

$\sigma$  = Boltzmann constant

$\sigma_u$  = ultimate strength (bar)

$\zeta$  = thermal diffusivity of the rock wool ( $\text{s m}^{-2}$ )

## Subscripts

$c$  = convective

$e$  = external

$f$  = fire

$i$  = internal

$j$  = liquid phase or vapor phase

$l-v$  = liquid-vapor

$\text{prop}$  = propane

$r$  = radiative

$t$  = total

$w$  = wall

## Superscripts

$1$  = liquid-vapor interface

$l-v$  = liquid-vapor

$\text{max}$  = maximum

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