BOILING LIQUID EXPANDING VAPOUR EXPLOSIONS (BLEVE); possible failure mechanisms and their consequences

J.E.S. Venart

Mechanical Engineering, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada

The detailed re-analysis of the catastrophic failures of four 4.5 - tonne water capacity LPG vessels of various fills subjected to jet fire attack indicates that the severity of the event and the intensity of the fireballs formed may be a function of the initiating mode of vessel failure and the thermo-hydraulic state of the contents. The mechanism of vessel failure appears to be a two-step process; the formation of an initiating overpressure crack in the high temperature vapour wetted walls of the vessel, followed by a final catastrophic 'unzipping' of the containment and the nearly instantaneous release of its contents. The distribution and flashing of the lading causes a fireball. The surface emissive power of the BLEVE fireball does not appear to be directly related to the 'superheat' of the contents at failure.

Possible reasons for the final rapid failure of the vessel are either crack instability, rapid overpressurization due to the dynamic 'head space' impact of the two-phase swell, and/or the rapid quenching of the crack tip, due to its two phase discharge, that results in large local thermal stresses.

Keywords: jet fires, Boiling Liquid Expanding Vapour Explosions (BLEVE), fireballs, pressure liquified gases (LPG), catastrophic pressure vessel failure, loss of containment (LOC), large scale experiments.

PREFACE

A BLEVE has been defined as 'an explosion resulting from the failure of a vessel containing a liquid at a temperature significantly above its boiling point at normal atmospheric pressure', CCPS 1994. It is the intent of this contribution to advance possible explanations for the very complex fluid structure interactions (FSI) observed in the BLEVE event and to support the hypotheses by detailed re-examinations of recent experimental data, Roberts et al 1995(a - d), and new physical interpretation and metallurgical appraisals of these same trials. The detailed re-analyses of the catastrophic failures of these four 4.5 - tonne water capacity LPG vessels with various fills subjected to jet fire attack indicates that the severity of the event and the intensity of the fireballs formed is **not** necessarily a function of the superheat of its contents but may have more to do with the initiating mode of vessel failure and the thermo-hydraulic state of the contents at final failure. The mechanism of vessel failure appears to be a two-step process; the formation of an initiating over-pressure crack in the high temperature vapour wetted walls of the vessel, followed by the final catastrophic 'unzipping' of the containment and a nearly instantaneous release of its contents. The distribution and flashing of the lading causes a fireball if the contents are flammable. The failure of the vessel and the surface emissive power of the BLEVE fireball does not appear to be directly related to the 'superheat' of the contents at failure and indeed may be most severe for conditions when the vessel fails while undergoing a pressure reduction at 'low' superheat.

Possible reasons for the final rapid failure of the vessel may be either structural instability of the vessel, rapid over-pressurization due to a dynamic 'head space' impact of the two-phase swell initiated upon a depressurization (initiated by the formation of a thermal crack or tear which arrests), and/or the rapid quenching of its crack tip, due to the two phase discharge, that results in large local thermal stresses which cause the uncontrolled vessel failure.

INTRODUCTION

A major objective of current research programs in pressure liquefied gas (PLG) safety, Roberts and Beckett 1996, has been to develop, verify and validate models for the loss of containment (LOC) failures in partially filled, accidentially heated PLG storage and process vessels whether for transport or in on- or off-shore situations (e.g. separators, blow-down tanks, etc.).

Some current work has seen the conduct of extensive and carefully designed and performed large scale field trials, Johnson et al 1990 and Roberts and Beckett 1996,, as well as other, less well characterized, smaller sized experiments, e.g. Venart et al 1993 and Birk and Cunningham 1994, in addition to the development and testing of hypotheses for the cause(s), Sumathipala et al 1992, Birk 1995, Birk and Cunningham 1996, Kielec and Birk 1997, and Miller and Birk 1997 that lead to the BLEVEs observed. Unfortunately most of this work has not been able to address the fundamental questions as to **how** the vessel fails and **why** the BLEVE event exhibits such diverse fluid-vessel reactions; failures range from total catastrophic loss of containment to only the venting of the contents through an arrested crack and a partial loss of containment. A further question is why the fireballs formed differ so markedly in form and intensity.

BACKGROUND

In the fire attack of a PLG vessel flames first heat up the vapour space walls and these increase in temperature more rapidly than the liquid wetted sides since heat transfer to them is resisted by the low thermal conductivity of the vapour and its lack of motion due to its thermal stability. On the liquid wetted walls heat transfer is initially by free convection, and later by subcooled and then saturated pool boiling; only rarely is the critical heat flux exceeded for most fluids and fire exposures. As heating progresses both the liquid and vapour portions of the lading stratify with the temperature at the liquid surface setting the vapour pressure inside the tank. With continued thermal exposure the sub-cooled liquid core can become homogeneous as boiling proceeds from sub-cooled to saturated boiling; this usually occurs within the stratified liquid zone after the pressure relief valve (PRV) opens and later within the bulk liquid upon falling pressure.

With time, the pressure rises to the set pressure of a PRV, which opens (the valve is theoretically sized to maintain the vessel at a safe pressure irrespective of its thermal exposure (API 520 1990, API 521 1993, ASME 1992 and NFPA 58 1998)). Then, dependent upon fill and heating, the valve may cycle or remain open in its attempt to maintain the pressure of the contents at its design setting. If fill is low - the liquid wetted area of the tank is small - the evaporation rate may not exceed the capacity of the valve and the pressure can remain constant with only partial valve lift or the valve may cycle. As fill increases, wetted surface area increases, and the evaporation rate now can exceed the valve's design relief capacity, especially since the exiting vapour may be severely superheated due to vapour stratification. In this case there will be an increase in pressure with time until the level falls, and along with it its evaporation rate. In all instances the opening of the valve will first depressurize the vapour which will then be followed by the formation of a two-phase swell within the now superheated liquid. If fill is sufficient, the valve intake can continue to be vapour or, with greater swell, two-phase; conditions that will vary with valve size and fire exposure (Sumathipala et al 1992).

Two-phase valve flow can be caused either by entrainment or because the vessel becomes two-phase full. In the entrained case, mist/droplet flow usually results. If the vessel becomes two-phase full, churn-turbulent bubbly two-phase flow through the valve may occur. In any case the choke pressure for such flows is greater, and the choke velocity substantially

less, than those for any prior superheated vapour flow. The pressure relieving capacity of the valve can now become compromised as the two-phase fluid exits with a much lower enthalpy, though greater density, compared to the earlier superheated vapour discharge, Sumathipala et al 1990.

With continuing fire attack the vapour metal walls weaken and commence plastic deformation at the hottest locations eventually leading to the formation of a crack which will cause further depressurization of the contents and an even greater two-phase swell of the contents. The size of initial fissure formed should be a function of the metal temperature, the fill level, and the available energy in the vapour as only it, the vapour, is immediately available to perform the necessary plastic work. Crack development during this process should be relatively slow with choked, nearly isothermal vapour flow ((, the isentropic index, is just slightly greater than one for superheated Propane vapour, Huber et al 1996) conditions being established as the crack lengthens. The crack should arrest locally in stronger, thicker and lower temperature but still very ductile metal upon the initial vapour pressure unloading, Venart 1998.

Once formed the structural stability of this opening now becomes a matter of vessel loading, the 'dynamics' of the subsequent thermo-hydraulics, exiting flow and/or the local cooling of the metal surrounding the crack. With a liquid over-pressure, a crack type of failure would most probably occur, whereas with a gas or vapour the failure is likely to be catastrophic due to the differences in the speed of sounds in the different media, liquid, vapour, or two-phase vs the speed of crack propagation. In subcooled liquid LPG the speed of sound is about 650 m/s and that of the vapour only approximately 200 m/s; in the liquid case the pressure vessel is able to 'unload' rapidly whereas in the vapour case this unloading is less rapid since the ductile crack propagation, or tearing, speed is the same order as the velocity with which the pressure wave is moving in the media. With the contents homogeneous two phase there is no unloading of the vessel as the speed of sound in the mixture is much less than that for the vapour and very much less than for the liquid and so the vessel walls cannot unload at all and any cracks will propagate the entire extent of the vessel and may indeed exhibit 'brittle' characteristics.

If, in the initial stages of crack development, mist/droplet flow issues through the opening cooling times of the adjacent hot vapour walls can be long since there will be little liquid contact with the heated metal. With sufficient fill impact of a low void fraction swell on the superheated head of the vessel and quenching of the hot metal by direct liquid contact and/or its water-hammer like pressure impulse can occur, Venart and Ramier 1998, perhaps catastrophically restarting the crack. These latter effects may be amplified by the interaction of both the thermal/hydraulic effects and the geometry of the head space (in both horizontal cylindrical and spherical vessels the vapour regions usually comprise convergent sections that lead to any crack) and the re-compression and shock of the contents, Venart and Ramier 1998 and Campbell and Pitcher 1954.

Whether the cooled crack is now stable, in a fracture mechanics sense due to its size (McClintock and Argon 1966), or becomes unstable due to pressure or fluid impact loading, and/or its imposed thermal stress (Goodier 1957) leads to differing fluid vessel interactions. On one hand we may have a long duration two-phase discharge through a stable crack with the vessel left intact. Alternatively, an apparent instantaneous catastrophic vessel failure can occur. A relatively long time two step LOC failure is also possible. Both of these latter cases will yield a BLEVE. There have been many examples of all types of these adaptive fluid-structure behaviours in the process safety BLEVE literature (e.g. Pietersen 1988).

It is our view that such a two-step process may be the **cause** of **all** BLEVEs. That is a 'leak before break' (LBB) crack initiator followed by a total loss of containment (LOC) of the PLG vessel is the normal sequence in the development of a BLEVE.

The consequence of such a progression of events is that the time delays involved can influence both the pressure at failure and the boiling process within the remaining liquid. If the contents are experiencing a continued increase in pressure, despite the additional relief provided by the crack, the bulk contents will still be sub-cooled and there will be few bubble nuclei within the fluid as boiling will only be occurring on the liquid wetted walls of the vessel. If the pressure is, however, constant or falling the contents will be homogeneously boiling and have many uniformly distributed bubbles within the bulk fluid. Catastrophic LOC under these conditions and with the liquid's abrupt depressurization and superheating allows the internal bubbles to play a significant role in the loading of the vessel **and** in the consequent development of the fireball. First since the contents are homogeneous vessel unloading is not possible due to the fact that the speed of crack propagation is greater than the speed of sound in the two-phase fluid and thus the vessel rapidly fails catastrophically. And then with the "unzipping" of the vessel, the now unconstrained high pressure bubbles expand and burst, shattering completely their surrounding superheated liquid host. The result of this will be a fine mechanically distributed high velocity evaporating aerosol. Any fireball formed from such a rapidly developing droplet cloud could thus involve the total contents of the vessel and not just the adiabatic flash fraction usually presumed for fire-ball development, Roberts 1982. The nearly instantaneous nature of its deflagration now perhaps could also develop significant over-pressures such as noted in Pietersen 1988.

Fireball characteristics (sizes, durations and surface emissive powers (SEP)) should therefor be functions not only of the mass of the liquid involved (Roberts 1982) but also the time delay from the LBB initiator to the final LOC **and** whether the LOC occurs with the contents still increasing in pressure and prior to the liquid contents becoming homogeneous. If vessel LOC occurs with a stratified liquid layer and a sub-cooled core under increasing pressure the fireball should be less buoyant and have an appreciable flash fraction and/or rainout and thus a lower SEP than in a case with dropping pressure and therefor homogeneous boiling.

Whether the vessel fails completely, as a result of severe 'quenching' of the superheated vapor-space metal, the imposed thermal stresses or the 'dynamics', i.e. the water-hammer like impact of the swell upon the already damaged shell and its fracture mechanic 'criticality', the time scales for the two-step processes envisaged could range from the near 'zero' to 10's of milliseconds (for an immediate quenching case) to the 10's of seconds (for the mist-flow cooling case). Indeed, two-step failures have been noted previously but not explained, Birk and Cunningham 1996.

Clear examples of all of the above types of BLEVEs have been found in the reexamination of the UK Health and Safety Laboratory (HSL) recent propane jet fire test records (Venart 1998). This information has been supplemented by additional analyses involving physical as well as macro and metallurgical examinations of the tank remnants, frame by frame analysis of the video records and a comprehensive thermo-hydraulic and metallurgical interpretation of the data and vessels (Venart 1996 and Sherrard 1997).

RECENT HSL LARGE-SCALE EXPERIMENTS

As part of the Commission of the European Community (CEC) Science and Technology for Environmental Protection (STEP) programme and with the United Kingdom Health and Safety Executive's (HSE) Technology and Health Sciences Division sponsorship, a joint project (STEP-CT90-098) was set up to investigate the hazard consequences of Jet-fire Interactions with **VE**ssels containing pressurized liquids (**JIVE**). The HSE's Health and Safety Laboratory (HSL) was contracted to investigate the thermal response of propane tanks when subjected to jet-fire attack and to assess the effectiveness of mitigation techniques.

The HSL's Process Safety Section undertook four field experiments on the thermal response of partially filled 4.5 tonne water capacity horizontal propane tanks to a jet fire. The jet fire consisted of an ignited, horizontal flashing liquid propane jet at a flow rate of about 1.5 kg/s from a nozzle equivalent to a 12.7 mm diameter hole. The nozzle was placed 4.5 m from the front surface and 1 m below the axial center of the tanks at about the still-air lift-off position of the flame. Vessel exposures were about 200 kW/m²; more than twice that for a fully engulfing hydrocarbon pool fire.

The target tanks were standard 1.2 m diameter 4546 litre water capacity (3864 litre propane (85% fill)) LPG vessels just over 4 m long with semi-ellipsoidal end caps. The center barrel was 3.276 m long and was constructed of two rolled and longitudinally butt welded plates with a band reinforced circumferential butt weld. The walls were almost all 7.1 mm thick low carbon low alloy steel (Bodycote 1997). The tanks were fitted with standard sized ($1\frac{1}{2}$ " NTP ASME/BS 500 3090) pressure relief valves.

All vessels were fitted with external wall thermocouples (3 mm stainless steel sheathed type K). Interior fluid temperatures, vapour and liquid, were measured on several levels at a single, near central, vertical position corresponding to the fill-level gauge connection with similar, though 1.5 mm diameter, thermocouples. Both vapour and liquid pressures were determined from remote calibrated pressure transducers. The target tank was mounted on a frame supported on four fire protected load cells; these were used to determine the variation in propane mass with PRV action.

All transducers were monitored using a remote computer data acquisition system. There were separate video (2 to 5 cameras) recordings made (Nind 1996) as well as infra red thermal image records of the fireballs formed (Hawksworth and Brearley 1996). British Gas additionally made wide- and narrow- angle thermal radiation measurements, Gosse and Pritchard 1996.

Commercial grade propane was utilized for both the jet fire fuel and tank contents. Vessel fills of 20, 41, 60, and 85 volume percent were examined under jet fire attack of the ignited flashing discharge of sub-cooled liquid propane at about 0.9 MPa.

Separate HSL documents (Roberts and Beckett 1997, Roberts et al 1995(a-d)) as well as the video records, Nind 1996 and Hawksworth and Brearley 1996, provide greater detail and archive the data obtained. Further physical, macro and micro metallurgical examinations of the tank remnants, in addition to extensive video and thermo-hydraulic analyses of the data sets, were also undertaken (Venart 1996 and Sherrard 1997) and are summarized by Venart 1998.

Vessel Failures

The vessels all failed catastrophically in less than five minutes and resulted in Boiling Liquid Expanding Vapour Explosions (**BLEVE**s) and fireballs.

Results

Detailed discussion of the results, derivations (Tables 1 to 3) and interpretations for only two of the trials, the 20% and 85% volume fills, follow; greater detail may be found in the original references and Venart 1998. Short summaries for the other trials (41 and 60 % volume fills) are also given.

Examination of the thermo-hydraulic data (Table 1) indicates that as fill level decreases time to first vent increases (multiple vents were observed for the 85% fill), the rate

of pressure increase prior to vent decreases, the rate of pressure increase after continuous venting decreases and that the pressure at failure diminishes. Most of this behavior can be explained in terms of the variation in liquid wetted wall with fill level (Sumathipala et al 1992) though some observations are in conflict with other workers, most notably Birk 1995 and his co-workers.

The times to vessel failure are similar (251 ± 28 seconds) all with comparable maximum and mean vapour wall temperatures ($810 \pm 74E$ and $611 \pm 90EC$, Table 2).

Table 3 records the sizes of the initial ruptures formed in these trials. The sizes of the openings were estimated from the tank remnants and taken to be the extent of the feather edged ruptures up to the point of fast fracture initiation as 45° shear lips with little plastic contraction. A derived equivalent Von-Mises stress (0.866 σ_{hoop}), for a vessel with end shells under pressure alone, and the rupture crack stress intensity factors at the commencement of fast fracture failure are also indicated. These indicators are, at best, only simple indicators of the actual stress and stress intensity levels due to the extreme temperature gradients present in the shell at the time of failure. There exist large radial, axial and circumferential temperature differences that impose significant local thermal strain upon the vessel (e.g. Tan et al 1999 and Tan and Venart 1999). So though approximate, and unlike the work of Kielec and Birk1997, this indicator should provide a better approximation for a failure criteria of LPG vessels under such extreme fire exposures since the 'mean' equivalent stress (142 MPa (Table 3)) does correspond to the ultimate stress at the maximum 'mean' temperature (~140 MPa at 684°C (Table 2)) for all tests. The importance of the role of the significant temperature variations in the span-wise directions of the tank's vapour walls (Table 2) should not, however, be overlooked as the source of the initiating rupture failures.

20% full trial (Tank C, Fig. 1(Roberts et al 1995 (c))

In this trial, a 1.52 kg/s flashing liquid propane jet fire brought the 20 % full tank, initially containing 453 kg of commercial propane, to failure in just over 250 seconds. The PRV opened at a pressure of 18.6 barg at 112 s and then remained partially open, venting its contents at the rate of 1.26 kg/s. At failure the pressure fell to 16.5 barg with a maximum recorded shell temperature of 870°C. Vessel failure was initiated by a longitudinal rupture just to the back side of the top of the tank. This crack was 556 mm long (Table 3) and commenced forming about 635 mm to the right of the left endcap weld some 200 mm circumferentially behind the top. Visual and video observations indicated that when the PRV operated this gave a vertical jet of flame approximately 10 m high with a lift-off distance of about 2 m. After 250 seconds the tank failed catastrophically at a pressure of 16.5 barg as this was slowly falling.

The composite figures of pressure, mass, internal fluid and exterior shell temperatures indicate that at approximately 197 s the recorded pressures (Figure 1(a)) gradually commence falling from 17.2 barg, where they had been constant for over 50 s, until at failure they were 16.5 barg. About the same instant, however, all internal temperatures (Figure 1(b)) rise at least 10 °C in about 8 s and then fall to regain their previous values or trends. These factors, in addition to the video record, suggest strongly that an initiating fracture developed, and the additional relief provided by its opening, allowed the valve to close; hence the momentary (approximately 16 s) excursion in internal temperatures. These observations suggest that the rupture crack formed around this time and then remained stable for about 40 s prior to catastrophic failure of the vessel by a fast (~ 50 ms, i.e. about one to two video frames) shear fracture.

The examination of the video records (Nind 1996) by time averaging (150 and 250 frames; 5 and 8.5 s respectively) at instances between 50 to 30 s prior to catastrophic rupture and then setting a threshold level between 150 and 160 out of 255 supports the above

possibility since the films, for all camera angles, show at least a 6 to 10 second period where there is a reduction in apparent PRV flare size and intensity for this interval; such a period very much exceeds the prior and later turbulent flare fluctuations, due to wind, and even suggests a jet with greater vertical momentum than with the original PRV discharge after crack formation. Figure 2(a) is an example of the time-averaged raw video extract for camera 2 and Figure 2(b) a similar image set with a threshold of 156 for camera 3. In both figures the reduction in flare size within the specified time frame is obvious.

The additional depressurization caused by the initial crack also helps explain the increase in liquid wetted wall temperatures of some 50 °C commencing 40 seconds prior to failure (Figure 1(c)); the progressive reduction in pressure, due to the additional area for discharge, causes more vigorous boiling and thus an increase in the fluid-wall temperature difference. There was a failure of the automatic recording system for mass and so this record (Figure 1(d)) was logged manually and little detail can be inferred from this record.

85% full trial (Tank D, Figure 3 (Roberts et al 1995 (d))

In this the last experiment of the test series, a 1.68 kg/s flashing liquid propane jet fire brought the 85 % full propane tank, initially containing 1932 kg of commercial propane, to failure in 254 seconds. The PRV opened at a pressure of 18.6 barg after 68 s and then cycled open and partially shut at least two times before remaining open (Figure 3(a)), venting its contents at the rate of approximately 1.28 kg/s. At failure the pressure was 24.4 barg with a maximum recorded shell temperature of just under 850 °C (Figure 3(c)).

Vessel failure was initiated by a small longitudinal rupture near the top of the tank. This crack, which was 290 mm long, commenced forming about 880 mm to the left of the center weld and about 50 mm circumferentially forward of the top.

Visual and video observations indicated that when the PRV operated this gave a vertical jet of flame approximately 10 m high with a lift-off distance of about 2 m. After 254 seconds the tank failed catastrophically.

The composite figures of pressure, mass, internal fluid and external shell temperatures, indicates no unusual characteristics in the recorded parameters such as were noted previously in the 20 % fill trial. However, a detailed frame by frame analysis of the video record clearly shows that the fast fracture phase of vessel failure was preceded, at about 1 to 2 seconds (approximately 25-50 video frames), with the formation of a crack which permitted a vapour and then two-phase discharge to occur through the rupture.

Figure 4 illustrates the development of the crack discharge and the resulting development of its supplemental flare taken from the frame by frame analysis of the video. At about 01:04 s, just to the left of the PRV flare, an ignited gas discharge is apparent which then proceeds to develop and enlarge (01:14 - 01:24 s), becomes two-phase (02:09 s) and somewhat diminishes (perhaps due to two-phase choking), until finally the vessel bursts just before 03:04 s. These video frame sequences seem again to confirm that a two stage process of rupture crack formation and arrest occurs prior to the catastrophic failure of the vessel by a fast plain stress shear fracture.

<u>41% and 60% full trials (Tanks A and B (Roberts et al 1995 (a) & (b))</u> In these two trials the flashing liquid propane jet fire brought the 40.9 % and 60 % full vessels to failure in just less than 5 minutes.

For the 40 % full case the PRV opened at a pressure of 18.8 barg at 130 s and then remained open, venting its contents at the rate of about 1.41 kg/s. At failure the pressure was 21.3 barg with a maximum shell temperature of just over 700 °C located near the center top of the shell. Vessel failure was initiated by a longitudinal rupture near the top of the tank and the

vessel failed catastrophically at about 285 s. This opening, which was originally 356 mm long, commenced forming about 420 mm to the right of the center weld and some 250 mm circumferentially forward of the top. The composite figures of pressure, temperatures, both interior fluid and exterior shell for this test indicated that at approximately 250 s there was an inflection point in the recorded liquid pressure and its rate of increase diminished. Further, commencing at about the same time there was an apparent progressive increase in the mass flow rate recorded through the PRV. These observations, taken with those determined from a frame by frame analysis of the visual record for two cameras, similar to that used earlier in the 20 % fill trial, indicated an increase in PRV flare size and intensity at 250 s and support the suggestion that a rupture crack formed around this time and then remained stable for some 30 s prior to catastrophic failure of the vessel. Additional, but perhaps less convincing, evidence comes from the audio track from the video for this trial; here the intensity and pitch of the PRV discharge dropped in level at about the same instance as the flare increased in intensity. This observation provides some confirmation to firemen's anecdotal adage when dealing with fires involving PLG's that 'when you hear a reduction in pitch of the PRV discharge, run like Hell!'.

In the 60% full experiment the jet fire brought the tank, originally containing 1364 kg of commercial propane, to failure in 217 seconds. The PRV opened at a pressure of 18.1 barg at 109 s and then remained open. At failure the pressure was 18.6 barg with a maximum recorded shell temperature of just under 800°C. Vessel failure appeared to have been initiated by a complex series of longitudinal rupture cracks near the top of the tank. These cracks had a combined feather-edged length of some 580 mm and commenced forming about 1200 mm to the right of the center weld and on the top center of the vessel. At 217 s the tank failed catastrophically at a pressure of 18.6 barg. On failure, the tank split into three sections with about the left hand two thirds of the vessel rocketing 447 m, an end cap being thrown 309 m and approximately one third of the barrel opening out flat in the target area. The composite figures of pressure, mass, internal fluid and external surface temperatures, indicated that at approximately 190 s the recorded liquid and vapor temperatures all dropped some 20 °C in about 15 s and then slightly recovered some 10 °C just at failure. The time averaged video record for this trial, with only one camera available for analysis is, however, less clear than in the previous instances. The observations though suggest that an opening developed about 15 seconds before failure and the crack so formed remained stable prior to catastrophic failure of the vessel by a fast shear fracture which bifurcated and caused two pieces of the tank to rocket off significant distances.

Other observations

All the vessels were fabricated from a low alloy low Carbon steel (0.21-0.25 % total C, 0.65-0.82 % Mn, 0.01-0.03 % Si, 0.015-0.021 % S, 0.014-0.035 % P, 0.02 % Cr, 0.01-0.02 % Ni, <% 0.01 Mo (Bodycote 1997)). Determined A₁ (Austenite start) and M_s (Martensite start) temperatures from these compositions were 715.8 (\pm 1.6) and 408.8 (\pm 9.3) °C respectively.

Vapour wall metal temperatures (Table 2) were extremely variable due to the impact of the jet fire. It was not unusual for temperatures to drop locally by up to 150 °C away (< 500 mm) from the initial rupture site. Metal strength would thus be affected and any over-pressure crack formed could possibly arrest in the cooler, thicker, stronger and tougher wall as the vessel unloads due to the initial local vapour depressurization prior to two-phase repressurization, Venart and Ramier 1999. The plastic deformation of selected initial crack cross sections exhibit progressive area reductions, with greater amounts occurring on the heated side Venart 1996 and Sherrard 1997. This can be attributed to wall thinning and bulging while under the initial complex triaxial stress state imposed by the internal pressure, support loads and thermal conditions. Micro-hardness examinations of the metal samples taken near the originating rupture crack tips for all four tanks showed statistically significant increases in hardness towards the crack tips. Metallographic macro and micrographs did not show any direct signs of quenching (i.e. an acicular structure of transformation products), although in earlier studies of a similar failure in a full size rail tank car transformation products were found at the sub-critical crack initiation region along with similar increases in hardness, Anderson and Norris 1974.

In the B (60% fill) tank samples a circumferential rolling direction for the plate forming the section of the barrel where the cracks originated was indicated (Venart 1996). The originating ruptures formed in this section may thus be possibly linked to the early crack bifurcation which was unique to this trial. This process caused a portion of the tank to circumferentially separate and rocket nearly 450 meters. It is well known that fracture toughness is a function of plate rolling direction; the low toughness direction is parallel to the rolling direction. In previous work on gas and liquid pressurized lines significant variations in strength and toughness were observed due to rolling direction sufficient to cause the bifurcation of longitudinal cracks so to form guillotine breaks (Wilkowski 1991) similar to the case of the 60 % full vessel.

<u>Summary</u>

The thermo-hydraulic, metallurgical and video film evidence for these experiments indicate that crack development and propagation during vessel failure occurred in two distinct steps:

- a rupture stage, where a crack opens up and becomes stable forming an opening for a vapour or two-phase jet discharge additional to that of the PRV,
- a final fast fracture stage, where the initial crack rapidly propagates into the metal as a plain stress shear failure along (usually) the entire length of the tank and then circumferentially at the end caps, and,
- rolling direction of the shell appears to be implicated in the 'rocketing' for one vessel.

The consequence of this type of failure is called a BLEVE (Boiling Liquid Expanding Vapour Explosion). The process causes the remaining contents of the vessel to be rapidly released as a superheated liquid aerosol which may then ignite and form a fireball.

Fireball Characteristics

The fireball characteristics, Table 4, show that as the mass of material involved in the BLEVE increases, the duration and size of the fireball becomes larger; however, its shape becomes less spherical and more vertically elongated. From the video analyses it is also apparent that there is a greater ground flash fraction for large fills and these require significant times before ignition. The mean Surface Emissive Powers (SEP) of the fireballs, at their maximum size, also decreases despite the significant increases in saturation pressure, and thus liquid superheat of the contents. The 85 % fill fireball develops much slower and exhibits both an average and a top 10 % SEP (max) that is nearly 20 % less than that exhibited in the 20 % fill experiment contrary to the expectation of the models of Roberts 1982, Shield 1993 and recent evidence from both deflagrating and detonating fuel - air clouds, Dorofeev et al 1995 and Makhviladze et al 1999.

DISCUSSION and CONCLUSION

The analyses and interpretations of the HSL JIVE tank failure data present a coherent and plausible case that can best be explained by the formation of a fracture which arrests and then

is re-initiated for some reason and now becomes critical. For the transitions to fast fracture that were observed in all these experiments, there must be some physical reason for crack reinitiation. Once cracks are arrested in a ductile material, re-initiation requires significant further energy. It is our view that the thermo-hydraulic, video and physical data support the possibility of a crack tip quenching mechanism as the most probable cause; the metallurgical data for this is less conclusive despite some earlier supporting evidence, however.

Taken together the situation described is not unlike that envisaged in the highly transient 'rewet' situation in high heat flux forced convective boiling; however, it now occurs within a stressed and damaged pressure vessel. The dependence of the time delay on liquid fill would appear to be a function of the heat transfer and the distance to the boiling LPG surface. Due to entrainment, flow through the initial rupture crack could be 'mist/droplet' two-phase flow in the case of low fills or for fills greater than about 50 percent 'churn-turbulent bubbly' flow. In this latter case impact of the two-phase swell on the hot vapour space walls, as a result of the additional pressure relief from crack formation, may be possible and very rapid cooling of the metal surface could therefore take place due to direct liquid-metal contact.

The influence of such a two-step vessel failure on fireball formation appears to be significant. Some of the observations made here contradict earlier works based upon liquid superheat and the results from single step failures and thus will have importance to the design of further experiments and the development of realistic fireball and BLEVE models.

ACKNOWLEDGMENT

The experimental field work described and interpreted here was performed as part of the Commission of the European Community (CEC) Science and Technology for Environmental Protection (STEP) program and with the United Kingdom Health and Safety Executive (HSE) Technology Sciences Division sponsorship. The programme (STEP-CT90-098) investigated the hazard consequences of Jet-fire Interactions with VEssels containing pressurized liquids (JIVE). Dr. T.A. Roberts, HSL, Buxton, provided access to the data sets and gave permission for the removal of samples and the metallurgical examinations. Marc LeBlanc and Jennifer Sherrard helped in the preparation and analyses of the metallographic and hardness specimens. Dr. C. Thornley, New Brunswick Research and Productivity Council, assisted in part of the examination and analyses of the metallographic samples. The views and interpretations put forward in this contribution are those of the author alone.

REFERENCES

Anderson, C & Norris, E B, 1974, "Fragmentation and metallurgical analysis of tank car RAX 20", Report No. FRA-OR&D 75-30, US DoT, FRA, April.

API, 1990, "Guide for pressure-relieving and depressuring systems", API Recommended Practice 521, 3rd Ed., Washington, DC, Nov..

API, 1993, "Sizing, selection, and installation of pressure-relieving devices in refineries, Part 1- Sizing and selection", API Recommended Practice 520, 6th Ed., Washington, DC, July.

ASME, 1992, "ASME boiler and pressure vessel code, Section VIII, Rules for construction of pressure vessels, Division 1", ASME, New York, NY, July.

Birk, A M, 1995, "Scale Effects with Fire Exposure of Pressure-Liquefied Gas Tanks", J. Loss Prev. Process Ind., **8**, 5, pp. 275-290.

Birk, A M & Cunningham, M H, 1994, "The Boiling Liquid Expanding Vapor Explosion", J. Loss Prev. Process Ind., **7**, 6, pp. 474-480.

Birk, A M & Cunningham, M H, 1996, "Liquid Temperature Stratification and its Effect on BLEVEs and their Hazards", J. Hazard. Materials, **48**, pp. 219-237.

Bodycote Materials Testing, 1997, Chemical Test Reports, Galt Laboratory, Aug. 26.

Campbell, I J & Pitcher, A S, 1958, "Shock waves in a liquid containing gas bubbles", Proc. Roy. Soc. A 243, pp 534-545.

CCPS, 1994, <u>Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash</u> <u>Fires and BLEVEs</u>, Center for Chemical Process Safety, AIChE, New York, NY, p 6.

Dorofeev, S B, Sidorov, V P, Efimenko, A A, Kochurko, A S, Kuzenetsov, M S, Chaivanov, B B, Matsukov, D I, Pereverzev, A K & Avenyan, V A, 1995, "Fireballs from Deflagration and Detonation of Hetrogeneous Fuel-rich Clouds", Fire Safety Journal, **25**, pp 323-336.

Goodier, J N; 1957, "Thermal Stress and Deformation", J. Appl. Mech., Trans. ASME, Sept. pp. 467-474.

Gosse, A J & Pritchard, M J, 1996, "A study of the radiative characteristics of the fireball produced following the BLEVE failure of a pressurised LPG vessel; a record of measurements made by British Gas as part of a CEC co-funded research project", British Gas Report GRC R 1197, January.

Hawksworth, S J and Brearley, D, 1996, "Thermal Imaging of Propane fireballs as part of the hazardous consequences of jet-fire interactions with vessels containing pressurised liquids project", HSL Report R04.029, IC/06/01, Feb.

Huber, M, Gallagher, J, McLinden, M & Morrison, G, 1996, "NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP)", Ver. 5.0, Feb., U.S. Dept. of Commerce, NIST, SRDP, Gaithersburg, MD

Johnson, D M, Pritchard, M J & Wickens, M J, 1990, "Large Scale Catastrophic Releases of Flammable Liquids", British Gas Report to the CEC, Contract EV4T.0014.UK.

Kielec, D J & Birk, A M, 1997, "Analysis of fire induced ruptures of 400-L propane tanks" ASME J Pressure Vessel Technology, **119**, pp365-373.

Makhviladze, G N, Roberts, J P & Yakush, S E, 1999, "Combustion of two-phase hydrocarbon fuel clouds released into the atmosphere", Combustion and Flame, **118**, pp 585-605.

McClintock, F A & Argon, A S, (Eds.), 1966, <u>Mechanical Behavior of Materials</u>, Addison-Wesley, Reading, MA.

Miller, T & Birk, A M, 1997, "A re-examination of propane tub rockets including field trial results", ASME J Pressure Vessel Technology, **119**, pp 356-364.

Nind, M J, 1996, "Video record BLEVE Tests (Great Longstone); all camera views from ignition to explosion", HSL Visual Presentation Services, Sheffield, UK, January, 1995 and video July.

NFPA, 1998, "NFPA 58, Liquefied Petroleum Gas Code", National Fire Protection Association, Inc., Quincy, MA.

Pietersen, C M, 1988, "Analysis of the LPG-Disaster in Mexico City", J. Hazard. Materials, **20**, pp. 85-107.

Roberts, T, Beckett, H, Cooke, G & Brown, D, 1995 (a), "Jet fire impingement trial on a 41% full, unprotected, 2 tonne Propane tank", HSL Report R04.029, IR/L/PH/95/11, Buxton, UK, July.

Roberts, T, Beckett, H, Cooke, G & Brown, D, 1995 (b), "Jet fire impingement trial on a 60% full, unprotected, 2 tonne Propane tank", HSL Report R04.029, IR/L/PH/95/12, Buxton, UK, Aug.

Roberts, T, Beckett, H, Cooke, G & Brown, D, 1995 (c). "Jet fire impingement trial on a 20% full unprotected, 2 tonne Propane tank", HSL Report R04.029, IR/L/PH/95/13, Buxton, UK, Oct.

Roberts, T, Beckett, H, Cooke, G & Brown, D, 1995 (d), "Jet fire impingement trial on a 85% full, unprotected, 2 tonne Propane tank", HSL Report R04.029, IR/L/PH/95/14, Buxton, UK, Oct.

Roberts, T & Beckett, H, 1996, "Hazard Consequences of Jet-fire Interactions with Vessels Containing Pressurised Liquids: Project Final Report", HSL Report R04.029, PS/96/03, Buxton, UK, Feb.

Roberts, A F, 1982, "Thermal radiation hazard from releases of LPG from pressurised storage", Fire Safety Journal, 4, pp. 197-212.

Sherrard, J, 1997, "Metallurgical and physical measurements of HSL JIVE samples", unpublished work, UNB FSC, Fredericton, NB, Sept.

Shield, S R, 1993, "A model to predict the radiative and blast hazards from LPG BLEVE's", AIChE Symp. Ser., **89**, pp 139-149.

Sumathipala, K, Venart, J E S & Steward, F R, 1990, "Two-phase swelling and entrainment during pressure relief valve discharge", J. Hazardous Materials, **25**, pp 219-236.

Sumathipala, K, Hadjisophocleous, G, Aydemir, N, Yu, C, Sousa, A, Steward, F & Venart, J E S, 1992, "*Fire Engulfment of Pressure-Liquefied Gas Tanks: Experiments and Modelling*", ASTM **STP 1150**, <u>Fire Hazard and Fire Risk Assessment</u>, pp. 106-121.

Tan, D M, Sollows, K F, & Venart, J E S, 1999, "Dragon: LPG Rail Tank Failure Analysis", ASME **PVP 396** (Ed. W L Cheng), pp.121-128.

Tan, D M & Venart, J E S, 1999, "LPG Tank Failure: Ste. Elizabeth de Warwick, Quebec, June 27, 1993; the lessons to be learnt", ASME **PVP 396** (Ed. W L Cheng), pp. 129-136.

Venart, J E S, 1996, "HSL JIVE Tank Failures; Physical and Metallurgical Examinations", UNB Fire Science Centre, UNB FSC: R-96-09-23 (revised), Fredericton, NB, Nov. 7.

Venart, J E S, 1998, "Boiling Liquid Expanding Vapor Explosions (BLEVE): possible failure mechanisms", ASTM **STP 1336**, <u>Very Large-Scale Fires</u> (Eds. N R Keltner et al), pp 112-132.

Venart, J E S & Ramier S A, 1998, "Boiling Liquid Expanding Vapor Explosions: the influence of dynamic re-pressurization and two-phase discharge", ASME **PVP 377-2** (Eds. C R Kleijn and S Kawano), pp 249-254.

Venart, J E S, Rutledge, G A, Sumathipala, K & Sollows, K, 1993, "To BLEVE or Not to BLEVE: anatomy of a Boiling Liquid Expanding Vapor Explosion", AIChE Process Safety Progress, **12**, 2, pp. 67-70.

Venart, J E S, Yu, C M & Xiao, J, 1999, "*PLGS99*", A thermo-hydraulic code to represent the thermal response of pressure liquefied gas vessels under fire attack, University of New Brunswick, Department of Mechanical Engineering.

Wilkowski, G M, 1991, "Anisotropic fracture toughness effects on failure modes of piping", ASME Journal of Pressure Vessel Technology, **113**, pp 154-158.

TABLE 1. Thermo hydraune Response of JIV E Vessels.							
Tank (fill %)	C (20)	A (41)	B (60)	D (85)			
1. Valve operation							
(a) cycles	1	1	1	1	2	3?	open
(b) $(P/T)_{initial}$ (barg/°C)	7.9/19	8.4/20	7.7/20	8.7/18			
(c) P _{open} (barg)	18.6	18.8	18.1	18.3	16.0	14.8	
(d) P _{close}	17.2	16.5	14.1	13.9	-	-	
2. Pressurization (dP/dt)							
(a) before valve open	0.095	0.092	0.106	0.15	-	-	
(b) after valve open	-ve	0.035	0.047				0.066

TABLE 1. Thermo-hydraulic Response of JIVE Vessels

TABLE 2. JIVE Vessel Thermal Response at Failure.

Tank (fill %)			C (20)	A (41)	B (60)	D (85)
Tank-wall thickness (mm)		7.1	7.5	7.1	7.1	
Liquid space outside metal temperatures (°C)		257±47	141±68	116±24	159±27	
Vapour	Front	T _{mean}	711±93	645±46	559±49	734±89
space		T _{min}	516	573	485	644
metal		T _{max}	870	704	641	848
temperatures						
(°C)						
	Back	T _{mean}	564±86	424±136	646±94	663±112
		T _{min}	479	304	531	508
		T _{max}	697	694	798	848
Failure Pressure (barg)		16.5	21.3	18.6	24.4	

TABLE 3: Initial crack size, failure stress and stress intensity factor; JIVE Tanks

Tank (fill %)	P _{fi} (barg)	t (mm)	σ_{eq} (MPa)	a _c (mm)	$\mathbf{K_1} \left(\mathbf{MPa} \sqrt{\mathbf{m}} \right)$
C (20)	17.2	7.1	126	278	166
A (41)	20	7.5	138	178	146
B (60)	17.5	7.1	128	290	174
D (85)	24	7.1	176	145	168
			mean		164±12

Legend:

Legend: $P_{f_i} \equiv$ initial failure pressure; $t \equiv$ wall thickness; $\sigma_{eq} \equiv 0.866(\sigma_{hoop})$; $K_1 \equiv$ equivalent elastic stress intensity factor (($K_1 = Y\sigma\sqrt{\pi a_c}$) $2a_c \equiv$ measured size of initial crack)

Tank (fill %)	Mass (kg)	SEP (kW/m ²)		duration (s)	diameter (m)	Height (m)	
		mean	max				
C (20)	279	410	640	3.5	45	45	
A (41)	710	278*	484*	5.5	45	70	
B (60)	1272	365	550	6.5	55	75	
D (85)	1708	350	580	7	45	45	
*British Gas Measurements							

Table 4. Fireball Surface Emissive Powers (SEP), duration and size



Figure 1. Selected composite results 20% fill trial: (a) pressure, (b) interior temperatures, (c) exterior wall temperatures, and (d) mass (manually logged): Roberts et al 1995 (c).



Test 3 - Camera 2 (Average for 8.5 sec.)

Figure 2(a). Time averaged (255 frame) raw video of PRV/crack jet fire, Camera 2, 20% fill, 50, 40, 35 and 30 s before catastrophic BLEVE failure.



Test 3 - Camera 3 (Average for 5 sec.)

Figure 2(b). Threshold (149) of time averaged video, Camera 3, 20% fill.



Figure 3. Selected composite results 85% fill: (a) pressure, (b) interior temperatures, (c) exterior wall temperatures, and (d) mass (manually logged); Roberts et al 1995 (d).



Figure 4. Selected video frame sequences; 85% fill PRV and crack discharge flares, time in seconds to commencement of BLEVE.