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Annex 1

The boiling liquid expanding vapour explosion (BLEVE): Mechanism, consequence assessment, management (Abbasi & Abbasi, 2006)



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The boiling liquid expanding vapour explosion (BLEVE): Mechanism, consequence assessment, management

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Abstract

Among the most devastating of accidents likely in chemical process industry is the boiling liquid expanding vapour explosion (BLEVE). It is accompanied by highly destructive blast waves and missiles. In most situations there is also a fireball or a toxic gas cloud. The damaging effect of BLEVEs is reflected in the fact that the 80-odd major BLEVEs that have occurred between 1940 and 2005 have claimed over a 1000 lives and have injured over 10,000 persons besides harming property worth billions of dollars. Release of toxic chemicals like chlorine and phosgene from BLEVEs have damaged large chunks of areas surrounding the BLEVE site.

This paper presents an overview of the mechanism, the causes, the consequences, and the preventive strategies associated with BLEVEs. © 2006 Elsevier B.V. All rights reserved.

Keywords: BLEVE; Fireball; Missiles; Blast wave; Domino effect

1. Introduction

1.1. Definition of BLEVE

The Centre for Chemical Process Safety [1] has defined boiling liquid expanding vapour explosion (BLEVE) as 'a sudden release of a large mass of pressurized superheated liquid to the atmosphere'. The sudden release can occur due to containment failure caused by fire engulfment, a missile hit, corrosion, manufacturing defects, internal overheating, etc. According to Birk and Cunningham [2] 'a BLEVE is the explosive release of expanding vapour and boiling liquid when a container holding a pressure-liquefied gas fails catastrophically'. They have further defined 'catastrophic failure' as the sudden opening of a tank to release its contents nearly instantaneously. The sudden release from confinement of a hitherto pressurized and liquefied vapour causes instantaneous and explosive boiling–vaporization, leading to a series of cataclysmic impacts.

A BLEVE gives rise to the following [1,3-5]:

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

After the Flixborough disaster which had destroyed most of the caprolactam plant of M/s Nypro Ltd. in 1974 [3,6], great attention was focused on vapour cloud explosions (VCEs) till Kletz [7] pointed out that BLEVEs can cause as much loss of life and property as VCEs and should not be neglected. This view is justified when we look at the record of accidents before and after Flixborough. Indeed one of the biggest accidents in chemical process industry – which occurred at the LPG plant at Mexico City in 1984 claiming over 650 lives – involved a succession of BLEVEs [3,4].

1.2. Coinage of the term BLEVE

The acronym BLEVE was coined in 1957 by three Factory Mutual Research Corporation workers J.B. Smith, W.S. Marsh,

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and W.L. Walls [8]. They had analyzed the likely mode of failure of a vessel containing an overheated mixture of formalin and phenol, and had believed that the container had suffered a 'boiling liquid expanding vapour explosion' [9]. Later, Walls [10,11] defined BLEVE as 'a failure of a major container into two or more pieces, occurring at a moment in time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure'. Even though BLEVE is now firmly entrenched in the lexicon of risk assessment, its appropriateness has been questioned from time to time. According to Marshall [12], the UK-based Institute of Chemical Engineering (IChemE) had advised that the term BLEVE is 'an acronym of uncertain meaning, and its usage should be avoided'. Reid [13] had defined BLEVE as 'the sudden loss of containment of a liquid that is at a superheated temperature.' Even though this definition served as a reference point for BLEVE through several years, the Centre for Chemical Process Safety [8] has reverted to the Wall's definition with the modification that 'failure of a major container into two or more pieces' has been replaced by 'failure of a vessel' [8]. Venart et al. [14] had coined the term BLCBE (boiling liquid collapsed bubble explosion) to describe one of the variants of BLEVE.

2. Mechanism of BLEVE

McDevitt et al. [15], Prugh [16,17], Leslie and Birk [18], Lees [3], Birk and Cunningham [2,19], Casal et al. [5] and Venart [20], among others, have given elaborate description of the occurrences which lead to a BLEVE. Based on their observations, and of Reid [21], Shebeko et al. [22] and Birk et al. [23], the steps involved in a typical BLEVE can be identified as under:

(a) A vessel containing pressurized liquid gas (PLG) receives heat load or fails due to a missile hit, fatigue, or corrosion. If a vessel containing 'pressure-liquefied gas (PLG)', in other words a liquid confined at a temperature above its atmospheric pressure boiling point, gets accidentally heated - say from the heat radiation emanating from a nearby fire the pressure inside the vessel begins to rise. When this pressure reaches the set pressure of the pressure relief valve, the valve operates. The liquid level in the vessel falls as the valve releases the liquid vapour to the atmosphere. The liquid is effective in cooling that part of the vessel wall which is in contact with it, but the vapour is not. The proportion of the vessel wall which has the benefit of liquid cooling falls as the liquid vaporizes. After a time, the portion of the metal which is not cooled by liquid also becomes exposed to the heat load, weakens, and may then rupture. This can occur even though the pressure relief valve may be operating correctly.

A vessel may also fail even in absence of fire-engulfment if it is accidentally hit by missiles originating from another vessel exploding nearby – as it happened during the serial explosions in the LPG facility at Mexico City [4,24,25] – or other forms of mechanical failure such as gland/seal loss, sample line breakage, fatigue, or corrosion [26].

- (b) The vessel fails. A pressure vessel is designed to withstand the relief valve set pressure, but only at the design temperature conditions. If the metal has its temperature raised due to heat load exerted by a nearby fire, it may lose strength sufficiently to rupture. For example, the steel normally used to build LPG vessels may fail when the vessel is heated to ~650 °C and its pressures reaches ~15 atm. The vessel may also rupture due to mechanical failure as stated in the preceding paragraph.
- (c) There is instantaneous depressurization and explosion. When a vessel fails, there is instantaneous depressurization. The liquid inside the vessel, which hitherto was at a temperature corresponding to a high pressure, is suddenly at atmospheric pressure but at a temperature well above the liquid's atmospheric pressure boiling point. In other words the liquid is superheated. But there is a limit - different for different liquids - up to with liquids can withstand superheating. If the temperature of the liquid in the suddenly depressurized vessel is above this 'superheat limit temperature' (SLT), there will be instantaneous and homogeneous nucleation. It would cause a sudden and violent flashing of a large portion of the liquid, resulting in a 'boiling liquid expanding vapour explosion' (BLEVE). This would occur within 1 ms of depressurization, causing a massive release of liquid-vapour mixture. If the liquid in a suddenly depressurized vessel is below its SLT, but is in a state of 'significant superheat', a BLEVE would still occur because factors such as depressurization waves agitating the liquid when the vessel first develops a crack, and presence of likely heterogeneous nucleation sites, would cause the explosive boiling-cum-vaporization which triggers BLEVE [26].

Prugh [16,17], was among the firsts who stressed that a BLEVE can occur even for initial temperatures below the superheat limit, but stated that the higher TNT (trinitrotoluene) equivalent for BLEVE occurs near or above the superheat limit temperature (SLT). Birk and Cunningham [2] state that BLEVEs have been observed with propane when the pressure-liquefied gas was at ambient temperature (20°C), well below its atmospheric superheat limit temperature of 53 °C. However, like Prugh [16,17], they, too, recognize that for violent, explosive, boiling to take place, there must be the potential for superheat in the liquid when it is suddenly exposed to a pressure below its saturation pressure as a result of the initial tank failure. Indeed the superheat aspect becomes implicit if the material under reference is a pressure liquefied gas (PLG)-i.e. a substance which would have been in gaseous state at atmospheric pressure but is held as liquid in a pressurized container. Numerous industrial chemicals such as liquid petroleum gas, compressed natural gas, liquefied chlorine, etc., confirm to this definition. So does superheated water in a boiler.

(d) The vessel is shattered. The suddenly vaporizing liquid – with several hundred-fold to over a thousand fold increase in its volume – plus the expansion of the already existing vapour, generate a powerful overpressure blast wave. The magnitude of the blast wave is much higher than the one caused by a vapour cloud explosion occurring in an identical

quantity of material. The vessel is shattered and its pieces are propelled outwards. Some of the liquid may be splashed and hit the ground nearby forming short-lived pools before vaporizing. These pools may be afire if the liquid happens to be flammable.

The shattering of the vessel sends big and small fragments shooting at high velocities in all directions. The missiles can, and often do, damage other vessels storing liquefied gas under pressure, causing them to undergo BLEVE as well. This 'domino effect' [27,28] was witnessed at its most tragic worst at the Mexico City in 1984, causing the largest number of loss of lives ever occurred in an explosion-cumfire accident in a process industry. At times a large part of the vessel itself turns into a missile and is shot over long distances. For example, at port Newark, a portion of a sphere went flying over 800 m and demolished a petrol bunk on which it landed.

(e) There is fireball or toxic dispersion. If the substance involved is not combustible or toxic, such as water in boilers - the pressure wave and the missiles are the only effects of the explosion. But if the substance is flammable, as is often the case, the mixture of liquid/gas released by the explosion catches fire, giving rise to a fireball. Past accidents analysis – such as the one reported by Prugh [16,17] covering 'notable BLEVE accidents (1926–1986)' and the compilation made by Lees [3]—reveal that over two-thirds of all BLEVEs involve flammable chemicals. With such chemicals, a BLEVE is almost always followed by a fireball, causing massive damage due to the intense thermal radiation that ensues. The shape, the size, and the heat load exerted by the fireball are a function of numerous factors. It may so happen that the whole mass of fuel can burn only at its periphery because there is no air inside the mass (the mixture being outside the flammability limits). Further, not all the fuel initially contained in the tank may be involved in the fire; some of the material might escape (from a crack or other opening in the vessel) before the explosion [5]. Some of the fuel may be entrained in the wake formed by the flying fragments. In the BLEVE disasters, such as the ones that occurred at Mexico City in 1984, and at Sydney in 1990—fragments of shattering vessels carried with them portions of the flammable liquid, causing fires all around and jeopardizing other vessels.

As the fireball grows, the turbulence of the fire entrains air into the fireball. Simultaneously the thermal radiation vaporizes the liquid droplets and heats the mixture. As a result of these processes, the whole mass turbulently increases in volume, evolving towards an approximately spherical shape that rises, leaving a wake of variable diameter. Such fireballs can be very large, causing a very strong thermal radiation [29,30].

The size, the life, and the radiation intensity of a fireball may also depend on the temperature of the liquid lading [31], and whether the loss of confinement of the flammable material had occurred when the pressure inside was still rising [32]. The BLEVE fireballs are spheroidal when fully developed; on lift-off they acquire a mushroom-like shape. Fireballs resulting from

two-step BLEVEs may be approximately ellipsoidal in shape [31].

Toxic dispersion. BLEVE accidents have occurred involving ammonia [5], chlorine [12], chlorobutadiene [6], and phosgene [12] wherein the explosion did not cause a fireball but was accompanied by dispersion of toxic material. Indeed of the one-third past BLEVE events not involving flammable liquids, the majority have been associated with toxic gases—chlorine (14%), ammonia (10%), and phosgene (2%) account for 76% of the BLEVEs involving non-flammables. With such chemicals, fatalities have been caused by the toxic clouds that accompanied the blast wave and the missiles when BLEVE occurred. BLEVEs without any fire or toxic dispersion have also occurred—involving carbon dioxide and water [4,6,24,25]. These authors believe that a lot of boiler explosions – and such explosions are far more common than explosions involving other chemicals - are BLEVEs, though not commonly acknowledged as such. Indeed if the boiler explosions which occur when holding superheated water are included in the BLEVE tally, it may well turn out that the substance most frequently involved in BLEVEs is none other than water!

Among major BLEVEs with toxic dispersion, the maximum cases have involved chlorine, accounting for 138 fatalities during 1926–1981 [16], followed by ammonia (49 fatalities in the corresponding period).

According to Lees [3], it is possible, though not common, for a BLEVE event not caused by an engulfing fire to provide the source for a large vapour release leading to a flash fire or a vapour cloud explosion.

3. Illustrative case histories

A few instances which illustrate the variety of situations under which BLEVEs have occurred and the destruction BLEVEs normally cause, are presented below. These and some other major BLEVE events that have occurred over the last 80 years are catalogued in Table 1.

3.1. BLEVEs involving stationary installations of flammable chemicals

3.1.1. Butane storage spheres, Montreal

On 8 January 1957, a leak occurred in an 800 m³ sphere storing butane at an installation at Montreal, Canada. The sphere had been overfilled due to a faulty level gauge, resulting in the leak. The escaping butane formed a vapour cloud which met with an ignition source, probably at a service station 180 m away. The flame flashed back to the leaking sphere, where a pool fire started. The heat load softened a 1900 m³ sphere located close by, which underwent a BLEVE within 30 min of the start of the pool fire. In other 15 min the 800 m³ sphere and another adjacent sphere of 2400 m³ capacity also exploded, causing devastation all round [33].

3.1.2. LFG storage farm, Feyzin

A leak in a propane storage sphere on 4 January 1966 at Feyzin, France led to one of the worst incidents involv-

Table 1 An illustrative list of some of the major BLEVEs (1926–2004)

An illustrative list of son	ne of the major BLEVEs (1926–20	04) 		0 (1 (tannon)	Death (d), injured (i)
Date	Location	Cause	Material	Quantity (tonnes)	
13 December 1926	St. Auban, France	Overfilling	Chlorine	25	19d 11d, 171i
28 May 1928	Hamburg, Germany	Runaway	Phosgene	10	· · · · · · · · · · · · · · · · · · ·
10 May 1929	Syracuse, NY, USA	Explosion (H2)	Chlorine	25	1d
24 December 1939	Zamesti, Romania	Overfilling	Chlorine	10	60d
29 July 1943	Ludwigshafen, Germany	Overfilling	Butadiene	16	57d
5 November 1947	Rauma, Finland	Overfilling	Chlorine	30	19d
28 July 1948	Ludwigshafen, Germany	Overfilling	Ethyl ether	33	209d
7 July 1951	Port Newark, NJ, USA	Fire	Propane (70)	2600	14i
•	Walsum, W. Germany	Overfilling	Chlorine	15	7d
4 April 1952	Institute, WV, USA	Runaway	Acrolein	20	-
4 June 1954	Ludwigshafen, FRG	Railroad accident	LPG	a	2i
1955 1955	Cottage Grove, OR, USA	Storage vessel failure	LPG	a	12d, 13i
1057	Montreal, Canada	Fire	Butane	5100	1d
8 January 1957		Overfilling	Butane	55	1d
1958	Michigan, USA	Damage (Derail)	Propane	55	23d
28 June 1959	Meldrin, GA, USA	Fire	Gasoline	70	5d
18 August 1959	Kansas City, MO, USA	LPG	Storage cylinder	a	2i
1959	McKittrick, CA, USA	Li	(six on site)		
	D D VV IIOA	Runaway	Ethylene oxide	25	1d
17 April 1962	Doe Run, KY, USA	Fire	Propane	1000	18d, 83i
4 January 1966	Feyzin, France	Fire (Derail)	Ethylene oxide	NA	5i
1 January 1968	Dunreith, IN, USA	Mechanical	Ammonia	20	5d
21 August 1968	Lieven, France	Overfilling	Carbon dioxide	35	9d
2 January 1969	Repcelak, Hungary	Fire (Derail)	Propane	65	2d, 976i
25 January 1969	Laurel, MS, USA	Damage (Derail)	Ammonia	65	8d
18 February 1969	Crete, NB, USA		Ammonia	a	a
1969	Cumming, IA, USA	Damage (Derail)	Vinyl chloride	55	
11 September 1969	Glendora, MS, USA	Fire	Propane (5)	275	66i
21 June 1970	Crescent City, IL, USA	Fire (Derail)	Ethylene	4	1
19 January 1971	Baton Rouge, LA, USA	Overpressure	Vinyl chloride	50	1d, 50i
19 October 1971	Houston, TX, USA	Fire (Derail)	Propane	28	NA
9 February 1972	Tewksbury, MA, USA	Collision		1000	37d
30 March 1972	Rio de Janeiro, Brazil	Fire	Propane	18	2d
21 September 1972	NJ Turnpike, NJ, USA	Collision	Propylene Carbon dioxide	0.01	
27 November 1972	San Antonio, TX, USA	Corrosion		9	2d, 5i
1972	Lynchburg, VA, USA	Propane	Road tanker	a	37d, 53i
1972	Rio de Janeiro, Brazil	LPG	Storage spheres		374, 331
			(five on site) and		
			cylinders	100	13d, 95i
5 July 1973	Kingman, AZ, USA	Fire	Propane		4d
11 January 1974	W. St. Paul, MN, USA	Fire	Propane	27	25i
12 February 1974	Oneonta, NY, USA	Fire (Derail)	Propane (4)	288	231
29 July 1974	Pueblo, CO, USA	Fire (test)	Propane	80	_ 16d
29 April 1975	Eagle Pass, TX, USA	Collision	Propane	18	
14 December 1975	Niagara Falls, NY, USA	Runaway	Chlorine	20	4d
1975	Des Moines, IA, USA	LPG	Rail tank car	a	3i
11 May 1976	Houston, TX, USA	Collision	Ammonia	20	6d
31 August 1976	Gadsden, AL, USA	Fire	Gasoline	4	3d
1976	Belt, MN, USA	LPG	Rail tank car	80	22i
1977	Cartegna, Columbia	Overpressure	Ammonia	ä	30d
1977	Dallas, TX, USA	Isobutene	Rail tank car	a	1i
1977	Goldona, VA, USA	LPG	Rail tank car	70	2d, 9i
22 February 1978	Waverly, TX, USA	Damage (Derail)	Propane	45	16d, 43i
11 July 1978	San Carlos, Spain	Overfilling	Propylene	25	211d
30 May 1978	Texas City, TX, USA	Fire	Butanes (6)	1500	7d, 10i
	Donnellson, IA, USA	LPG	Pipeline	435	2d, 2i
1978	Good Hope, LA, USA	Ship collision	Butane	120	12d
30 August 1979	Pazton, TX, USA	Chemicals	Rail tank car	a	8i
1979	Los Angeles, CA, USA	Gasoline	Road tanker	a	2d, 2i
1979		Damage (Derail)	Chlorine (2)	110	29d
1 August 1981	Montanas, Mexico	Overheating	Water	0.3	7d
19 January 1982	Spencer, OK, USA	Runaway	Acrolein	250	**
11 December 1982	Taft, LA, USA	Runaway	Chlorobutadiene	1	3d
12 July 1983	Reserve, LA, USA	Lunaway			

Table 1 (Continued)

Date	Location	Cause	Material	Quantity (tonnes)	Death (d), injured (i
4 October 1983	Houston, TX, USA	Overfilling	Methyl bromide	28	2d
19 November 1984	Mexico City, Mexico	Fire	Propane (20)	3000	650d, 6400i
1984	Romeoville, IL, USA	Propane	Process vessel	- 24	15d, 22i
28 January 1986	Kennedy Space Center, FL,	Fire	Hydrogen	115	7d
20 January 1700	USA				
1 April 1990	Boral LPG distribution depot,	Fire	LPG	>240	35,000 affected
	Sydney, Australia				
1 April 1990	Cairns gas terminal,	Fire	LPG	a	1d
1	Queensland, Australia				
28 August 1992	Japan	Damage	Nitrogen	ä	\$5 million loss
August 1993	Panipat, India	Pressure build-up	Ammonia	a	6d, 25i
19 April 1993	Waco, TX, USA	Fire	LPG	a	¥
27 June 1993	Quebec, Canada	Fire	Propane	2.3	4d, 7i
4 March 1996	Weyauwega, WI, USA	Derailment	Propane, LPG	a	· 55
18 March 1996	Palermo, Italy	Collision in a	Propane	a	5d, 25i
	-	highway tunnel			
2 October 1997	Burnside, IL, USA	Fire	LPG	3.8	2d, 2i
9 April 1998	Alberta City, IA, USA	Fire	Propane	40	2d, 7i
30 April 1999	Between Athens and Lamia,	Traffic accident	LPG	a	4d, 13i
	Greece				
23 September 1999	Toronto, Canada	Derailment	LPG	>60	\ -
30 December 1999	Quebec, Canada	Derailment,	Hydrocarbons	2700	2i, 350 evac.
		collision			
27 May 2000	Eunice, LA, USA	Derailment	Flammable PLGs	a a	2000 evac.
19 July 2000	Ohio, USA	Overfilling	Propane	66	3i
7 January 2001	Kanpur, India	Highway accident	LPG	a	12d, 6i
20 October 2000	Downey, CA, USA	Leak	Propane	2	2d
22 October 2000	Texas, USA	Improper	Propane	17	2d
		unloading			
1 July 2001	Jamnagar, India	Damage	LPG	*	12d
20 February 2002	Cairo, Egypt	Fire caused in a	Butane		373d, 7500i
201001011, 200-	, -671	passenger train by			
		a butane tank			
		BLEVE			
22 June 2002	Tivissa, Spain	Overturned	LNG	$48\mathrm{m}^3$	1d, 2i
25 June 2002	Gronton, CT, USA	Overheating	Borane-	0.1	2i
25 Julio 2002	, , , , , , , , , , , , , , , , , , ,		tetrahydrofuran		
11 April 2003	Louisville, USA	Overheating	Maltodextrin and	*	1d
11 71pm 2005	2000.	C	other chemicals		
13 January 2004	Baltimore, Washington	Traffic accident	Propane	(*)	10d
	Highway, USA				
19 January 2004	Skikida, Algeria	Explosion	LNG	90	13d, 74i
9 August 2004	Mihama, Japan	Steam pipe	Steam		4d, 7i
) 1 tag a 5 t 200 1	and the second second	depressurization			

^a Information not available.

ing LFG (liquefied flammable gases) that has ever occurred [34].

An operator had to drain water from a 1200 m³ spherical storage vessel nearly full of propane. There were three valves underneath the vessel. The first valve, nearer to the vessel bottom, led to the other two valves further below, connected in parallel. The operator opened the first valve and one of the two lower ones. When traces of oil showed that the draining was nearly complete he shut the first valve, then cracked it to complete the draining. No flow came. So he opened the first valve fully. The choke – presumably hydrate – cleared suddenly and the operator and the two other men were splashed with liquid. The handle came off the valve and they could not get it back on. The lower valve had been frozen and could not be moved. Access was poor because the drain valves were immediately below the

tank, which was only 1.4 m above the ground [34]. The continuing propane leak soon formed a visible cloud of vapour, 1 m deep. It spread for 150 m and was ignited 25 min after the leak started by an automobile that had stopped on a nearby road. The fire flashed back to the sphere but there was no immediate explosion. The sphere was fitted with water sprays but the supply was inadequate to cool the vessel. When the fire brigade began using their hoses, the water supply to the spheres ran dry. Apparently, the firemen had used off the available water for cooling the neighboring spheres to prevent the fire from spreading, in the belief that the vessel on fire shall be protected by the relief valve!

Ninety minutes after the fire started, the sphere went through a BLEVE. Ten out of 12 firemen within 50 m were killed. Men 140 m away were badly burned by a wave of propane which came

over the compound wall. Altogether 15–18 men were killed and about 80 injured. Flying debris broke the legs of an adjacent sphere which fell over. Its relief valve discharged liquid which added to the fire, and 45 min later it also BLEVEd, leading to more BLEVEs. Altogether five spheres and two other pressure vessels burst and three were damaged. The fire spread to gasoline and fuel oil tanks [3].

3.1.3. The PEMEX LPG terminal disaster, San Juan Ixhantepec, Mexico City

The PEMEX LPG terminal in San Juan Ixhuatepec, Mexico City, was a large installation which received supplies from three gas refineries every day. On the morning of 19 November 1984, when the vessels at the PEMEX terminal were being filled with LPG arriving in a pipeline from a refinery 400 km away, a drop in the pipeline pressure was noticed by the control room and a pumping station. It occurred because an 8 in. pipe connecting one of the spheres to a series of cylinders had ruptured but the operators did not think of such a possibility and the release of the LPG from the leaking pipeline continued for 5-10 min. The escaping gas formed a 2 m high cloud covering an area of \sim 200 m \times 150 m. The cloud then drifted towards a flare tower, caught fire and precipitated the first BLEVE. The explosion hurled vessel fragments wrapped in burning LPG in all directions. Some of the projectiles hit other vessels, damaging them, or caused local fires which engulfed other vessels. This led to the failure of one vessel after another; most exploding vessels caused nearby vessels to fail.

Four LPG spheres, each containing 1500 m³ of LPG, and several other smaller cylinders holding between 45 m³ and 270 m³ of the liquid suffered BLEVEs. Each BLEVE generated a fireball; such fireballs raged through the streets of Ixhuatepec for about 90 min. A block of perhaps 200 houses built mostly of wood, cardboard, and metal sheets was demolished by these fireballs. Masses of fragments of tanks and pipes, some of them weighing 40 tonnes, were blown into air and landed as far as 1200 m away. The PEMEX terminal was devastated.

The accident was responsible for 650 deaths and over 6400 injuries. Damages due to the explosion and the resulting fire were estimated at approximately \$31 million [35].

3.1.4. Boral LPG distribution depot, Sydney

On all-fools day (1 April) in 1990, at approximately 8.45 p.m. at a Sydney suburb, a BLEVE occurred in a LPG storage-cumdistribution terminal. It led to further accidents and one BLEVE after another occurred through the night. The unintended fireworks began with the explosion of a small gas tank. The fire then spread along the ruptured gas pipes to the four main 100-t steel storage tanks, each at least 60% full, holding ~40,0001 of LPG. It heated-up the tanks until their 15 cm thick steel wall failed, generating massive BLEVEs. The resulting fireballs and gas flares shot hundreds of meters into the night sky. Hundreds of portable gas cylinders kept inside a storeroom at Boral, sized 2–240 kg also BLEVEd. Power blackouts occurred after the first thundering explosion, which shattered windows. Two fire officers who were close to the unattended depot, whose main entrance was padlocked, were thrown against a wall after one

of the explosions. The exploding vessels generated rocketing fragments; the shock waves sent other objects which came into their paths, flying like missiles. One such missile, an uprooted telegraphic pole, just missed crushing a woman who was standing almost 0.5 Km away from an exploding vessel. One of the 30 m long fractured cylinders shot off its mooring, and rocketed through the air with an ignited tail of flames. On landing it gouged a huge 2 m crater in the earth, before bouncing through a wire fence into three, 40-t tanks, which were propelled into the nearby Alexandria Canal. The rocketing cylinder then hit and flattened an electrical substation and a panel-beating workshop before nose-diving into the canal, 300 m away from its original position.

Luckily it all happened on a Sunday or else the toll in the form of human lives would have been massive as the accident occurred in a very busy section of the city, where thousands of persons went to work on weekdays. If the wind had been blowing in a different direction, it could have carried the fire to the jet fuel storage 20 m away and might have set it ablaze.

The Mascot International Airport is located just a few hundred meters away from where this accident occurred and a passenger plane on its final approach into Mascot was buffeted by shockwaves when one of the tanks BLEVEd. Plane passengers, the airport and a nearby hotel were evacuated and airport fire crews placed on full alert. The chain of BLEVEs was eventually broken when Boral engineers released relief safety valves of the surviving tanks to depressurize them.

Factory storage buildings close to the explosions were destroyed. Those that survived had doors blasted off hinges, roofs lifted and windows shattered. Underfoot, thick grey mud had formed. Elsewhere, on the depot's 10 ha site were the charred ruins of 10 gas trucks, 3 gas tanker semi-trailers and a row of storerooms which backed onto the main row of cylinders. An adjacent bitumen production plant was destroyed. The Boral plant was built in 1968 to satisfy standards which by 1990 had become outdated [4].

3.1.5. Burnside, Illinois

A 38001LPG tank underwent a BLEVE after coming in contact with fire from a nearby grain dryer. The tank was venting when the fire services unit were applying water to the tank from a distance of approximately 20 m, taking shelter behind a storage building [36]. The tank exploded within minutes. The tank pieces and the secondary projectiles formed when the explosion shock waves impinged upon the nearby structures, struck several fire fighters and a fire engine. Two fire fighters were killed and another two were seriously injured.

3.1.6. Turkey farm, Albert City, IA

On 9 April 1998, two fire fighters were killed and seven seriously injured in a BLEVE that also caused a massive destruction of infrastructure [36]. The incident began at 11:10 p.m. when a fire was accidentally started at a large Turkey farm near Albert City, IA. The fire had begun when teenagers driving a vehicle struck two pipelines carrying liquid propane from an 18,000 gal tank to two vaporizer units. The ensuing cloud of vapour was ignited by a nearby ignition source. The teenagers were able to

escape the area prior to ignition and rang up the Fire Department which rushed its team within 11 min of the rupture.

The fire fighters quickly set up operations to protect the exposed buildings with hose lines. There was no water supply in the area so a tanker shuttle operation was established, with a portable tank left at the scene.

Two fire fighters advanced a hose line from the engine setup northwest of the jeopardized LP tank. They positioned themselves at the west corner of the storage building immediately north of the LP tank.

Another group of two fire fighters advanced a hose line from the engine staged north of the LP tank between the building north of the tank and the large coop east of the tank. These men were approximately 27.5 m north from the LP tank.

The venting gas from the LP tank created a loud noise similar to a jet engine, making communications on the fire ground difficult. The fire chief indicated that the plan was to allow the fire to burn itself out and to protect exposures.

As this strategy was being implemented at approximately 11:28 p.m. a tremendous explosion occurred, sending large sections of the LP tank flying in four different directions.

The largest portion of the tank, a piece approximately 7.3 m long, was hurtled over 91.5 m into the large coop east of the LP tank. Another piece was propelled directly north, narrowly missing the two fire fighters positioned north of the LP tank. This piece went through the north building and was stopped by a silo over 46 m from the LP tank's original location. The force of this piece passing by the two fire fighters carried one of the men into the building and up against the far wall. He crawled out of the wreckage and re-joined the others. The third large piece traveled northwest from the LP tank's location and struck the two fire fighters operating the hose line at the west corner of the north building. The impact killed the two fire fighters instantly. This piece also narrowly missed the fire chief as he stood near the two men that were killed. He was burned badly by the blast.

Other pieces of the LP tank were scattered in the open field across the street from the tank. Some traveled almost 80 m from the site of the blast. A piece of one of the vent pipes was found embedded over 1 m deep into a gravel driveway over 61 m west of the tank's original location.

Two fire fighters were killed, and the fire chief, five fire fighters and a sheriff's deputy were injured in the blast.

3.2. BLEVEs during transportation of LFG

3.2.1. Railroad tank cars, Laurel, USA

On 25 January 1969, a freight train with 15 tank cars of LFG derailed in the centre of Laurel, Mississippi. The impact caused a crack in the tank which was then torn apart in a BLEVE. It ruptured another tank which also exploded. Both explosions generated fireballs. During the next 40 min one car after another burst or rocketed. The initial fireball set fire to buildings 200–400 ft away. Other fires were initiated by burning fragments up to 10 blocks away. All structures lying within about 400 ft of the accident site were damaged. Window-panes were shattered in buildings located as far away as 5 km. Two people died and 976 were injured.

Much of the damage was caused by the impact of rocketing tank cars and the fires which they set going. One 37 ft section traveled through the air and bounced first at 1000 ft distance, then bounced again at 300 ft, and again at 200 ft, and finally went another 100 ft, before coming to rest at a total distance of 1600 ft, where it set fire to houses [3].

3.2.2. Tractor tank, Eagle Pass, USA

On 29 April 1975 a tractor tank carrying LPG on a highway near Eagle Pass, Texas, swerved to avoid a car in front which had slowed suddenly to make a turn. The tank semi-trailer separated from the tractor, struck a concrete wall and ruptured, releasing LPG. Witnesses described a noise like that of a violent storm, followed immediately by an explosion, fire, and a second explosion.

The large front section of the tank rocketed up, struck an elevated sign, traveled 1029 ft and struck the ground; bounced up and traveled 278 ft; struck and demolished a mobile home; bounced up again and traveled 347 ft over another mobile home, causing it to burst into flames and be destroyed; finally rested 1654 ft from its starting point [3].

Sixteen people, including the driver, were killed and 512 suffered burns.

3.2.3. Highway tunnel, Palermo (Italy)

On 18 March 1996, a tank truck was involved in a car crash in a highway tunnel near Palermo, Italy. The sequence of events was as follows [37]: (a) a vehicle skidded about 100 m from the tunnel entrance, causing a pile-up of cars; (b) the engine of one of the cars caught fire as a result of collision with another car; (c) a tank truck entered the tunnel and stopped about 50 m from the exit to avoid collision with the cars ahead; (d) a bus, arriving at high speed, skidded and crashed into the tank truck, causing a leakage in the upper part of the tank shell, just below the manhole. A few seconds later a soft rumble was heard, followed by a hot wind that caused serious burns to the people in the tunnel; (e) everyone ran out of the tunnel, except for five who had fainted as a result of the crash; (f) 4 min later the tank went through a BLEVE. The resulting blast wave seriously damaged the cars in the tunnel and killed the five persons remaining there. Dense black clouds billowed from the tunnel. Many relics of the explosion are still found on the tunnel walls.

3.2.4. Highway, Tivissa (Spain)

The accident took place on 22 June 2002—on a highway near Tivissa, Catalonia (Spain). A tanker carrying compressed natural gas lost control while speeding downhill. It turned over, tipping onto its left side, and finally came to a halt beside a sandy slope. Immediately flames appeared between the truck cabin and the trailer due to the ignition of either leaking diesel, or CNG, or perhaps both. The fire increased in size as, perhaps, the CNG escaping from the PRV caught fire. There was a small explosion, then a strong hissing sound, and then the tank BLEVEd, generating a huge fireball [38]. Even though the accident occurred in a remote location, it still led to one death and burn injuries to two persons who happened to be at points about 200 m away from the blast site.

3.3. BLEVEs in stationary installations of non-flammable but toxic chemicals

3.3.1. Phosgene storage tank, Hamburg, Germany, 1928

On 28 May 1928, a tank containing phosgene went through a BLEVE at the Stolzenburg factory near the harbor area of Hamburg, releasing an estimated 12 tonnes of the deadly gas. Eleven people were killed and 171 required hospital treatment. People were affected by the gas at locations up to 11 miles from the accident site [4].

If the northerly wind, which later changed to the south-east, had blown over populous areas, the fatalities would have been much higher.

3.3.2. Colorant manufacturing unit, Louisville, KY, USA

On 11 April 2003 a tank containing caramel color liquid, maltodextrin, and water was unintentionally overheated at the D.D. Williamson & Company, Louisville, KY. The tank had on two earlier occasions, had been deformed due to misapplication of vacuum and the repairs had not been certified to meet the ASME code requirements. It most probably failed due to structural weakness, as the pressure at the time of vessel burst was less then the design pressure, and exploded, killing the lead operator. The explosion propelled the top head of the tank about 100 m to the west. The shell was also propelled off its foundation and stuck a 12,000 gal aqua ammonium storage tank, knocking it sideways and resulting in a 12,000 kg leak. The shell then ricocheted, hit the bottom of a five-story-tall spray drier, toppling it. Twenty-six persons were evacuated and 1500 were sheltered-in-place [39].

3.4. BLEVEs during transportation of non-flammable but toxic chemicals

3.4.1. Tractor tank carrying ammonia, Houston, USA, 1976

On 11 May 1976 in Houston, Texas, a tractor tank semi-trailer carrying ammonia went through a bridge rail on an interstate highway and fell some 15 ft onto a freeway. The interchange was the busiest in the state and at the time the traffic was quite heavy. The tank, which held 19 tonnes of liquid anhydrous ammonia, suffered a BLEVE [25].

The ammonia which had flashed off, formed a cloud 30 m high. It gradually took in air and reached a width of about 300 m and a length of 600 m. One photograph showed a tail to the left-hand side, indicating the typical slumping behavior of heavy gas. It is estimated that the ammonia evaporated and the cloud dispersed within about 5 min. The driver of the truck and five other people were killed, 78 taken to hospital and about another 100 injured. Apart from the driver's, all the casualties were due to the toxic impact of ammonia.

3.4.2. Freight train transporting chlorine, Montana, Mexico, 1981 [25]

A train consisting of 38 wagons, including 32 rail tank cars filled with liquid chlorine was moving down a steep and winding valley at a 3% gradient when its brakes failed. The train derailed at over 80 km/h on a bend 350 m beyond Montana sta-

tion, resulting in a pile-up that included 28 of the 32 chlorine cars. Most were badly damaged and suffered BLEVEs one after another. One tank car lost its dished end and the shell was propelled 2000 m. A second was split along its side. A third had a 0.5 m diameter hole, probably the result of an iron-chlorine fire, which could well have resulted from ignition of the cork insulation by red hot brakes. Four other tank cars suffered damage to their valves, which were ripped off or dislodged so that they leaked. It is estimated that 100 tonnes of chlorine escaped in the first few minutes and 300–350 tonnes in all.

Seventeen persons died, 4 in the caboose of the train and 13 from gassing. Another 1000 people were impacted. The vegetation up the valley was bleached by the gas cloud passing up it; there was also discoloration some 50 m down the slope and up the sides for a vertical distance of about 50 m. The highest concentrations appear to have occurred in a strip $1000\,\mathrm{m}\,\mathrm{long} \times 40\,\mathrm{m}$ wide.

3.5. BLEVEs involving non-flammable, non-toxic chemicals

BLEVEs leading to multiple fatalities and severe property damage have occurred even in tanks storing non-flammable and non-toxic chemicals [35]. For example at Repcelok, Hungary, nine persons died when a 35-t cylinder containing carbon dioxide BLEVEd on 2 January 1969. Another catastrophic failure of CO₂ storage vessel at the citrus process plant of Procter & Gamble GmbH at Worms, Germany, caused three deaths and damage of property worth \$20 million [40]. The blast hurled parts of the vessel over the factory's compound wall and into the nearby river Rhine. At Spencer, USA, seven persons were fatally hit when a tank containing overheated water suffered a BLEVE.

On 28 August 1992 there was a failure of a storage vessel containing liquefied nitrogen at a manufacturing facility in Japan. The catastrophic failure of the vessel and the resulting BLEVE caused the collapse of almost half of the factory, damage to the walls of 25 houses and 39 cars, buses and trucks, all within a 400 m radius. Fragments of the vessel were projected up to 350 m—including part of the top head of the outer shell which was 1.5 m wide and 8 mm in thickness [40]. The estimated property loss was \$5 million.

At Mihama Nuclear Power Reactor, Japan, on 9 August 2004 a large pipe carrying superheated water developed a leak, and exploded. The resulting two-phase release of superheated water and steam scorched 11 workers, killing or maiming them. The antique boiler explosion in Medina, USA, which occurred on 29 July 2001, and the explosion abroad the cruise ship S.S. Norway at Miami, USA, are both likely to be BLEVEs which occurred when vessels containing superheated water developed cracks. The combined death toll of the two accidents was 15, and several times this number were left seriously injured [41].

4. Initiating events which have triggered BLEVEs and some of the lessons learnt

From the tables of notable BLEVE incidents compiled by Prugh [16,17], Lees [3], and our survey of BLEVE events

covering 1995–2004, we calculate the frequency of causative events as under:

Fire	36%	
Mechanical damage	22%	
Overfilling	20%	
Runaway reactions	12%	
Overheating	6%	
Vapour space contamination	2%	
Mechanical failure	2%	

This is a broad assessment, limited to a sample size of 88, comprising only of some of the major BLEVE incidents that have occurred across the world from 1926 onwards. Unfortunately no comprehensive catalogue of all, or even most, of the BLEVEs that have occurred in this period exists.

The indicative frequency distribution pertains to the causes leading to the first BLEVE in an accident event. If we count the first BLEVE as the *initiating* event of the subsequent BLEVEs that often accompany the first blast, it may perhaps turn out that a BLEVE is the most common trigger for other BLEVEs!

Among the most important of lessons learnt from the postmortem of past BLEVEs are:

- (i) Contrary to popular perception [42] BLEVEs are not limited to flammable chemicals. All pressure liquefied gases can, and often are, associated with BLEVEs. Boilers which hold superheated water can also suffer BLEVE.
- (ii) All BLEVEs lead to shock waves and rocketing fragments of ruptured vessels. In addition, BLEVEs cause fireball if the exploded vessel had contained a flammable chemical, and/or dispersion of hazardous material (such as chlorine/superheated steam/phosgene) if the stored chemical was non-flammable.
- (iii) It is well-neigh impossible to forecast with any certainty as to how much time a jeopardized vessel may take before undergoing BLEVE. The 'time to BLEVE' may be a few seconds to several hours. This fact makes it very dangerous for the fire fighters to go near a fire-engulfed vessel containing a pressure-liquefied gas. There have been many instances when a vessel has exploded even after the pressure-relief valves have been venting the vessel for several minutes.
- (iv) Of all the harmful effects of BLEVE, the one with the greatest range of impact is of rocketing fragments. Quite often death of bystanders and secondary accidents in other process units are caused by such missiles.

5. The BLEVE theory

How severe and prolonged has to be the fire engulfment in order to precipitate a BLEVE? How long a vessel jeopardized by fire, or mechanical damage would hold itself before falling apart in a BLEVE? What are the factors that enhance or dampen the severity of a BLEVE?

Attempts have been made to answer these questions with the hindsight of past accident analysis, controlled experiments, and by the application of numerous concepts of chemical and mechanical engineering. Together, these attempts constitute the BLEVE theory which is in a continuous state of refinement.

5.1. The superheat limit theory (SLT)

Reid [13,21,43] proposed the oft-used, oft-quoted, and oft-contested explanation to the question, "what triggers a BLEVE?" According to Reid's explanation, which has come to be known as the superheat limit theory (SLT), a BLEVE originates as follows: when a vessel containing a pressure liquefied gas ruptures, the vapour which was hitherto in equilibrium with its liquid, begins to blow off. As a result the liquid pressure drops rapidly, equilibrium is lost, and the liquid is suddenly rendered 'superheated' as its temperature is now way above its boiling point at the accidentally reduced pressure.

There are two ways of reaching the superheat limit or homogeneous nucleation temperature. At constant pressure the superheat limit is reached when the temperature exceeds a threshold value, which is the minimum temperature at which the liquid gets homogeneously nucleated in the absence of nucleation sites. At constant temperature superheat occurs if there is a sudden depressurization of a vessel containing a PLG, rendering the PLG suddenly at a temperature way above its boiling point at the now suddenly reduced pressure. At constant pressure, superheat limit temperature is the highest temperature below critical temperature and at constant temperature it is the lowest pressure that a liquid can sustain without undergoing phase transition.

In such a situation, instantaneous flash of a fraction of the liquid and a superheated liquid vapour explosion takes place, releasing a biphasic liquid/vapour mixture. These events occur very swiftly, within a few milliseconds. The increase in volume caused by the instantaneously vaporizing mass of liquid is enormous, which, added to the expansion of the pre-existing compressed vapour, generates a strong pressure wave. The resulting massive explosion can often shatter the container into several pieces, and propel the pieces to considerable distances.

The superheat limit theory (SLT) can be explained with the illustrative examples of ammonia, chlorine, and butane (Fig. 1), in which the degree of superheat available if vessels containing these pressure liquefied gases (PLGs) accidentally rupture at 308 K or 350 K, has been computed. The figure also gives the pressure–temperature curves for the three PLGs along with the corresponding superheat limit loci (tangents drawn at the corresponding points of critical pressure).

It may be seen that the values of boiling point and superheat limit at 1 atm pressure are 239.8 and 347.21 for ammonia, 239.1 and 247.22 for chlorine, and 272.7 and 362.61 for butane, respectively. When the sudden depressurization takes place due to rupture of the vessel, the liquid inside the vessel which was in equilibrium with vapour suddenly comes to atmospheric pressure, losing its equilibrium. Depending upon the degree of superheat (which, in turn, depends on the initial temperature) as shown in Fig. 1, violent flashing would take place generating a pressure wave. As per SLT, the intensity of the pressure wave thus generated would depend upon the degree of superheat. Thus, according to the SLT, the severity of a BLEVE depends upon the degree of superheat which, in turn, depends upon the

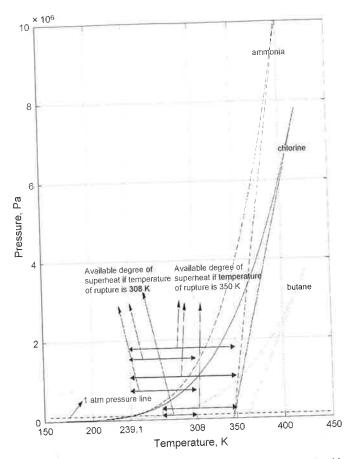


Fig. 1. Pressure-temperature curves and superheat limit loci for ammonia, chlorine, and butane, showing degrees of superheat at different stages of container

temperature of the PLG before the sudden rupture of its container.

5.2. Determination of SLT

Even as a precise knowledge of superheat limit temperatures (SLTs) of the substances used in nuclear power plants and chemical process industries is essential for designing and controlling the operations involving those substances [44], for reasons elaborated below it is exceedingly difficult to accurately determine SLT by experimentation.

5.2.1. Experimental approaches

The most commonly used experimental approach for determining SLT is based on the 'droplet explosion technique' introduced by Wekeshima and Takata [45] and Moore [46]. This technique involves introducing small droplets of the test liquid up the bottom of a column filled with a lesser volatile (host) liquid. The host liquid must be immiscible with the test liquid, and should have a boiling point well above the critical temperature of the test liquid. A temperature gradient is maintained in the column, progressively greater from the bottom up. As the test drop rises through the column it is progressively overheated till it reaches its SLT at which stage it explodes into vapour. The temperature at which the drop explodes is recorded.

The main problem associated with the droplet explosion technique is that when the temperature approaches the superheat limit the unstable bubble nuclei attain sizes reaching molecular proportions and it is probable that even in the finest experiments, microscopic fluctuations would initiate the formation of a nucleus bubble at a temperature below the superheat limit. Another problem to be considered is thermal equilibrium between the rising droplet and the host liquid. The increase in temperature of the rising droplet may depend on the droplet size, rise velocity of the droplet, temperature gradient in the host liquid column, and the heat diffusivity of the droplet. There is the likelihood of under cooling of the droplet which can introduce some error in the measurement of SLT.

Nevertheless, the droplet explosion technique is the best available method for the experimental determination of SLT and the uncertainties can be minimized by sophisticated experimentation.

Another experimental method for determining SLT is based on immersion of very fine wires in a very clean test liquid and subjected to very rapid heating. The temperature of the liquid adjacent to the wires at the time of explosive vaporization of the liquid is noted. For this approach to succeed the dynamics of the thermocouple/temperature measuring device must be faster than the dynamics of the heating of wires for precise measurements, which is not always possible. The nature of the wire surface also influences nucleation. Nevertheless, as in case of 'droplet explosion technique', this method also gives fairly reproducible results, though not with the most desirable accuracy and preci-

5.2.2. Theoretical approaches

Once the temperature of a liquid crosses the superheat limit, the liquid must totally vaporize. This can occur only if the liquid gets homogenously nucleated across its entire body. The factors which precipitate homogeneous nucleation in a superheated liquid are dealt by the 'homogeneous nucleation theory' which has its roots in the work of Gibbs [47]. He had outlined and defined the minimum work required for the formation of vapour voids in the body of a pure liquid. The theory was subsequently developed by Volmer and Weber [48], Farkas [49], Becker and Doring [50], Blander and Katz [51], and others [52,53].

The classical theory can be used to explain the causes and some of the fundamental mechanisms associated with the explosive boiling in liquids. It can also be used to predict the bubble size and steady-state nucleation rates. But theoretical results are often at variance with the experimental data; the later, in itself, could harbor some uncertainty as discussed earlier. Attempts to improve upon the classical homogeneous nucleation theory, especially in terms of modeling the behavior of droplets consisting of 100 molecules or fewer have led to complex statistical-mechanical treatments but even as these treatments rest upon a more elaborate theoretical foundation, they do not give any better agreement with the experimental data then the classical models [54]. The situation has been summarized by Li et al. [53], noting that even though the classical kinetic theory presents some difficulties in dealing with nanoscale nucleation embryos, the theory is the only one that connects the phase change mechanism in microscale with the observed macroscale phenomena.

In summary, in spite of continuous advancements in the homogeneous nucleation theory, occurring in tandem with more and more fine experimentation [55], it is not possible to use the theory in predicting superheat limit temperatures with reasonable degree of certainity. We have recently made an attempt to develop a theoretical framework with which SLT of various substances can be predicted. The details are reported elsewhere [44].

The SLT had aimed to provide a framework with which the likelihood as well as the severity of a possible BLEVE can be predicted. The logical safety strategy, as per SLT, is that the pressure relief valve of the PLG vessel should be set to operate in such a manner that it depressurizes the vessel before the vessel contents cross the superheat limit temperature.

5.3. Exceptions to the superheat limit theory (SLT)

A great deal of work, notably by Birk and co-workers [56,2,19,31], McDevitt et al. [15], Prugh [16,17], Venart and co-workers [26,20,32,57], besides others, has brought to the fore the limitations of SLT. It is more or less agreed that 'significant superheating' of the pressure liquefied gas (PLG) is necessary for a BLEVE to occur [5,58,59] but more and more evidence has piled up which indicates that a BLEVE can occur well below the SLT. Interestingly Reid himself has observed (as quoted in McDevitt et al. [15]) that a vessel would certainly undergo BLEVE if it suffers LOC at the SLT; BLEVE may still occur but with less than 100% certainity if the initial temperature of the liquid is below the SLT.

Prugh [16,17] has pointed out on the basis of a study of past accidents (for example McDevitt et al. [15]) that BLEVE'S can occur well below the superheat limit temperature but the blast effect may be much higher when a BLEVE occurs near the SLT.

As superheat limit temperature (SLT) is a focal reference point in the matters of BLEVE, it may be pertinent to dwell upon it a little.

5.4. Boiling liquid collapsed bubble explosion (BLCBE)

Underlining the complexity of the mechanism of loss of confinement (LOC) - an occurrence essential for a BLEVE - Venart et al. [14] proposed the concept of 'boiling liquid compressed bubble explosion' (BLCBE; later the word 'compressed' was replaced by 'collapsed' in Yu and Venart [26]) to explain the severity of some of the past BLEVE accidents. BLCBE has been postulated [26] to result from a complex multi-step adaptive and coherent bubble formation-growth-collapse process in a pressure liquefied gas and its interaction with the containment vessel, as follows: (i) a partial vessel failure (i.e. a 'sub-critical' sized crack or opening), (ii) rapid depressurization of an already nucleated and now superheated liquid, (iii) rapid bubble growth and then the constraint of the expanding two-phase system (by either physical, acoustic, or inertial means), (iv) the repressurization, back to nearly the original containment pressure (or values in excess) followed by, (v) adaptive and coherent bubble collapse resulting in the formation of a power amplified liquid shock wave. As a result (vi) wall-pressure wave interaction causes the total and rapid vessel destruction, with (vii) an explosive mechanical distribution of the liquid contents as a finely divided aerosol, and (viii) heat transfer and total evaporation (and if flammable, auto-ignition) of the aerosol.

The authors further postulate that the bubble growth and collapse phenomena results in a power amplification of the bubble energy and hence dynamic pressures which may greatly exceed the original thermodynamic containment pressure dictated by its original temperature. It follows that a BLCBE may cause much greater blast effect than may be indicated by the 'extent of superheating' of the vessel contents just before the loss of confinement.

The BLCBE concept apparently had some of its roots in the homogeneous nucleation theory of superheated liquids [52,53]. Refinement of the BLEVE concept in the light of the information available from the past accidents, and substantiation by controlled experiments, has led Venart and co-workers [20,32,57] to suggest that a complex two-step failure process involving fluid–structure interaction may be the cause of all the BLEVES. The first step is a crack in the vessel causing a 'leak before break'. In the second step there are waves of depressurization, repressurization and crack propagation leading to the final failure. Based on experimentally simulated BLEVEs, Birk, and co-workers [2,60–62] have also developed the theory of 'two-step BLEVE' described later in this section.

According to Venart and co-workers, the severity of the final failure may not necessarily be a function of the extent to which the contents get superheated but may have more to do with the initiating mode of the vessel failure and the thermo-hydraulic contents of the final failure. The delay times, between crack initiation and catastrophic failure, range from about 40 s to 1.4 s as fill increases from 20% to 85%. The distribution and flashing of the loading causes a fireball if the contents are flammable and the surface emissive power of the these do 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 BLEVEs while undergoing a pressure reduction at 'low' superheat.

According to Venart [20], the 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 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 case the uncontrolled vessel failure. The size, shape, and radiation intensity of the fireballs which are formed when flammable liquids undergo BLEVE also do not appear to be directly related to the liquid's superheat but rather the thermal-hydraulic contents just at failure.

The studies of Venart and co-workers support the observations made earlier by McDevitt et al. [15] and Prugh [16,17] with the major modification that BLEVEs can not only occur well below the SLT, but also the destructive power of the BLEVE may be unrelated to the extent of superheat.

5.5. Time to BLEVE

Once a vessel containing pressure liquefied gas (PLG) suffers from a minor or major failure, it can lead to a BLEVE even if pressure relief valves (PRV) may be operating [23,32]; indeed if the PRVs are wide open and the PLG is escaping so fast that siren-like sound is generated, it is a signal that BLEVE can occur any moment. But in most other situations there is no simple indicator that can tell that a jeopardized vessel would eventually suffer a BLEVE and, if so, when. During the accidents that have occurred in the past, some vessels have exploded within a few minutes of fire engulfment or missile hits, some other have done so after several hours. In some cases vessels have suffered a BLEVE as many as 24 h after being jeopardized! At the Feyzin BLEVE, described earlier in this paper, the time between ignition of the leak and vessel rupture was about an hour and a half. At the PEMEX LPG Terminal catastrophe of 1984, also referred earlier in this paper, vessels took anywhere between 3 min and 30 min before exploding.

It is important to estimate the time that may elapse between the initial jeopardization of a vessel and its eventual BLEVE as this may help in devising damage-control strategies. Blything and Reeves [63], studying horizontal cylinders, 75% full with butane and suffering partial fire engulfment or jet flame impingement, estimated that BLEVE would occur between 4 min and 48 min. Selway [33] obtained 7–11 min, 25–38 min, and 5.5–7 min as time spans likely for a full 1000 tonnes LGP storage sphere to experience a BLEVE if it has suffered total fire engulfment, partial fire engulfment, and jet flame impingement, respectively. According to Selway these times would be shorter if the vessel is less than full. In vessels subjected to jet fire by Roberts et al. [29], the pressure relief valves opened after 1–2 min of fire impingement and the vessels BLEVEd after another 3 min.

In fire-induced or projectile-induced vessel damage, a tear can propagate long enough to induce a BLEVE or can stop short leading to a transient jet release [19]. The second of the situations can yet lead to a BLEVE if the crack restarts again. This kind of event has been named 'two-stage BLEVE' [64].

Birk and Cunningham [2,19] conducted a series of tests with 4001 propane tanks, subjecting the tanks to fire engulfment and studying the pattern and the duration of vessel failure. They observed that a tank will suffer total loss of confinement (TLOC) when the pressure stresses in the tank wall exceed the level required to propagate a fracture along the entire length of the vessel. The energy necessary for the TLOC is supplied by the vapour and the liquid in the tank. Of these, the vapour space energy is available immediately on initial failure of the vessel. However, the liquid energy is only available after a phase change (i.e. the liquid must boil or flash to generate vapour), which requires a finite period of time. Due to very rapid depressurization, the boiling proceeds in a non-equilibrium fashion and very large liquid superheats can occur as a result. These large superheats can result in very energetic and powerful boiling which could theoretically cause rapid pressure recovery or overshoot in the tank. It was also observed that BLEVEs of very weak tanks were very short-duration events and were driven by vapour space energy. The liquid temperature was not important in these types of BLEVEs. Indeed high-speed video of BLEVE occurring in a weak tank when the average liquid temperature in the tank was 20 °C, revealed that complete tank failure occurred even before the liquid had begun to react. Evidently the energy for the failure was derived almost exclusively from the vapour space.

In contrast, Birk and Cunningham [2,19] suggest, very long-duration BLEVEs of stronger tanks are possible, and these are driven by violent boiling in the tank after initial tank failure. The phenomenon was later named 'two step BLEVE' (see following section). The vapour space energy may only be contributing to the initial failure of the vessel and might play little or no role in the long-duration BLEVEs.

Between the two extremes of the BLEVE process, there are intermediate events in which both the vapour space energy and the liquid energy contribute to the BLEVE. These intermediate events have durations greater than the short-duration BLEVEs but much less than the long-duration events. A summary of the test results acquired by Birk and Cunningham [2] is presented in Table 2. The authors observe that if the energy stored in the compressed gas in the vapour space were large enough and the tank weak enough, the initial crack would not stop and would grow until a BLEVE occurred. In the tests conducted by them, this type of BLEVE was very rapid and the tank failure process was over in less than approximately 10 ms. The duration suggests a crack-propagating velocity of approximately 200 ms⁻¹ which is in reasonable agreement with the crack velocities in propagating shear failures of pipelines.

Birk and Cunningham [2,19] further observe that if the energy in the vapour space were not enough to force TLOC, then the crack could stop. In such a situation, the liquid energy content may play a major role in determining whether a BLEVE would eventually take place. The initial crack (now arrested) would result in venting and depressurization and this may lead to a boiling of the liquid with a severity which would depend on how much superheat is generated by the initial depressurization. If the initial liquid temperature is high enough, the boiling response and its associated pressure transient may be sufficient to restart the crack and cause TLOC and BLEVE. A BLEVE may also be preceded by a jet release of significant duration. Such a jet release may have a significant impact on the geometry of the resulting fireball, and its rapid rise.

The long-duration BLEVE is a transition event between a BLEVE and a non-BLEVE (i.e. partial failure and jet release) and is probably fairly rare, requiring specific conditions of tank and lading properties. About 20% of the BLEVEs observed by Birk and Cunningham [2] were of long duration. Such events probably occur in tanks that are almost strong enough to resist TLOC, but are 'pushed over the edge' by the violent boiling of the depressurization-induced superheated liquid. The long-duration BLEVEs are strongly related to the PRV setting because this ultimately determines the liquid temperature.

The maximum possible liquid superheat that can be attained occurs when the liquid is at the atmospheric superheat limit (53 °C for propane) and this could potentially lead to the most violent boiling response. Birk and Cunningham [2] have drawn

Table 2 Summary of test outcomes [2]

Test	Fire conditions	No. of events	Outcome	Comments
Vent to empty	Pool only	5	Entire tank contents lost through the PRV	Fire conditions were not severe enough to initiate a local failure
	Pool and torch	2		
Partial failure	Pool and torch	7	Partial failure occurred in the tank causing a two-phase liquid/vapour mixture to be released from the tank	Local thermal weakening was such that pressure stresses in the wall exceeded local tank wall strength causing a failure (crack)
	Torch only	4	In two cases, the jet was angled such that it propelled the tank up to 30 m	The tank wall was strong enough to arrest the crack
TLOC and BLEVE	Pool and torch	9	The tank failed catastrophically releasing the entire contents as expanding vapour, boiling liquid and dispersed droplets	Not all BLEVEs were the same
	Torch only	2	Failures resulted in blast and fireballs	The characteristics of BLEVEs varied with tank properties and lading conditions at the time of failure

a pressure—temperature diagram for propane which shows the theoretical superheat limit spinodal for propane in the context of the results of BLEVE tests done by the authors. It was found that BLEVEs occurred in almost all of the tanks above the atmospheric superheat limit, and some of these were the long-duration or transition type. This suggests that, even if the tank is strong enough to survive a partial failure, if the PRV is set near or above the superheat limit, then the boiling response will push the event into a long-duration BLEVE. This was first suggested by Reid [21].

Birk and Cunningham [2] and Birk et al. [23] have also presented a 'BLEVE map' which displays the relationship between the estimated burst strength of the vessel and the liquid energy at the time of failure. The map shows that the BLEVE and non-BLEVE situations occur in distinct regions which are divided by a line with a positive slope indicating that increase in liquid energy per unit volume of the tank will result in an increased likelihood of BLEVE occurring in strong tanks. In addition, for the cases where the tank strength is relatively high, there appears to be a transition region between BLEVEs and non-BLEVEs. This transition region contains all BLEVEs of long duration where it is the liquid boiling response that drives the TLOC and BLEVE.

The BLEVE maps also carry a shaded region of uncertainty because no test results appear in these areas. Of this shaded region, the most interesting is the part at higher liquid temperatures. If this region proves to be part of the BLEVE region, then it suggests that the liquid temperature is very important and that the PRV set pressure selection is of critical importance.

With additional data and analysis, Birk and Cunningham [2,19] and VanderSteen and Birk [61] have shown that pressure release valve (PRV) set pressure and vessel wall thickness have a significant impact on the probability of a BLEVE occurring; in case of a thin-walled tank with its wall temperature raised to 700 °C due to fire engulfment, doubling the wall thickness and reducing the PRV set pressure from 2150 kpsig to 1725 kpsig would reduce the susceptibility of a tank to BLEVE by a factor of 3 or more.

Even though these authors, nor others who have studied the factors responsible for 'delayed BLEVE', have explicitly correlated the severity of the blast effects with 'time to BLEVE', it

appears from the discussions that some of the delayed BLEVES may be as severe; or even more so, than instantaneous BLEVES. A different postulation has been made by Van den Berg et al. [65], on the basis of acoustic and gas dynamic blast modeling validated by them using the data of Giesbrecht et al. [66] on exploding vessels of liquefied propylene. According to Van den Berg et al. [65], a rupture in a vessel containing a pressure liquefied gas in free space develops a blast of significant strength only if the vessel disintegrates nearly instantaneously; if the rupture and the catastrophic vessel failure are delayed even for a short duration, the blast effects are minor.

5.6. Two-step BLEVE, pressure relief value (PRV) blow down, thermal stratification and effect of thermal insulation

Further light on BLEVE mechanism, which provides useful insights for BLEVE prevention, has been shed by the recent fire tests, on PLG-containing vessels, by Birk et al. [23], Birk and VanderSteen [64], Roberts et al. [29], Stawczyk [58] and VanderSteen and Birk [61]. The tests of Birk and VanderSteen, which augment the ones done earlier by Birk and Cunningham [2], and Kielec and Birk [60], indicate that for a BLEVE to occur, the tank must first be weakened to the point where an initial pin hole rupture is formed. For the case of a fire heated tank this narrow rupture may form due to plastic thinning of the wall in the heated area or it may form at a flaw in the tank wall. This opening must then grow to cause a total loss of containment (TLOC), and BLEVE.

The initial rupture normally grows in a direction perpendicular to the principal stress (in this case hoop stress). As the rupture widens, vapour initially escapes from the tank and the pressure drops. If the tank has been rendered very weak due to heating over a large area then the crack may rapidly (>200 m/s) grow across the full length of the tank to give a TLOC and BLEVE. In this case the failure may be so rapid that the liquid may not have enough time to undergo phase change and pressurize the tank wall. In other words the TLOC may be caused solely due to the wall loading by vapour space energy.

In other cases the crack may stop in stronger material or it may stop because of the decreased pressure in the tank. In this

case the vapour space energy is spent without failing the vessel. But the stoppage in the crack propagation may not mean the accident is over. With the pressure dropping in the tank, the liquid may go to a state of superheat. If the pressure drop is very rapid (large hole and/or small vapour space) a significant amount of superheat may be established in the liquid before the bulk of the liquid responds by flashing. This and the resulting pressure transient may cause sufficient loading of the tank wall to restart the crack and cause TLOC. It has been shown in many experiments that there can be a significant pressure recovery in a tank holding a pressure liquefied gas after initial depressurization by a rupture. Once a massive flash response is initiated the rapid phase change can send liquid droplets up to impact the top of the tank wall [67]. The flashing may cause liquid to be entrained into the vented stream and this two-phase material may reduce the vented material enthalpy flux to the point where the pressure may begin to recover in the vapour space. The increase in pressure from the pressure recovery may add to the wall loading and may contribute to restarting the failure crack and sending the tank to TLOC and BLEVE.

In BLEVE accidents in which the crack has stopped and then is restarted may be called a two-step BLEVE. These kinds

of BLEVEs are deemed to be in a transition region between a finite failure and a rapid BLEVE (i.e. the failure process almost stopped before a TLOC; Fig. 2). On the basis of the eyewitness accounts of a BLEVE involving a LNG road tanker which occurred at Tivissa, Spain, on 22 June 2002, Planas-Cuchi et al. [38] opine that it was a two-step BLEVE. There was a minor explosion, then a strong hiss, and then a major explosion, suggesting that an initial crack had formed by thermal stress at a very hot location on the LNG tank wall which was arrested in a cooler and stronger zone, followed by a discharge (probably two-phase flow which created the hiss). The crack then restarted due to further thermal stress at the crack tip originated by the cooling effect of the two-phase release through crack, leading to the catastrophic BLEVE.

Birk and VanderSteen [64] further observe that if there is only local heating of the vapour space wall then the crack is likely to stop in stronger cool material. If the final hole size is kept below some critical size then the pressure forces on the flaps produced by the failure opening may not be sufficient to propagate the failure. However, if the hole size is larger than the critical size then the crack can sometimes be restarted and driven through cool strong wall material.

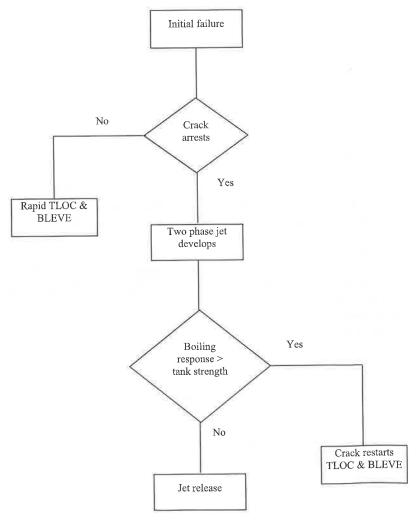


Fig. 2. Two-step BLEVE [2,64].

The tests on nine, 1.8 m³ propane tanks [64], all started 80% full with commercial propane at 10–20 °C, revealed that:

- (i) The time to initial failure depends on the fire condition and on the design of the tank and pressure relief system.A large blow down PRV may delay a failure due to the reduced average stress state in the tank.
- (ii) If a rupture takes place in a vessel holding a liquid at or near its atmospheric superheat limit, it may not always produce a BLEVE; the vessel must open completely if a BLEVE has to occur, and this will only happen if the tank has been weakened sufficiently to initiate a rupture and if the pressure transient during failure is sufficient to drive the failure crack to fully open the vessel.
- (iii) If the length of the severely heated (weakened) part of the vapour space exceeds some critical value, then a BLEVE outcome is likely over a range of fill conditions (10–50% in the present tests). This critical length was around one diameter in the tests of Birk and VanderSteen [62]. However, if the heated zone is smaller than this critical value (in these tests the smaller heated zone was 0.8D) a BLEVE will not happen for lower liquid fill levels. It is possible that higher fill levels with higher liquid energies may cause a BLEVE failure even with small heated zones.
- (iv) It was possible to produce a plot based on a modified Folias parameter that divided BLEVE from non-BLEVE outcomes.

In the course of BLEVEs simulated by heating LPG cylinders of 5 kg and 11 kg capacities, Stawczyk [58] has observed that during the initial stage of the tank heating process the pressure within the tank followed the vapour pressure curve for propane. At 85 °C and 35 bar the tank pressure began to deviate from the curve, apparently due to the exceeding of the critical tank load. The vessels failed at temperatures >115 °C when 80% full and >150 °C when 40% full; the internal pressure before the vessel failure was in the range 75–120 bar. The tank failure began with a precipitous drop in the tank pressure due to the onset of tank unsealing. The author assumes that adiabatic expansion of supercritical propane then took place. Part of the supercritical fluid vaporized through the crack which had developed. The pressure drop caused by the crack rendered the liquid in a superheated state which then boiled over. It led to violent pressure increase as boiling generated far more vapour than could escape through the small opening in the tank. The tank shattered explosively. Stawczyk [58] further notes that internal tank pressure does play an important role in the formation of the initial local creep rupture; in a thermally weakened tank, a failure will occur when the local pressure-induced hoop stress exceeds local strength of the tank wall material.

BLEVEs were simulated by jet fire impingement on 2-t vessels, filled to the extent of 20%, 41%, 60%, and 85% with propane by Roberts et al. [29]. It was observed that the vessels failed within 5 min of jet-fire impingement and at pressures ranging from 16.5–24.4 bar. In all cases except for the 20% full vessel there was an initial pressure drop on pressure relief valve (PRV) opening, followed by a pressure shoot up to above PRV

opening pressure. For the 20% full vessel, the pressure fell from 18.6 bar to 16.5 bar. In all cases the temperature of the vessel wall just above the liquid level was much higher than just below the liquid level suggesting that there was little liquid swelling, hence wetting of the wall. On vessel failure considerable portion of the liquid immediately flashed to vapour which ignited giving large fireballs.

It has been surmised [68–70] that when a fire engulfs a PLG tank, the liquid near the wall is heated, becomes less dense and rises to the top, rendering the liquid thermally stratified. As this top liquid dictates the tank pressure, the actual tank pressure in such a situation would be higher than the one expected from the average liquid temperature.

Another series of tests, simulating tank cars jeopardized by pool fire [61] in which the cars were fortified with thermal protection systems with or without defects of varying magnitudes, have revealed:

- (i) Using only the steel jacket provides thermal protection as it behaves as an effective radiation shield. In these tests, the jacket was found to cut the wall heating rate to approximately half of an unprotected wall (53 °C/min versus 24.5 °C/min) assuming that there is an air gap between the wall and the jacket.
- (ii) Thermally protecting the tank wall with a steel jacket and a blanket of 13 mm ceramic insulation provides substantial thermal protection. The fully protected tank may reduce the wall heating rate to approximately 1/10th of an unprotected wall (53 °C/min versus 5 °C/min).
- (iii) Larger defect sizes resulted in higher average and peak wall temperatures in the area of the defect for a given heating time. As defects got larger, the peak temperature of the defect approached the wall temperature with no insulation (i.e. very large defect). The transition defect length was found to be about 40 cm. If the defect was smaller than 40 cm, the peak temperature was reduced by the surrounding protected material. If the defect was larger than 40 cm, there was little or no benefit from the surrounding material as far as peak temperature was concerned.

All said and done, safety professionals still echo the words of Leslie and Birk [18] that even as BLEVEs are widely accepted as being the most damaging of the pressure-liquefied gas release accidents, we still do not have accurate methods of predicting when and where they will occur. Nor can we say with much certainty how quickly a jeopardized vessel will BLEVE—in the past, vessels have taken anything between a few seconds to a few hours before BLEVE occurred. What is beyond much debate is that the damage caused by a BLEVE is much larger than of a vapour cloud explosion involving an identical material in identical quantity [4,6,71,72].

6. Impact or consequences of BLEVE

6.1. Introduction

The assessment of the impact or the consequences of a BLEVE revolves round two factors:

Table 3 Methods of estimating BLEVE explosion en

Methods of estimating BLEVE explosion energy	VE explosion energy			
Identification of the method	Basis of the method	The key expressions	Explosion energy estimates relative to Prugh's method (kJ)	Reference
Prugh's method or the TNT equivalent method	(1) Assumes that the flashing fraction of the liquid and the pressurized gas expand isentropically as an ideal gas in a BLEVE; (2) equates the work done by the expanding vapour with a charge of TNT; (3) Works out the explosion energy, WTNT, as if it is	$W_{\text{TNT}} = \frac{2.4 \times 10^{-4} PV^*}{k - 1} \left[1 - \left[\frac{101}{P} \right]^{(k-1)/k} \right] \text{ where}$ $V^* = V_{\text{T}} + W_{\text{L}} \left[\frac{f}{D_{\text{V,T}}} - \frac{1}{D_{\text{L,T}}} \right], f = 1 - \exp \left[-\Omega \frac{C}{L} (T_c - T_b) \right],$ $\Omega = 2.63 \left(1 - \left[\frac{T_c - T_0}{T_c - T_b} \right]^{0.38} \right)$	If the burst energy of a vessel filled with propane is 1 KJ as per Prugh's method, according to other methods it is:	Prugh [16]
SVEE (specific volume, entropy and enthalpy) method	(1) Does not assume ideal gas behavior; (2) assumes isentropic expansion; (3) explosion energy, e_{ex} , is computed from the difference in internal energy of the expanding gas between its initial and the final stage	$e_{ex} = m_{f1}u_{f1} - m_{f2}u_{f2} + m_{g1}u_{g1} - m_{g2}u_{g2} \text{ where}$ $m_{f2} = (1 - X_f)m_{f1} + (1 - X_g)m_{g1}, m_{g2} = X_fm_{f1} + X_gm_{g1},$ $u_{f1} = h_{f1} - p_{1}v_{f1}, u_{g1} = h_{g1} - p_{1}v_{g1}, u_{f2} = h_{f2} - p_{a}v_{f2},$ $u_{g2} = h_{g2} - p_{a}v_{g2}, X_g = \left(\frac{s_{g1} - s_{f2}}{s_{g2} - s_{f2}}\right), X_f = \left(\frac{s_{f1} - s_{f2}}{s_{g2} - s_{f2}}\right)$	1.1	CCPS [8] and TNO [73]
Irreversible adiabatic expansion method of Planas-Cuchi et al.	(1) Does not assume ideal gas behavior; (2) expansion is considered to be an adiabatic, irreversible process; (3) the change in internal energy due to the adiabatic irreversible expansion is equated to the work done by the fluid expanding at constant atmospheric pressure. The expressions for both are solved for getting x, the vapour fraction at the final state of the expansion process. This is then substituted in the expression for change in internal energy; (4) from the change in internal energy; the TNT equivalent mass is calculated	$e_{\rm ex} = -\Delta U = P_0 \Delta V \text{ where } \Delta U = (u_{\rm L} - u_{\rm G}) m_{\rm T} x - m_{\rm T} u_{\rm L} + U_i,$ $P_0 \Delta V = P_0 [(v_{\rm G} - v_{\rm L}) m_{\rm T} x + m_{\rm T} v_{\rm L} - V_i],$ $x = \frac{m_{\rm T} P_0 v_{\rm L} - V_i P_0 + m_{\rm T} u_{\rm L} - U_i}{m_{\rm T} [(u_{\rm L} - u_{\rm G}) - (v_{\rm G} - v_{\rm L}) P_0]},$ $W_{\rm TNT}(kg) = 2.14 \times 10^{-7} \times \beta \times \Delta U$	0.4	Planas-Cuchi et al. [59]

(J/kg); u_{k2}, u_{G} : Internal energy of the vapour at the final state (J/kg); U_i : Internal energy at initial state (J); V'': Total vapour volume (m³); v_{f1} : Specific volume of the liquid at the initial state (m³/kg); v_{f2}, v_{L} : Specific volume of the liquid at the final state (m^3/kg) ; v_{g1} : Specific volume of the vapour at the initial state (m^3/kg) ; v_{g2} , v_G : Specific volume of the vapour at the final state (m^3/kg) ; V_i : Volume of the vessel (m^3/kg) ; W_L : C: Average specific heat of the liquid over temperature interval To to Tb (J/kg K); DL, T: Density of vapour at temperature at burst (kg/m³); Dv, T: Density of vapour at temperature at burst (kg/m³); ex, ex. Explosion energy (J); f. Fraction of liquid flashing into vapour (no unit); h_{l1} : Enthalpy of the liquid at the initial state (J/kg); h_{l2} : Enthalpy of the liquid at the final state (J/kg); h_{g1} : Enthalpy of the vapour at the initial state (J/kg); h_{g2} : Enthalpy of the vapour at the final state (J/kg); k: Ratio of specific heats at constant pressure and constant volume (no unit); L: Average latent heat of vaporization over temperature interval T_0 to T_b (J/kg); m_{ℓ_1} : Mass of the liquid at the initial state (kg); m_{ℓ_2} : Mass of the liquid at the final state (kg); m_{g_1} : Mass of the vapour at the initial state (kg); m_{g_2} : Mass of the final state (kg); m_{g_1} : Total mass of the vessel contents (kg); P: Pressure in the vessel at the time of burst (KPa); p_1 : Pressure in the vessel at the time of burst (Pa); P_0 , p_2 : Atmospheric pressure (Pa); s_{fl} : Entropy of the liquid at the initial state (J/kg K); 5/2: Entropy of the liquid at the final state (J/kg K); 5/3: Entropy of the vapour at the initial state (J/kg K); 5/3: Entropy of the vapour at the final state (J/kg K); 7/5: Boiling point (K); 7/5: Critical temperature (K); 7/6: Initial temperature of the vessel contents (K); u_{fl} : Internal energy of the liquid at initial state (J/kg); u_{fl} . Internal energy of the liquid at the final state (J/kg); u_{fl} . Internal energy of the vapour at the initial state Mass of liquid in the vessel (kg); W_{TNT}: Equivalent mass of TNT of the explosion energy (kg); X_f. Fraction of liquid flashing into vapour; X_g. Fraction of vapour condensing into liquid; \(\beta\): Fraction of explosion energy converted into a pressure wave; ΔU : Change in internal energy (J); ΔV : Change in volume (m^3); Ω : Correction for flash fraction f. Note: Initial state: At the instant of explosion. Final state: After explosion.

- (a) The energy of explosion, or 'burst energy'. This determines the severity of the blast wave generated by the BLEVE and the velocity (hence the range and the penetration) of the missiles formed out of the shattered vessel fragments;
- (b) The manner of release of the vessel contents. This determines the size, duration, and heat flux of the fireball if the contents are flammable, or the pattern of atmospheric dispersion if the contents are toxic.

Whereas more rigorous treatments are available, and with greater degree of consensus on their applicability, for explosion of vessels containing pressurized gases, cased explosives, and VCE (vapour cloud explosions), there is much greater degree of uncertainty associated with BLEVE situations wherein superheated liquids together with pressurized gases are involved.

When a vessel containing a superheated liquid fails catastrophically in a BLEVE, the 'boiling liquid' as well as the 'expanding vapour' together provide the burst energy but it is very difficult to estimate which phase contributes how much. This is because, as detailed in the preceding section, the events between the initial crack and the crack's propagation up to the occurrence of BLEVE would influence the state of both the phases. Further, a portion of the burst energy is used up in shattering the vessel, another portion in propelling the vessel fragments, and yet another in the generation of blast wave. The cooling effect of the flash vaporization of the liquid and the adiabatically expanding vapour further complicate the scenario. Once a vessel is shattered, some of the contents can also form transient pool fires by getting splashed on the floor before evaporating. This may reduce the quantity of the vessel contents which form the fireball.

We present below an overview of the state-of-the-art of BLEVE consequence assessment.

6.2. BLEVE energy

Classically two treatments have been used to estimate the burst energy accompanying a BLEVE: the so called 'TNT equivalent method' developed by Prugh [16] which treats the expanding vapour as an ideal gas, and the method which relies on entropy, enthalpy, and specific volume data when treating the expansion as occurring in a non-ideal gas. The second method has been described by Prugh [16], CCPS [8], Lees [3], and TNO [73], among others without giving it any name. As it is a thermodynamic method like the Prugh's but is distinguished by its use of specific volume, entropy and enthalpy (SVEE), we give it the name SVEE method. The manuals of CCPS [1,8] and TNO [73] mention only the latter but Prugh's method continues to receive consideration owing to its simplicity [74]. Recently, Planas-Cuchi et al. [59] have proposed a new method for calculating BLEVE energy on the basis of their contention that the liquid-vapour flashing in a BLEVE ought to be treated as irreversible adiabatic expansion rather then as isentropic expansion an in the Prugh method.

The essence of the three methods is presented in Table 3. The Prugh's and the SVEE forecasts run close to each other—as presented in Table 3. If the burst energy of a vessel filled with

propane is 1 kJ as per Prugh's method, it will be about 1.1 kJ as per SVEE. But the estimate as per the method of Planas-Cuchi et al. [59] for the same event yields burst energy less than half of the Prugh's/SVEE methods. Further refinement of the burst energy estimation methods is necessary as the forecast of the kinetic energy of the vessel fragments, hence the initial fragment velocity and the fragment striking range, are directly dependant on burst energy estimates.

6.3. Overpressure

Once the explosion energy of a BLEVE is estimated by one of the methods summarized in the preceding section (Table 3), overpressure can be determined by employing the correlations available in literature which link overpressure with explosion energy, and the distance from the accident epicenter. CCPS [8] and TNO [73] use the graphical method of Baker et al. [75], in conjunction with the SVEE estimate of explosion energy. But Prugh [16,17] has calculated overpressure by employing the graphs in CCPS [76] while Planas-Cuchi et al. [59] have used the graphs proposed by van den Berg and Lannoy [77]. The approaches are summarized below.

6.3.1. The method of Baker et al. [75] as used by CCPS [8] and TNO [73]

The explosion energy, $e_{\rm ex}$, obtained from the SVEE method is multiplied by a factor of 2 if the burst is a ground level, to obtain the working explosion energy, $E_{\rm ex}$ (J). The scaled distance, z, is then obtained from

$$z = R \left(\frac{P_0}{E_{\rm ex}}\right)^{1/3}$$

where R is the distance of the target from the vessel undergoing BLEVE (m), P_0 the atmospheric pressure (Pa), and $E_{\rm ex}$ is the explosion energy. The scaled overpressure is read from the curves in which scaled overpressure ($P_{\rm s}$) is plotted versus scaled distance [75].

Once the scaled overpressure is read from the graph, adjustments have to be made for cylindrical vessels and for vessels slightly elevated above the ground by using the appropriate multipliers, as given in Tables 4 and 5.

Table 4
Adjustment factor for *Ps* for cylindrical vessels [73]

Value of z	Multiplier for P_{S}
<0.3	4
0.3–3.5	1.6
>3.5	1.4

Table 5 Adjustment factor for P_s for vessels slightly above ground [73]

Multiplier for $P_{\rm s}$
2
1.1

The scaled overpressure, P_s (which is read off from the graph), is related to the overpressure (p_s) :

$$P_{\rm S} = \frac{p_{\rm S}}{P_0} - 1$$

6.3.2. Overpressure calculation as described by Prugh [16,17]

Prugh has outlined the following steps to determine overpressure:

1. The maximum overpressure at the surface of the bursting container ($P_{\rm sb}$, in kPa) is determined from [78]:

$$P_{\rm b} = P_{\rm sb}[1 - \theta]^{-2k/(k-1)}$$

where

$$\theta = \frac{0.035(k-1)(P_{\rm sb} - 101)}{\sqrt{[1+0.058P_{\rm sb}](kT/M)}}$$

 $P_{\rm b}$ is the pressure in the vessel at the time of burst (kPa), k the ratio of specific heats at constant pressure and constant volume, T the temperature of the vapour in the container (K), and M is the molecular weight of the vapour. The equation is solved iteratively to obtain $P_{\rm sb}$.

2. An entity, 'virtual distance', is next determined by first reading the scaled distance corresponding to overpressure $P_{\rm sb}$ from the curves given in CCPS [76], and calculating the distance (R) from the scaled distance by using the formula:

$$z = \frac{R}{\sqrt[3]{W_{\rm TNT}}}$$

On subtracting the radius of the vessel from R, the 'virtual distance', is obtained.

3. To determine overpressure at any distance from the vessel, the value of the 'virtual distance' is added to the distance at which the overpressure has to be determined. This value (distance + virtual distance) is used in the place of *R* in the formula for calculating scaled distance. Once the scaled distance is calculated, the curves given in CCPS [76] are used to obtain overpressure at the given distance.

6.3.3. Graphs give in van den Berg and Lannoy [77] as used by Planas-Cuchi et al. [59]

Unlike the graphs of Baker et al. [75] and CCPS [76] the graphs of Van den Berg and Lannoy [77] relate the scaled distance to overpressure directly, instead of scaled overpressure. Thus, for the calculated scaled distance, the overpressure can be obtained directly from the graphs.

6.4. Missiles

In most BLEVEs, except the ones involving non-flammable chemicals, fireballs are generated along with the explosion. But the range-of-impact of the missiles which result from the fragmented vessel is much larger than that of fireball [56,58].

Missiles also pose much greater danger of causing domino effect than the fireball or the blast wave. In disasters like the one that occurred in the Mexico City, 1984, the first vessel which BLEVEd had let off missiles wrapped with burning propane. These missiles struck other vessels, damaging them, and causing them to BLEVE. The resulting missiles precipitated further explosions.

Missiles are also known to be a major cause of death and destruction. In the Turkey farm episode at Albert City, IA, described earlier (Section 3.1.6), both the fatalities were by missile hits, as were the more serious of the injuries. At Deer Lake, PA, most of the 11 deaths and 10 injuries were caused by the flying fragments of an LPG road tanker which had BLEVEd. Many of the hits occurred on persons standing over 200 m away and beyond the range of the thermal hazard [3]. In the Laurel railroad tank car accident mentioned earlier (Section 3.2.1), a missile in the form of a rocketing fragment from one of the tank cars had hit a pump house, rupturing an 8 in. water main, thereby reducing the water supply to the fire fighters. The BLEVEs at Puebla, Mexico (1977) and at Texas City (1978) also produced rocketing fragments which damaged water tanks meant for supply to fire fighters [3].

The likely consequence of a BLEVE in terms of the duration and propagation of missiles depends on the following factors:

- 1. likely number and mass of missiles,
- 2. velocity and range of the missiles,
- 3. likely direction of propagation of the missiles,
- 4. penetrative ability and destructive potential of the missiles.

6.4.1. Likely number and mass of missiles

6.4.1.1. Cylindrical vessels. In a study of 27 BLEVEs involving LPG vessels, the maximum number of missiles per vessel, was found to be four and it occurred in 15% of the explosions [79]. The most frequently encountered number of missiles per vessel was three (37% cases) followed by one (30% cases) and two (26% cases). These authors have proposed the following correlation between the number of fragments, and the vessel capacity $(V, \, \text{m}^3)$ on the basis of involving vessel's a of capacities $700-2500 \, \text{m}^3$: n = 3.77 + 0.0096 V.

Stawczyk [58], in a study of LPG cylinders of 5 kg and 11 kg capacities, found that each BLEVE generated three to five main projectiles and several single, smaller fragments.

As per earlier studies [3] the most likely initiation of the failure of a cylindrical vessel is in axial direction; the crack may then turn and propagate circumferentially. Stawczyk [58] found that in the LPG cylinders studied by him, the upper part of the cylinder usually detached along with a large fragment of a side wall; the latter formed two or three projectiles.

6.4.1.2. Spherical vessels. Spherical vessels generate much larger number of fragments. A study of seven BLEVEs involving spheres revealed as many as 19 fragments in one of the explosions, followed by 16, 6, 5, 5, 4, and 3 in other explosions giving an average of above eight missiles per explosion [3]. Three tests

by Schulz-Forberg et al. [80] on 4.85 m³ vessels, half full with liquid propane, produced three, five and nine missiles, respectively.

Interestingly, other studies on missiles generated by vessel bursts, which evidently involve both BLEVE and non-BLEVE explosions, have reported much larger number of missiles per explosion than BLEVE-specific studies. A post-mortem of seven major explosions that had occurred between 1957 and 1988 [81] reveals that the explosion involving 53 m³ of a central section of a 200 m³ vinyl acetylene distillation column at Texas City, 1969, generated over 50 fragments. Another explosion at Antwerp, 1987, which had involved a 162 m³ ethylene oxide distillation unit, let off 35 fragments. The average number of fragments produced in the seven bursts analyzed by Scilly and Crowther [81] was 26.6. Another study of 25 accidental explosions by Baker et al. [82], leads to an average of 6.6 fragments per explosion. Three argon-filled spheres produced 14 fragments whereas a single propane cylinder split into 11.

In general a vessel may undergo either a brittle failure or a ductile failure; the latter type occurs more frequently than the former. But, whereas a brittle failure is likely to generate larger number of missiles then a ductile failure, it is the hits from the latter that have much greater potential to cause damage [3,83].

6.4.1.3. Missile fragment mass estimation. For fragment mass distribution, broad estimates may be obtained using the method of Held [84], developed for cased explosives. The mass m of the nth fragment is given by

$$M = \frac{\mathrm{d}M(n)}{\mathrm{d}n} = M_0 B \lambda n^{\lambda - 1} \exp(-Bn^{\lambda})$$

where M(n) is the overall (cumulative) mass of fragments of number n, M_0 the total mass of fragments, n the number of the nth largest fragment, and B and λ are constants.

6.4.2. Velocity and range of the missiles

An assessment of the momentum of the rocketing fragments likely from a BLEVE, and the distance likely to be traveled by such fragments is essential for determining the likely impact area of a BLEVE. Apart from designing the layout of a plant, this knowledge is also very important in deciding how far away fire fighters must be located when trying to save a fire-engulfed vessel from suffering a BLEVE [56,58].

When a vessel undergoes a BLEVE, a fraction of the explosion energy of the vessel is transformed as the kinetic energy of the vessel fragments which then shoot out as missiles. Experimental determinations on light-weight containers detonated with TNT have indicated that most fragments fall at distances between 0.3 and 0.8 of the maximum. The probability that there would be at least one fragment which would travel the maximum possible distance increases with the number of fragments and is therefore greater for a large explosion [3]. In the simulated BLEVEs on LPG cylinders of 5 kg and 11 kg capacities, Stawczyk [58] observed that the biggest elements of a cylinder were found at a distance of about 70 m from the shattered vessel. Flat fragments, and compact elements of small mass, such as the head, went up to four times farther.

Stawczyk [58] also notes that even though past reports in literature put 200 m as the maximum distance to which projectiles from a 11 kg LPG tank can reach, he has found that projectiles from his 11 kg cylinders undergoing BLEVE went up to 300 m.

There are many instances when large chunks of an exploded vessel have traveled long distances. At Murdoch, IL [9], portion of a rail container was hurled as much as 1.7 km away after a BLEVE! In the explosion at the American Oil Company refinery at Whiting, Indiana, one 60-t piece landed on a tank of gasoline, smashing it severely and igniting and scattering its contents. Other vessel fragments were scattered for several hundred feet away from the unit site. In one ship explosion investigated by Clancey [85] a deck cover of 400 tonne was thrown 100 ft. During the serial BLEVEs at Sydney which occurred on April Fool's day in 1990, a 30 m long cylinder rocketed after its top was ripped off in a BLEVE. It struck three 40-t tanks, an electrical substation, and a workshop before nose-diving into a canal 300 m away from the origin of its flight [86].

For vessels filled with ideal gases, Baum's [87] treatment of Baker's equation for explosion energy [82], used in conjunction with experimental data, yields a factor in the range 0.2–0.5 by which explosion energy of a vessel is transformed to kinetic energy of the fragments in which the vehicle is shattered. But for non-ideal gases, and for vessels partially filled with liquefied gas as in BLEVE situations, this treatment can give grossly inaccurate forecasts. The Centre for Chemical Process Safety [1] has suggested the Moore [88] equation for obtaining the initial velocity of the fragment, μ (ft/s), emanating from the rupture of a pressurized vessel as a function of rupture pressure of the vessel, P (psig), fragment diameter D (in.), and weight of the fragment, W (lb):

$$\mu = 2.05 \sqrt{\frac{PD^3}{W}}$$

Fragments with spheroidal shape have the least drag coefficient, followed by edge-on cubes and end-on rods [1]; missiles with shapes and orientation similar to these geometries travel the farthest. Baum [89] has presented a model for velocities attained by end-caps of cylindrical vessels upon vessel burst. The model assumes that the action of the escaping vapour/liquid on the end-cap is analogous to a missile driven by a gas jet from a constant pressure source. The missile velocities are derived via a simple approximation to the impulse applied to the internal face of the closed end of the 'rocket'. Similar logic was used later by Baum [90] for predicting the velocity achieved by an axially split cylindrical vessel. The author also describes experiments which validate the model.

6.4.3. Likely direction of propagation of the missiles

Given the fact that vessel fragments which are shot off as missiles upon a BLEVE have much longer range of impacts than other hazards caused by BLEVE – fireballs and shock wave – it may enormously help in BLEVE damage control (following section) if the most probable directions in which the missiles may fly can be known.

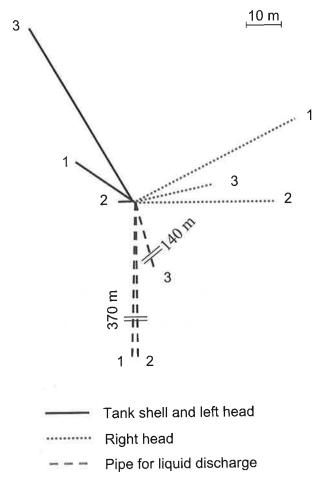


Fig. 3. Schematic view of the direction of flight and range of fragments of three vessels – nos. 1–3 – after a BLEVE. *Source*: Drawn from the data of Schulz-Forberg et al. [80].

In the BLEVE test on three vessels, Schulz-Forberg et al. [80] found that the tank shell and the left head of each of the vessels were propelled in a north-westerly direction, between 0° and 45° (Fig. 3). The right head of all the three vessels propelled in the opposite direction north-east, in the 135–180° arc. The liquid discharge pipe of each of the vessel was hurled southward and went more than thrice farther then the other two pieces. In other words similar type of vessel fragments tended to be hurled in similar directions.

Missile maps of 11 incidents (Fig. 4), involving 15 vessels, mainly LPG, indicate that about half the fragments were projected into about a third of the total area, in arcs of 30° to either side of the vessel front and rear axial directions [3,79].

Considering that the findings of Holden and Reeves [79] do not match with that of Schulz-Forberg et al. [80], and the very scanty nature of information on the direction of missiles in the past accidents, it is not possible at present to draw even a broad guideline *vis-á-vis* likely direction of fragment propagation in BLEVE events. Nevertheless, Hauptmanns [91,92] has proposed the following probabilities of projectile directions on the basis of the data of Holden and Reeves [79]: 30–150°: 0.2; 150–210°: 0.3; 210–330°: 0.2; 330–30°: 0.3.

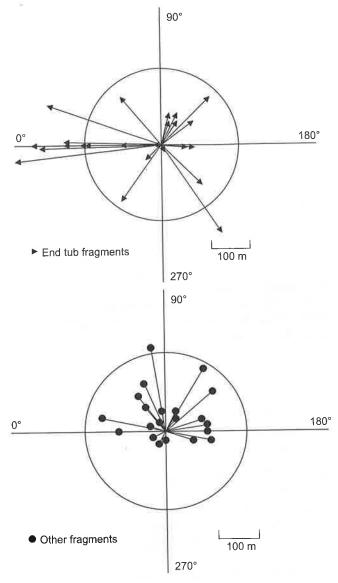


Fig. 4. Map of missiles generated from the bursting of LPG vessels (from the data of Holden and Reeves [79]).

6.4.4. Penetrative ability and destructive potential of missiles

A great deal of work has been done on the penetrative power of cased explosives but information pertaining to vessel-burst missiles is less extensive. Missiles generated from process plant, such as high pressure vessels, are of irregular shape and relatively low energy density, and their penetrative or destructive power depends on their orientation at the moment of impact with a target. Due to their irregular shape, fragments usually produced by the bursting of a pressure vessel have much lower penetrating power, often only half, than compact blunt fragments, while pointed projectiles have appreciably more [3].

For penetration by small fragments, the depth of penetration is given by the relation (Cox and Saville [93], quoted in Lees [3]):

$$t = Km^{n_1}V^{n_2}$$

where m is the mass of the fragment (kg), t the thickness of the barricade needed just to stop the fragment (m), V the velocity of the fragment (m/s), K a constant and n_1 , and n_2 are the indices. For brickwork, concrete, and mild steel the values of K, n_1 and n_2 are in the range 6×10^{-5} to 23×10^{-6} , 0.33-0.4, and 1.0-1.5 respectively.

The above equation is valid for compact blunt steel fragments such as solid cylinders with the fragment length approximately equal to the cylinder diameter, and a mass of not more than 1 kg.

For penetration by larger fragments, of mass exceeding 1 kg, the depth of penetration may be calculated from

$$t = \frac{Cm}{A} \log_{10}(1 + 5 \times 10^{-5} V^2)$$

where A is the presented area of the fragment (m²) and C is a constant. The value of C ranges between 0.3×10^{-4} to 3.5×10^{-4} for alloy steel, mild steel, and reinforced (1.4%) concrete; it is $\sim 25 \times 10^{-4}$ for brickwork.

For penetration of concrete by rod shaped missiles:

$$t = 2 \times 10^{-7} \frac{mV^{1.5}}{d^{1.8}}$$

and for mild steel plate:

$$t = \left(0.33 \times 10^{-9} \frac{mV^2}{d^3}\right)^{1/1.41}$$

where d is the diameter of the fragment (m).

As the size of the projectile increases, the response of the target becomes increasingly significant. Kennedy [94] has proposed that the target response may be modeled by assuming it to be subject to a rectangular pulse forcing function. With this assumption it is then possible to apply conventional structural response techniques to estimate the susceptibility of a structure to a missile hit.

Out of the models developed for the penetration of reinforced concrete by missiles, the modified NDRC correlation [95] has found widespread acceptance. It is applicable to a flat-faced cylindrical missile:

$$G\left(\frac{x}{d}\right) = 2.74 \times 10^{-5} \left(\frac{Dd^{0.2}}{\sigma_c^{0.5}}\right) V^{1.8}$$

with

$$G\left(\frac{x}{d}\right) = \left(\frac{x}{2d}\right)^2 \quad \left(\frac{x}{d} \le 2\right),$$

$$G\left(\frac{x}{d}\right) = \frac{x}{d} - 1 \quad \left(\frac{x}{d} > 2\right), \qquad D = \frac{m}{d^3}$$

where d is the diameter of the missile (m), D its caliber density (kg/m³), m its mass (kg), V its velocity (m/s), x the penetration depth (m) and σ_c is the compressive strength of concrete (Pa).

To assess the likely penetration by a flat-nosed cylinder the formula developed by the Commissariat å I'Energie Atomique/Electricite de France (CEA/EDF) (quoted in Lees [3]), on the basis of extensive testing, is also often used, though no comparison has been reported in literature of the results obtainable

by this method and with the NDRC correlation:

$$V_{\rm p}^2 = 1.7\sigma_{\rm c} p^{1/3} \left(\frac{de}{m}\right)^{4/3}$$

where V_p is the perforation velocity (m/s), e is the perforation thickness (m) and p is the density of the concrete (kg/m³); the other symbols are as defined above.

It has been reported, that hemispherical nosed projectiles with a diameter approximately equal to the target thickness require up to 30% higher velocities to perforate a reinforced concrete target than a flat-faced or a flat nosed projectile having the same mass and diameter. Similar observations were obtained for other projectiles with sharp noses [96].

For penetration by missiles of steel plate, the model described by White and Botsford [97], appears to have found wide acceptance:

$$\frac{e_{\rm c}}{d} = \frac{u}{10.29}(42.7h^2 + wh)$$

where d is the diameter of the missile (m), e_c its critical impact energy (J), h the thickness of the target panel (m), u the ultimate tensile strength of the panel (Pa) and w is the width of the panel (m).

Vessel rupture by a BLEVE fragment: Pietersen [98] has proposed a method which involves calculating (i) the force at the point of impact to deform the sphere up to the yield point, and the corresponding energy E_y and (ii) the energy E_r to deform the sphere in the plastic region between yield and rupture. Utilizing equations given by Roark and Young [99] and taking the impact area as five times the vessel wall thickness, these two energies were found to be $E_y = 7 \, \text{kJ}$ and $E_r = 64 \, \text{kJ}$. Assuming that plastic deformation of the impacting fragment uses up an amount of energy equal to that used in the sphere itself, the total energy required for rupture is 135 kJ. From simple kinetic energy considerations, for a fragment of mass 20 tonnes (1/10th of a sphere) the velocity required to effect rupture is then 3.7 m/s and for 1 of 2 tonnes (1/100th of a sphere) it is 11.6 m/s.

Pietersen's calculation indicates that the projectile velocities needed to rupture another vessel are well below the initial velocities the fragments actually acquire when a sphere undergoes BLEVE. In other words, missiles from a vessel undergoing BLEVE are highly likely to rupture other vessels lying close by. Accident histories confirm this surmise.

Acknowledging the stochasticity associated with the nature of fragmentation of a vessel undergoing BLEVE, orientation and initial velocities of the fragments, direction of fragment propagation, etc., Hauptmanns [91] has developed a procedure for analyzing such missiles on the basis of probability density functions. The Monte Carlo simulation is done to propagate the effect of the stochastic and uncertain input parameters through the calculation.

Probability theory has also been used by Gubinelli et al. [100] to estimate the likelihood of a fragment hitting a target if a vessel explodes. Their model is based on the analytical solution of the ballistic equations for fragment trajectory, and on the introduction of probability distribution functions for the initial direction of projection of the fragments. The authors

have made a 'preliminary validation' of their model with the data of Holden and Reeves [79].

6.5. Fireball

The 'Yellow Book' [73] defines fireball as 'a fire, burning sufficiently rapidly for the burning mass to rise into the air as a cloud or ball.' In all BLEVEs involving flammable material, there is a near instantaneous two-phase release of the material which auto-ignites to form a fireball. As fireball is an inevitable consequence whenever a vessel containing a flammable material undergoes BLEVE, it is often presumed to be an integral part of all BLEVEs. But about one-fifth of all BLEVEs involve non-flammable material (including fire suppressants like nitrogen, carbon dioxide, and water) and no fireballs are generated in such cases [40].

Fireballs are also formed when vapour clouds are ignited but whereas such fireballs are governed by buoyancy forces, those from BLEVEs are predominantly influenced by momentum forces.

In rare cases a vessel containing a flammable PLG may first release sufficient mass of vapour which may form a cloud and get ignited before the vessel fails in a BLEVE generating a far bigger fireball.

For a typical fireball resulting from an accidental release of some 100 tonnes of flammable material, combustion energy of the order of $5 \times 10^{12} \, \mathrm{J}$ is released within a time span of $10\text{--}20 \, \mathrm{s}$ [101]. About one fourth of this energy is emitted as radiation—powerful enough to scorch people, damage property, and trigger secondary fires. For these reasons fireballs are considered as one of the major hazards in process industry.

Frame by frame analysis of full-scale fireball photographs by Crawley [102] show that the fireball passes through the phases of (a) growth, (b) steady burning and (c) burnout. The growth phase has two intervals, each spanning about 1 s. During the first time span, during which the fireball grows to about half its final diameter, the fireball boundary is bright with yellowish-white flames indicating a flame temperature of about 1300 °C. In the second time span of the first phase, the fireball attains its maximum volume, but about 10% of the surface is dark and sooty with the rest being white, yellowish-orange or light red, indicating flame temperatures in the range 900–1300 °C, with an estimated effective flame temperature of 1100–1200 °C.

In the second phase, which lasts some $10 \, \mathrm{s}$, the fireball, which is now roughly spherical, is no longer growing. At the start of this phase it begins to lift off. It rises and changes to the familiar mushroom shape. The estimated effective flame temperature remains at $1100-1200 \, ^{\circ}\mathrm{C}$.

In the third phase, which lasts some $5\,\mathrm{s}$, the fireball remains the same size, but the flame becomes less sooty and more translucent.

To forecast the size, duration, and radiation of a likely fireball from a BLEVE, the following issues must be addressed:

- (a) the mass of flammable substance released on BLEVE,
- (b) the mass of the substance contributing to the fireball,

- (c) the fireball development as a function of time,
- (d) the fireball size and duration,
- (e) the heat load generated,
- (f) the 'view factor',
- (g) the likely harm to the life forms or inanimate objects exposed to the heat load generated by the fireball.

The 'Yellow Book' [73] presents a 14-step calculation with which the size and the impact of a BLEVE fireball can be predicted. The steps are associated with calculations of: (a) the amount of flammable material likely to be released on vessel failure, (b) fireball radius, (c) fireball duration, (d) fireball lift-off height, (e) distance of impact point X from the center of the fireball, (f) maximum value of view factor at point X, (g) heat generated by the fireball, (h) net available heat for radiation, (i) absorption factor for water vapour (likely to be present between the fireball and X), (j) absorption coefficient of carbon dioxide (also likely to be present between the fireball and X), (k) atmospheric transmisivity (based on (i) and (j), above), and (l) the heat flux. Further assessments can be done of the damage likely at point X in terms of degree of burns.

Of the 12 parameters mentioned above, the view factor is defined as the ratio between the received and the emitted radiation energy per unit area [73]. Put another way, it is the fraction of the fireball that can be 'seen' by the target [103]. The view factor incorporates the orientation of the object relative to the fireball, and its distance from the fireball center.

As is the case with other aspects of BLEVE forecasting, wide variations are possible in most of the aspects associated with fireball calculations mentioned above, and treatments by different authors can give widely varying estimates. The uncertainty begins with the estimation of the material that would be released instantaneously on the vessel failure, or the 'flashing fraction'. Some treatments, including the 'Yellow Book' [73] and Ref. [1] assume that the entire lading will flash over to contribute to the fireball whereas other treatments, for example Roberts [104] and Marshall [12] put the fraction of the fuel that participates in the fireball at about a third of the fraction that is released in a BLEVE.

The work done so far on the estimation of fireball diameter and duration is summarized in Table 6. The available expressions for estimating the height of the fireball from the ground are listed in Table 7.

Of greater relevance is the assessment of the surface emissive power of the fireball and the incident radiation (heat load) exerted by it at a reference point (the target). Models for these treatments are summarized in Table 8. The point source models assume that a certain fraction of the heat generated (F_r) by the fireball is radiated uniformly in all directions. This heat is usually taken to be the heat of combustion of the fireball. CCPS [8] cautions that the point source models should not be used for those instances where the plane of the target (receptor) intercepts the fireball.

The estimates and models for the fraction of heat radiated (F_r) , view factor (v_F) the atmospheric transmissivity (τ) , are given in Tables 9–11.

Thermally induced BLEVEs in 4001 automotive tanks filled with liquefied propane, carried out by Maillette and Birk [31],

Table 6 $\,$ Empirical and analytical methods for estimating fireball diameter and duration

Source	Material	Diameter, D_{max} (m)	Duration, $t_{\rm B}$ (s)
Empirical correlations			
Hardee and Lee [116]	Propane	$5.55M^{0.333}$	=
Fay and Lewis [117]	Propane	$6.28M^{0.333}$	$2.53M^{0.167}$
Hasegawa and Sato [118]	Pentane	$5.28M^{0.277}$	$1.10M^{0.097}$
Hasegawa and Sato [119]	n-Pentane	$5.25M^{0:314}$	$1.07M^{0.181}$
Williamson and Mann [120]	7=	$5.88M^{0.333}$	$1.09M^{0.167}$
Lihou and Maund [121]	Butane	$5.72M^{0.333}$	$0.45M^{0.333}$
Lihou and Maund [121]	Rocket fuel	$6.20M^{0.320}$	$0.49M^{0.320}$
Lihou and Maund [121]	Propylene	$3.51M^{0.333}$	$0.32M^{0.333}$
Lihou and Maund [121]	Methane	$6.36M^{0.325}$	$2.57M^{0.167}$
Moorhouse and Pritchard [122]	Flammable liquid	$5.33M^{0.327}$	$1.09M^{0.327}$
Lihou and Maund [121]	Propane	$3.46M^{0.333}$	$0.31M^{0.333}$
Duiser [123]	Flammable liquid	$5.45M^{.1}$ 30	$1.34M^{0.167}$
Marshall [12]	Hydrocarbon	$5.50M^{0.333}$	$0.38M^{0.333}$
Gayle and Bransford [124] and	Flammable liquid	$6.14M^{0.325}$	$0.41M^{0.340}$
Bagster and Pitblado [125]	1		
Pietersen [98], CCPS [76], Prugh	Flammable liquid	$6.48M^{0.325}$	$0.852M^{0.260}$
[105] and TNO [73]	1		
Robert [104] and CCPS [1]	Flammable liquid	$5.80M^{0.333}$	$0.45M^{0.333}$ ($M < 3 \times 10^4$), $2.60M^{0.167}$ ($M \ge 3 \times 10^4$)
Martinsen and Marx [126]	Flammable liquid	$8.66M^{0.25}t^{0.333}, 0 \le t \le t_{\rm B}/3$	$0.9M^{0,25}$
Analytical models			
Bader et al. [127]	Propellant	$0.61 \left(\frac{3}{4\pi a}\right)^{1/3} W_{\rm b}^{1/3}$	$0.572W_{\rm h}^{1/6}$
Hardee and Lee [116]	LNG	$0.61 \left(\frac{3}{4\pi\rho}\right)^{1/3} W_{\rm b}^{1/3}$ $6.24 M^{0.333}$	$1.11M^{0.167}$
Fay and Lewis [117]	Flammable liquid	$\frac{g\beta t^2(\rho_0 - \rho_p)}{7\rho_p}$	$t = \left(\frac{14\rho_{\rm p}}{g\beta(\rho_{\rm u} - \rho_{\rm p})}\right)^{0.5} \left(\frac{3V}{4\pi}\right)^{0.167}$

M: mass of fuel in fireball (kg), t: time elapsed after BLEVE (s), ρ : density of fireball gas (lb/ft³), W_b : mass of propellant (lb), g: acceleration due to gravity (m/s²), β : entrainment coefficient, ρ_a : density of air (kg/m³), ρ_p : density of products of combustion (kg/m³).

Table 7 Correlations for estimating height of the center of the fireball from the ground, H

**	
Reference	H (m)
TNO [73] CCPS [1] Martinsen and Marx [126]	6.48 $M^{0.325}$ 4.35 $M^{0.333}$ 4.33 $M^{0.25}t^{0.333}$ for $0 \le t \le t_B/3$

Table 8 models for estimating the surface emissive power and incident radiation on target

Reference	Surface emissive power, E (W/m ²), E	Heat radiation received by target, $E_{\rm r}$ (W/m ²)
Point source models		0.67
Hymes [128]	=	$E_{\rm r} = \frac{2.2\alpha \tau F_{\rm r} H_{\rm c} M^{0.67}}{4\pi l^2}$
CCPS [76] and Prugh [105]	$E = \frac{F_{\rm r} M H_{\rm c}}{\pi D_{\rm max}^2 t_{\rm B}}$	23
Lees [3]	-	$E_{\rm r} = \frac{\alpha \tau F_{\rm r} Q}{4\pi l^2}$
TNO [73]	$E = \frac{\Delta HMF_{\rm r}}{\pi D_{\rm max}^2 t_{\rm B}}$	m.
Solid flame models TNO [73] and CCPS [1]	illax D	$E_{\rm r} = E \tau v_{\rm F}$

 ΔH : Net heat available for radiation (J/kg), H_c : Heat of Combustion (J/kg), α : Absorptivity of the target, Q: Heat release rate (W), l: Distance of fireball centre from the target/receptor (m).

Table 9 Estimates and models for the fraction of heat radiated by fireballs, F_r

Source	F_{τ}
Roberts [104]	$0.25P_{\rm v}^{0.32}$, for $P_{\rm v} < 6{\rm MPa}$
Hymes [129]	0.3 for fireballs bursting below the relief valve set pressure, 0.4 for fireballs bursting at or above the relief
	valve set pressure
TNO [73]	$0.27P_{\rm v}^{0.32}$
Makhviladze and Yakush [130]	0.18–0.27
Roberts et al. [29]	0.25-0.4

 $P_{\rm v}$ is the vapor pressure at the moment of burst (MPa).

Table 10 Expressions for view factor, v_F

Expressions for their factors, of				
Source	Position of object	v_{F}		
CCPS [8]	Horizontal	$\frac{H(D_{\text{max}}/2)^2}{(L^2+H^2)^{3/2}}$		
CCPS [8]	Vertical $(L > D_{\text{max}}/2)$	$\frac{L(D_{\text{max}}/2)^2}{(L^2 + H^2)^{3/2}}$		
CCPS [76] and TNO [73]	Highest value of view factor	$\left(\frac{D_{max}}{2X}\right)^2$		

X: Distance of fireball centre from the target/receptor (m), L: Distance of point on ground directly below the fireball centre, from the target/receptor (m).

Table 11 Expressions for atmospheric transmisivity, τ

Source	τ
Pietersen and Huerta [131] and CCPS [1]	$2.02(P_{\rm w}X_{\rm s})^{-0.09}$
TNO [73]	$1 - \alpha_{\rm w} - \alpha_{\rm c}$

 α_c : Absorption coefficient for carbon dioxide, α_w : Absorption factor for water vapour, P_w : Water partial pressure (Pa), X_s : Distance from surface of fireball to the target (m).

revealed that while the projected fireball area is more or less circular for one-step BLEVEs, the shape of the fireball tended to be cylinder-like in two-step BLEVEs. They found that fireballs resulting from cooler lading created greater hazards because they generated larger ground fires; took longer to lift off, and lasted longer.

Roberts et al. [29] compared the results of their BLEVE tests with the predictions of the models proposed earlier by Roberts [104], and Prugh [105] for fireball diameter and duration (Table 6). They found that the expression proposed by Prugh [105] gave a slightly better fit.

Based on numerical modeling of the formation, evolution, and combustion processes in a fireball, Makhviladze et al. [101] suggest that when the released fuel is ignited near the source, the burning gas could rapidly assumes a nearly spherical shape, rising as a fireball. The temperature and combustion product concentration fields gradually become similar to each other. Diffusion combustion of a fuel-rich cloud is localized in a thin zone on the cloud surface where the fuel mixes with the ambient air. The authors further observe that for two-phase releases of volatile liquefied gases, droplet evaporation proceeds much more rapidly than combustion, so that the main influence of prerelease condition is through changing the outflow velocity. The distributions of net emissive power calculated for small fuel mass (optically thin fireball) and for large fuel mass (optically thick cloud) showed that in the small cloud, the emission of radiation occurs throughout the volume of the fireball, whereas a large cloud emits mostly from its surface. The calculated fractions of combustion heat emitted as a radiation for all cloud sizes and storage conditions were in the range 0.2–0.25, which matched well with the available experimental data for turbulent propane flames.

7. BLEVE prevention and damage control

As discussed in Section 5 of this paper, it is well-neigh impossible to say with certainty whether a jeopardized vessel will suffer a BLEVE or not. Likewise it is not possible to forecast with any measure of confidence when a vessel will suffer a BLEVE after getting jeopardized. These aspects, and the uncertainty associated with forecasting the size, range, direction, and momentum of missiles likely from a BLEVE, pose special challenges towards preventing a BLEVE or in containing the damage a BLEVE may cause. There have been several tragic incidents when fire fighters arrive to save a fire-engulfed vessel only to be killed by the expanding fireball or the rocketing fragments when a vessel suddenly bursts [4,106].

The strategies required to minimize the occurrence and the adverse impact of BLEVE, have been reviewed by Prugh [16],

Khan and Abbasi [4], and Casal et al. [5]. Pointers can also be drawn from the studies on simulated BLEVEs described in Section 5, and from the studies such as effect of pressure relief value (PRV) functioning [23,56,107,108], survivability of steel cylinders in comparison to aluminum cylinders [62] and projectile range [29]. The strategies can be broadly classified into three categories:

- (a) Reducing the probability of a vessel getting jeopardized by a hit, a fire, an increasingly pronounced structural weakness, a runaway reaction, or a transportation accident.
- (b) Cushioning the impact of the above so that the perturbation does not escalate to a BLEVE.
- (c) Minimizing the damage if a BLEVE does occur.

We summarize below the strategies possible under each of these categories.

7.1. Preventing the causes which can make a vessel vulnerable to BLEVE

7.1.1. Preventing exposure to fire

Keeping the PLG containing vessel a safe distance away from likely source of fire. Fire engulfment being the most common of the causes due to which PLG vessels undergo BLEVE, it is imperative that a reasonably large distance should separate a PLG vessel from another vessel handling a flammable material or from other sources of fire. Of course this can at best reduce the probability of a PLG vessel being heated by the radiation load from another vessel which has caught fire. The PLG vessel may still be jeopardized by blast waves or projectile hits from another exploding vessel. Raj [109] has examined the efficacy of over 60-year-old NFPA (National Fire Protection Association) codes specifying minimum separation distance between storage tanks on the basis of a radiation heat transfer model. The author has calculated temporal variation of the vapour-wetted tank-wall temperature of a vessel exposed to an external, non-impinging, highly radiative 30.5 m diameter pool fire. The results indicate that the vessel wall temperature will never reach critical condition and that the NFPA codes are still valid for non-impinging fires.

Sloping of the nearby ground. To prevent a pool fire occurring after an accidental spill from a PLG vessel, the ground radially away from a fixed installation should have a downward slope of not less than 1% so as to lead the spill away to a safe area.

Water barriers. These may be installed close to the PLG containers. These consist of sprayer system which generates curtains of fine water mist. The barriers can capture flammable vapour if released from the PLG container and disperse it without getting ignited. Water mists can also dissolve some of the released material if it happens to be ammonia, chlorine, or some other water soluble substance, thereby reducing the toxic dispersion.

7.1.2. Preventing mechanical damage

Trucks and railroad cars carrying PLGs should be protected from accidental damage with double containers, equipped with insulation in the annular spaces. Collision or overturning during transportation damages the outer shall. This makes it essential to fabricate the outer container with a material which would provide protection for the inner tankage.

7.1.3. Preventing overfilling and overpressure

Rigid compliance with standards during the filling and weighing of the BLEVE-prone tanks alongside very careful installation and testing of relief devices have reduced the frequency of BLEVEs on account of overfilling. But accidents continue to occur during pumping of PLGs as happened at Moombas, South Australia, on 16 June 2001, killing one person, injuring three, and damaging the infrastructure.

The relief-devices are prone to plugging; this problem is circumvented by the installation of rupture disks in series as pluggage protection under relief valves. Rupture disks are also installed "in parallel" to relief valves as a last resort protection.

7.1.4. Prevention of runaway reaction

The accident which led to the coinage of the acronym BLEVE was a runaway reaction. But BLEVEs due to runaway reactions are much less common than BLEVEs which occur when a PLG storage vessel suffers accidental damage. Instrumentation should be provided for continuous monitoring of temperature and pressure within all process equipment likely to contain self-reactive materials. Such equipment should have facilities for counteracting overpressure or overtemperature; for example internal cooling coils or external jackets, remote-controlled venting valves, inhibitor—injection systems, and internal deluges, as well as high-temperature and/or high-pressure alarms for control-room and field personnel.

7.1.5. Prevention of vapour–space contamination with reactive material

Vessels containing highly reactive gases such as hydrogen and chlorine in liquefied form should be safeguarded against contamination by other substances with which they can react. Inerting vapour spaces with nitrogen or other nonreactive gas and installing explosion–suppression systems may prevent vapour–space explosions thus reducing the risk of vessel damage and, consequently, a BLEVE [16].

7.1.6. Prevention of internal weakening of vessel structure due to fatigue, creep, corrosion, etc.

Proper design and pre-use testing of containers can prevent distortion and possible rupture of containers. Periodic wall-thickness measurements, internal inspection for corrosion, acoustic emission testing for the possible cracking of the container, etc., should be performed to ensure the fitness of the containers. Preventive maintenance should be done along with 'predictive' maintenance [16].

7.1.7. General protection from fire as well as accidental hits, by container burial

Vessels containing PLGs can be protected from fire, or external hits, to a very great extent if they are partially or totally buried. But such vessels are difficult to inspect and are particularly vulnerable to corrosion.

7.1.8. Prevention of excessive superheat which may prevent explosive boiling

Taking a cue from distillation systems and reactors in which nucleation devices such as sharp-edged ceramic material or an aluminum mesh is placed in the liquid being distilled to assist boiling and prevent superheating, similar devices have been explored for PLG containers. But a well tried and tested strategy along these lines is yet to evolve.

7.2. Managing a jeopardized vessel to prevent it from undergoing BLEVE

7.2.1. Thermal insulation

The PLG containers should be thermally insulated to the maximum extent possible as it would reduce the rate of heating of the vessel when it receives heat load and delay the pressure increase inside. If the container wall is protected with a steel jacket and a ceramic insulation of adequate thickness (13 mm or more), it provides substantial thermal protection [61]. Even steel jackets with an air gap between the jacket walls can cut the wall heating rate to approximately half of the unprotected wall. But such fire proofing cannot by itself prevent a BLEVE; it can at best delay the catastrophic event by four to 5 h giving time for the fire fighters to remove the heat load. In fixed installations, even the vessel support system should be insulated so that it does not cave in when subjected to heat. Likewise, the valves, pipes, and other safety elements used in the PLG vessel must have the ability to resist the action of fire and withstand the high temperatures that may be reached in a crisis situation. The thermal insulation system should be installed in such a way that it does not interfere with the periodic inspection of the tank surface and support systems.

Fireproofing can be even more effective in delaying a BLEVE if the pressure relief valve (PRV) operates correctly.

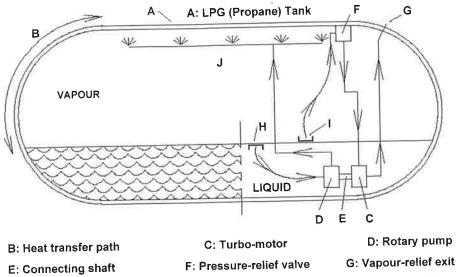
7.2.2. Directed water deluge

To cut off the heat load once a PLG vessel gets engulfed in fire, it has to be subjected to what is called 'directed water deluge' [110]. Water must be applied as soon as possible, with a layer of adequate thickness which should totally cover the vessel wall, especially those areas directly covered with flame. A water flow rate of $10\,\mathrm{m}^{-2}\,\mathrm{min}^{-1}$ is recommended, which should be upped to $15\,\mathrm{m}^{-2}\,\mathrm{min}^{-1}$ in areas directly being licked by a flame [111,112].

If the flame is highly turbulent, which can generate a heat flux of the order of $350 \,\mathrm{kW}\,\mathrm{m}^{-2}$, flow rates even larger than $25 \,\mathrm{m}^{-2}\,\mathrm{min}^{-1}$ may be required. But if the PLG vessel is being impinged by jet fire the water deluge is less effective; it cannot be relied upon to maintain a water film over the whole tank surface [110]. The dry patches, where the water film broke down got heated to about $350\,^{\circ}\mathrm{C}$ in 10 min during the course of full-scale tests reported by Shirvill [110].

7.2.3. Cooling of the unwetted part of the PLG tank wall by internal liquid spray

Young [113] has patented an 'anti-BLEVE safety system' in which a turbo-charger is placed inside the PLG vessel. If the



H: Self-righting liquid intake I: Self-righting vapour intake J: Liquid spray nozzles

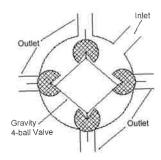


Fig. 5. The 'anti-BLEVE safety system' patented by Young [113].

vessel were to get engulfed in a fire, the turbo-charger, according to the patent, would take in the liquid from just below the surface near the shell of the tank, and spray it vertically upwards to cool the unwetted part of the tank (Fig. 5).

The charger is claimed to be driven by the vapour escaping through the pressure relief value. The system is expected to prevent the unwetted part of the tank well from getting heated to the point of weakening the part, thus preventing a crack to develop for the eventual BLEVE. According to the patent, the system can be readily built into all new LPG tanks, as well as retro-fitted to all existing transportation (rail, road and sea) tanks and storage tanks. For mobile tanks, the patentee has devised a gravity-valve assembly to ensure that the liquid is always sprayed upwards, and that only vapour is emitted from the pressure relief valve.

7.2.4. Rapid depressurization

Another step must be taken along with the start of 'directed water deluge' to reduce the probability of a BLEVE—depressurization of the vessel with remote operated 'fireproof' valves bypassing the installed PRV. Such devices should be able to reduce the vessel pressure to half of the design pressure within 15 min [5]. The released material should be eliminated in a safe manner, for example with a torch. The depressurization should not be too rapid either as it may lead to extremely low

temperature and fragility in the steel. For a 54 m³ tank holding 23 tonnes of LPG which underwent a BLEVE at Alma-Ata, Kazakhastan, in 1989, Shebeko et al. [22] theorize that the tank would not have exploded if its safety value had a cross sectional area not less than 77 cm² and operating pressure not exceeding 1.6 MPa. Attempts to develop pressure relief devices specific to the substance stored as PLG have also been made, for example liquefied ammonia [114]. The authors have modeled thermal response of a horizontal ammonia tank severely engulfed in fire.

7.3. Minimizing the damage if a BLEVE does occur

If a vessel suffers a BLEVE within a few minutes after getting jeopardized, very little can be done to reduce the damage it would cause. But even if a BLEVE is delayed – which could be by several hours – such delay is a mixed blessing. If care is not taken to prevent emergency responders or bystanders from going within 'striking distance' of the possible fireball, shock wave, or projectiles, the toll from a delayed BLEVE may even be higher than from the rapid one. Damage from projectiles is of the greatest concern because their impact area is much larger then of the fireball or shock-wave. In Sections 4 and 6.4 we have quoted several instances which reflect the great danger from missiles associated with BLEVEs.

7.3.1. Cushioning the missile damage

The first concern towards minimizing the damage caused by a BLEVE is to prevent the accident from triggering secondary and higher order accidents. Indeed the past accident analysis of BLEVEs tells us that very few BLEVEs occur as stand-alone accidents; in a large number of instances BLEVEs cause 'domino effect', triggering serial blasts [27,28]. To prevent domino effect, other vessels, which may explode on being heated or mechanically damaged, should be kept as far away from PLG-containing vessels as possible.

Barriers may also be placed around the vessels to cushion the impact of outgoing or incoming missiles. It is relatively easy to provide a barricade for vessels with energy contents in the range $10^3 - 10^5$ J, but it becomes progressively more difficult as the energy content rises, and for energy contents capable of giving a shock wave of $(50-100) \times 10^6$ J, putting a barricade would require sophisticated design and benefit-cost optimization.

The preferred form of barricade is a closed cubicle. For protection against blast using the equivalent static pressure method, the High Pressure Safety Code ([93], quoted in [3]) gives the relevant pressure as

$$P = 7.6 \left\lceil \frac{E \times 10^{-6}}{V} \right\rceil^{0.72}, \quad P < 70$$

where E is the shock wave energy (J), P the equivalent static pressure (bar) and V is the volume of the enclosure (m³). This equation is applicable where the aspect ratio of the enclosure does not exceed two.

Barricades can also take the form of thin-walled pressure vessels. Small enclosures can be made of angle iron and steel plate. Large barricades should be of reinforced concrete. Since the shock wave has positive and negative phases, reinforcement is required on both inner and outer faces. The barricade should have the provision to allow dispersion of small leaks by ventilation.

7.3.2. Fireball suppression

This is a possibility yet to be translated into practice but its potential is obvious. If fire suppressants can be released in a way that they get mixed with the flashing material when a vessel suffers a BLEVE, the fireball formation can be tempered with and its intensity reduced significantly. Systems can also be put in place so that the fireball, at the moment of its formation, gets surrounded by a cloud of certain fire suppressant. Then, the suppressant would be sucked into the fireball by strong air entrainment. As a result, the flame may be completely suppressed, or at least the fireball size would be significantly reduced.

The use of water mist as a fireball suppressant is an obvious possibility but the liquid droplets may completely evaporate before they are sucked into the fireball. This may reduce the suppressing effect. Aerosol fire extinguishing agents (AFEAs) may be a better substitute, because aerosol particles are not subjected to a phase change. They work by destroying the active centers which are necessary to sustain the flame. AFEAs can be generated by the combustion of solid propellants [30,115].

7.3.3. How close emergency responders can go to a jeopardized vessel

Birk [106] has proposed that fire fighters should not go closer to a jeopardized vessel than four fireball radii (which can be estimated on-the-spot using the expression $R = 3m^{0.33}$ where m is the lading mass in kg and R is the fireball radius in m), to a minimum of 90m. If it is possible the distance should be longer to reduce the hazard from rocketing fragments. Further, the emergency responders should be wearing protective clothing that can withstand radiation load of 21 kW m⁻² for the anticipated duration of a fireball (to be estimated as 0.15R, s). For large-scale tanks the 'safe' distance may be too long to enable fire fighters from directing water onto fire impinged tanks. For such large tank installations, water spray systems should already be in place and operating when responders arrive. However, delayed BLEVE remains a major risk to fire fighters dealing with uninsulated transport tanks and small stationary tanks; the responders are exposed to serious risk from fireball, blast and projectile effects. Responder should also expect danger from potential secondary projectiles (such as attached pipes, nearby equipment, etc.) which can be sent large distances by the waves which accompany a BLEVE.

7.3.4. Evacuation

The public should be evacuated to a distance of at least 15 fireball radii, preferably 30 fireball radii away from jeopardized tanks. This distance should be increased downwind of a potential BLEVE. At this distance there is little threat from the fireball thermal radiation or blast. As tank size increases above 5 m^3 the 30R distance becomes more and more conservative and the 15R distance becomes more appropriate [56].

If the PLG involved in a BLEVE happens to be toxic – such as chlorine, ammonia, methyl isocyanate, or phosgene – its initial dispersion would be influenced by the blast wave effects and would even carry it upwind to some distance before the usual meteorological factors and density effects become influential in the plume dispersion. Emergency preparedness for accidents involving such PLGs should factor in the blast-mediated dispersion.

8. Summary and conclusion

- (1) BLEVE is one among six classes of explosions that can occur in the process industry—vapour cloud explosion, dust explosion, condensed phase explosion, confined explosions, and 'physical' explosions' being the other five. Of these, BLEVE is a particularly destructive type and the world's second worst process industry accident the Mexico refinery disaster of 1984 had involved a chain of BLEVEs.
- (2) Aside producing highly destructive blast waves and fire-balls (or toxic dispersion), BLEVEs propel the fragments of the ruptured vessel in all directions at high velocities. Such missiles are often enveloped in fire if the ruptured vessel had contained a flammable chemical. The greatest damage in most BLEVE events has been caused by such missiles either by directly hitting (often killing) people, or by trig-

gering fires, or by damaging other process units leading to secondary accidents.

- (3) A BLEVE can occur in any situation where a vessel or a conduit carrying a pressure-liquefied gas (PLG) is accidentally depressurized. The depressurization suddenly renders the PLG into a superheated state, leading to instantaneous nucleation and explosive flashing. A number of factors introduce complexity in this otherwise simple-looking phenomena. For example the initial depressurization due to a minor crack may just cause the release of a gaseous or a liquid jet and the crack may either not propagate further or do so after a great deal of time. Just as well a crack may propagate rapidly. A great deal of effort, reviewed in this paper, has been made to understand the nature and the magnitude of the forces and counter-forces which are generated in a jeopardized vessel containing a PLG. A great deal of new knowledge has been acquired, on the basis of analysis of past accidents as well as experimental BLEVEs, but we still are not in a position to forecast whether a jeopardized vessel will suffer BLEVE and, if it does, when. This remains an area where a great deal of further R&D is required.
- (4) In a like manner a great deal of knowledge, reviewed in the paper, has been accumulated on the likely energy of explosion of a BLEVE, the likely size, duration, and heat load of the fireball a BLEVE may produce, and the number, size, orientation, and kinetic energy of missiles generated from the shattering vessel. But the forecasts one may arrive by using different methods may differ from each other significantly, at times by one or more orders of magnitude.
- (5) Even do-how manuals produced by coordinating agencies such as TNO, The Hague, and the Centre for Chemical Process Safety, New York describe different consequence assessment methods with little commentary on their relative merits. This state of affairs creates situations wherein the risk assessment conducted by an industry and a regulatory agency may differ widely from each other in spite of both sides having used legitimate consequence analysis models. There is urgent need to rectify this problem by the standardization and codification of procedures as has been done, say, in most areas of clinical analysis or environmental analysis.
- (6) Considering that BLEVE is a fairly well-known and well-documented phenomenon, a misconception is surprisingly prevalent that BLEVE occurs only with flammable chemicals. The fact is that one-fifth of all BLEVEs occur with non-flammable PLGs.
- (7) Among the questions which call for investigations is: what is the probability that a BLEVE will cause a secondary and higher order accident (domino effect)? A recall of BLEVE history indicates that a BLEVE is rarely a stand-alone event and is more often than not a trigger for other accidents. Studies on this aspect of BLEVE would refine our assessment of the risk posed by PLG-holding units.
- (8) A great deal of R&D is also needed to find more reliable methods than available for preventing a jeopardized vessel form undergoing BLEVE.

References

- CCPS, Guidelines for Consequence Analysis of Chemical Releases, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, 1999.
- [2] A.M. Birk, M.H. Cunningham, The boiling liquid expanding vapor explosion, J. Loss Prev. Process Ind. 7 (1994) 474–480.
- [3] F.P. Lees, Loss Prevention in the Process Industries-Hazard Identification, Assessment, and Control, vols. 1–3, Butterworth-Heinemann, Oxford, 1996
- [4] F.I. Khan, S.A. Abbasi, Risk Assessment in the Chemical Process Industries: Advanced Techniques, Discovery Publishing House, New Delhi, 1998
- [5] J. Casal, J. Arnaldos, H. Montiel, E. Planas-Cuchi, J.A. Vilchez, Modelling and understanding BLEVEs, in: M. Fingas (Ed.), Handbook of Hazardous Spills, McGraw Hill, New York, 2001.
- [6] F.I. Khan, S.A. Abbasi, Major accidents in the process industries and analysis of their causes and consequences, J. Loss Prev. Process Ind. 12 (1999) 361–374.
- [7] T.A. Kletz, Unconfined vapour cloud explosions, Loss Prev. 11 (1977) 50.
- [8] CCPS, Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVE's, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, 1994.
- [9] D.F. Peterson, BLEVE: facts, risk factors, and fallacies, Fire Eng. 155 (2002) 97-103.
- [10] W.L. Walls, What is a BLEVE, Fire J. 31 (1978) 46-47.
- [11] W.L. Walls, The BLEVE—part 1, Fire Command. 17 (1979) 35-37.
- [12] V.C. Marshall, Major Chemical Hazards, Ellis Horwood, Chichester,
- [13] R.C. Reid, Superheated liquids, Am. Scientist 64 (1976) 146-156.
- [14] J.E.S. Venart, K.F. Sollows, K. Sumathipala, G.A. Rutledge, X. Jian, Boiling Liquid Compressed Bubble Explosions: Experiments/Models, Gas-Liquid Flows, vol. 165, ASME, New York, 1993, pp. 55-60.
- [15] C.A. McDevitt, C.K. Chan, F.R. Steward, K.N. Tennankore, Initiation step of boiling liquid expanding vapor explosions, J. Hazard. Mater. 25 (1990) 169–180.
- [16] R.W. Prugh, Quantitative evaluation of "BLEVE" hazards, J. Fire Protect. Eng. 3 (1991) 9–24.
- [17] R.W. Prugh, Quantify BLEVE hazards, Chem. Eng. Prog. 87 (1991) 66–72.
- [18] I.R.M. Leslie, A.M. Birk, State of the art review of pressure liquefied gas container failure modes and associated projectile hazards, J. Hazard. Mater. 28 (1991) 329–365.
- [19] A.M. Birk, M.H. Cunningham, Liquid temperature stratification and its effect on BLEVEs and their hazards, J. Hazard. Mater. 48 (1996) 219– 237
- [20] J.E.S. Venart, Boiling liquid expanding vapor explosions (BLEVE); two-phase aspects of failure, in: Proceedings of the 39th European Two-phase Flow Group Meeting, Aveiro, 2001, p. 9.
- [21] R.C. Reid, Possible mechanism for pressurized-liquid tank explosions or BLEVEs, Science 203 (1979) 1263–1265.
- [22] Y.N. Shebeko, A.P. Shevchuck, I.M. Smolin, BLEVE prevention using vent devices, J. Hazard. Mater. 50 (1996) 227–238.
- [23] A.M. Birk, J.D.J. VanderSteen, M.H. Cunningham, C.R. Davison, I. Mirzazadeh, Fire tests to study the effect of pressure relief valve blow-down on the survivability of propane tanks in fires, Process Saf. Prog. 21 (2002) 227–236.
- [24] S. Shivaji, Forecasting the dispersion and impacts of accidental release of hazardous materials, MTech Thesis, Sri Venkatateswara University, Tirupati, 2004, 171 pp.
- [25] N.N. Desai. Risk assessment in the transport of hazmats, MTech Thesis, Vishweshvaraya Technological University, Belgaum, 2004, 74 pp.
- [26] C.M. Yu, J.E.S. Venart, The boiling liquid collapsed bubble explosion (BLCBE): a preliminary model, J. Hazard. Mater. 46 (1996) 197–213.

- [27] F.I. Khan, S.A. Abbasi, Models for domino effect analysis in the chemical process industries, Process Saf. Prog. 17 (1998) 107–123.
- [28] F.I. Khan, S.A. Abbasi, DOMIFFECT: a new user friendly software for domino effect analysis, Environ. Model. Softw. 13 (1998) 163–177.
- [29] T. Roberts, A. Gosse, S. Hawksworth, Thermal radiation from fireballs on failure of liquefied petroleum gas storage vessels, in: Proceedings of the IChemE Symposium Series No. 147, 2000, pp. 105–120.
- [30] V. Novozhilov, Some aspects of the mathematical modeling of fireballs, in: Proceedings of the IMechE, Part E, J. Process Mech. Eng. 217 (2003) 103–121.
- [31] J. Maillette, A.M. Birk, Effects of tank failure mode and lading properties on propane fireball geometry and fire hazard, in: Proceedings of the International Conference and Workshop on Modeling and Mitigating the Consequences of Accidents Releases of Hazardous Materials, Louisiana, 1995.
- [32] J.E.S. Venart, Boiling liquid expanding vapor explosions (BLEVE); possible failure mechanisms and their consequences, in: Proceedings of the IChemE Symposium Series No. 147, 2000, pp. 121–137.
- [33] M. Selway, The predicted BLEVE frequency of a selected 2000 m³ butane sphere on a refinery site. UK Atomic Energy Authority, Safety and Reliability Directorate, Report SRD/R492, 1988, 57 pp.
- [34] T.A. Kletz, What Went Wrong, Gulf Publishing, Houston, 1985.
- [35] S.K. Kuriechan, Causes and impacts of accidents in chemical process industries and a study of the consequence analysis software, MPhil Thesis, Pondicherry University, 2005, p. 175.
- [36] A. Wolf. BLEVE kills two. NFPA (National Fire Protection Association), 2006. http://www.nfpa.org/assets/files/PDF/AlbertCity.PDF.
- [37] M. Masellis, Fire disaster in a motorway tunnel, Prehosp. Disaster Med. 15 (2000) 74–78.
- [38] E. Planas-Cuchi, N. Gasulla, A. Ventosa, J. Casal, Explosion of a road tanker containing liquefied natural gas, J. Loss Prev. Process Ind. 17 (2004) 315–321.
- [39] US-CSHIB. Investigation Report—Catastrophic Vessel Failure, United States Chemical Safety and Hazard Investigation Board, Washington, NTIS No. PB 2004-103035, 2004, 53 pp.
- [40] R.M. Chelvi, Accidents in chemical process industries with a special reference to BLEVE, MTech Thesis, Coimbatore Institute of Technology, 2006, p. 163.
- [41] G. Vijayraghavan, Impact assessment, modeling, and control of dust explosions in chemical process industries, MTech Thesis, Coimbatore Institute of Technology, 2004, p. 131.
- [42] T. Abbasi, S.A. Abbasi, The expertise and the practice of loss prevention in the Indian process industry some pointers for the third world, Trans. IChemE 83 (2005) 413–420.
- [43] R.C. Reid, Some theories on boiling liquid expanding vapor explosions, Fire (1980) 525–529.
- [44] T. Abbasi, B.C. Clarke, S.A. Abbasi, Accidental risk of superheated liquids and a framework for predicting the superheat limit. J. Loss Prev. Process Ind., in press.
- [45] H. Wekeshima, K. Takata, On the limit of superheat, J. Phys. Soc. Jpn. 13 (1958) 1398–1403.
- [46] G.R. Moore, Vaporization of superheated drops in liquids, AIChE J. 5 (1959) 458–466.
- [47] W. Gibbs, The Scientific Papers, vol. 1, Dover Publications, New York, 1961
- [48] M. Volmer, A. Weber, Keimbildung in Übersättigten Gebilden, Z. Phus. Chem. 119 (1926) 277–301.
- [49] L. Farkas, The velocity of nucleus formation in supersaturated vapors, J. Phys. Chem. 125 (1927) 236.
- [50] R. Becker, W. Doring, The kinetic treatment of nuclear formation in supersaturated vapors, Ann. Phys. 24 (1935) 719–752.
- [51] M. Blander, J.L. Katz, Bubble nucleation in liquids, AIChE J. 21 (1975) 883.
- [52] C.E. Brennen, Phase change, nucleation, and cavitation, in: Cavitation and Bubble Dynamies, Oxford University Press, London, 1995.
- [53] J. Li, G.P. Peterson, P. Cheng, Mechanical nonequilibrium considerations in homogeneous bubble nucleation for unsteady-state boiling, Int. J. Heat Mass Transf. 48 (2005) 3081–3096.

- [54] I.J. Ford, C.F. Clement, The effects of temperature fluctuations in homogeneous nucleation theory, J. Phys. A 22 (1989) 4007–4018.
- [55] H.-C. Park, K.-T. Byun, H.-Y. Kwak, Explosive boiling of liquid droplets at their superheat limits, Chem. Eng. Sci. 60 (2005) 1809– 1821.
- [56] A.M. Birk, Scale effects with fire exposure of pressure-liquefied gas tanks, J. Loss Prev. Process Ind. 8 (1995) 275–290.
- [57] S. Ramier, J.E.S. Venart, Boiling liquid expanding vapor explosions: dynamic re-pressurization and two-phase discharge, in: Proceedings of the IChemE Symposium Series No. 147, 2000, pp. 527–537.
- [58] J. Stawczyk, Experimental evaluation of LPG tank explosion hazards, J. Hazard. Mater. B 96 (2003) 189–200.
- [59] E. Planas-Cuchi, J.M. Salla, J. Casal, Calculating overpressure from BLEVE explosions, J. Loss Prev. Process Ind. 17 (2004) 431–436.
- [60] D.J. Kielec, A.M. Birk, Analysis of fire-induced ruptures of 400-1 propane tanks, J. Pressure Vessel Technol.: Trans. ASME. 119 (1997) 365– 373.
- [61] J.D.J. VanderSteen, A.M. Birk, Fire tests on defective tank-car thermal protection systems, J. Loss Prev. Process Ind. 16 (2003) 417–425.
- [62] A.M. Birk, J.D.J. VanderSteen, The survivability of steel and aluminum 33.5 pound propane cylinders in fire, Process Saf. Prog. 22 (2003) 129–135.
- [63] K.W. Blything, A.B. Reeves, An initial prediction of the BLEVE frequency of a 100 tonnes butane storage vessel. UK Atomic Energy Authority, Safety and Reliability Directorate, Report SRD/R488, 1988, 88 pp.
- [64] A.M. Birk, J.D.J. VanderSteen, On the transition from non-BLEVE to BLEVE failure for a 1.8 m³ propane tank, Am. Soc. Mech. Eng. Pressure Vessels Piping Div. PVP 446 (2002) 143–152.
- [65] A.C. Van den Berg, M.M. van der Voort, J. Weerheijm, N.H.A. Versloot, Expansion-controlled evaporation: a safe approach to BLEVE blast, J. Loss Prev. Process Ind. 17 (2004) 397–405.
- [66] H. Giesbrecht, K. Hess, W. Leuckel, B. Maurer, Analysis of explosion hazards on spontaneous release of inflammable gas in the atmosphere. Part 1. Propagation and deflagration of vapor clouds on the basis of bursting tests on model vessels, German Chem. Eng. 4 (1981) 305– 314
- [67] C. Ogsio, N. Takagi, T. Kitagawa, On the mechanism of vapor explosion., in: Proceedings of the Loss Prevention and Safety Symposium, PACHEC, 1972.
- [68] G.V. Hadjisophocleous, A.C.M. Sousa, J.E.S. Venart, Mathematical modeling of LPG tanks subjected to full partial fire engulfment, Int. J. Numer. Meth. Eng. 30 (1990) 629–646.
- [69] G.V. Hadjisophocleous, A.C.M. Sousa, J.E.S. Venart, A study of the effect of the tank diameter on the thermal stratification in LPG tanks subjected to fire engulfment, J. Hazard. Mater. 25 (1990) 19–31.
- [70] Y.W. Gong, W.S. Lin, A.Z. Guo, X.S. Lu, A simplified model to predict the thermal response of PLG and its influence on BLEVE, J. Hazard. Mater. A108 (2004) 21–26.
- [71] F.I. Khan, S.A. Abbasi, TORAP-a new tool for conducting rapid risk-assessments in petroleum refineries and petrochemical industries, Appl. Energy 65 (2000) 187–210.
- [72] F.I. Khan, S.A. Abbasi, An assessment of the likelihood of occurrence, and the damage potential of domino effect (chain of accidents) in a typical cluster of industries, J. Loss Prev. Process Ind. 14 (2001) 283– 306
- [73] C.J.H. van den Bosch, R.A.P.M. Weterings, Methods for the Calculation of Physical Effects, Committee for the Prevention of Disasters, CPR 14E (TNO 'Yellow Book'), The Hague, The Netherlands, 1997.
- [74] C. Tellez, J.A. Pena, Boiling-liquid expanding vapor explosion (BLEVE): An introduction to consequence and vulnerability analysis, Chem. Eng. Educ. 36 (2002) 206–211.
- [75] W.E. Baker, J.J. Kulesz, R.E. Richer, R.L. Bessey, P.S. Westine, V.B. Parr, G.A. Oldham, Workbook for predicting pressure wave and fragment effects of exploding propellant tanks and gas storage vessels, NASA CR-134906, NASA Scientific and Technical Information Office, Washington, 1975 and 1977.

- [76] CCPS., Guidelines for Chemical Process Quantitative Risk Analysis, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, 1989.
- [77] A.C. Van den Berg, A. Lannoy, Methods for vapor cloud explosion blast modeling, J. Hazard. Mater. 34 (1993) 151–171.
- [78] W.E. Baker, P.A. Cox, P.S. Westine, J.J. Kulesz, R.A. Strehlow, Explosion Hazards and Evaluation, Elsevier, New York, 1983.
- [79] P.L. Holden, A.B. Reeves, Fragment hazards from failures of pressurized liquefied gas vessels, Chem. Eng. Symp. Ser. 93 (1985) 205–217.
- [80] B. Schulz-Forberg, B. Droste, H. Charlett, Failure mechanisms of propane-tanks under thermal stresses including fire engulfment, in: Proceedings of the International Symposium on Transport and Storage of LPG and LNG, Antwerp, 1984.
- [81] N.F. Scilly, J.H. Crowther, Methodology for predicting domino effects from pressure vessel fragmentation, in: Proceedings of the International Conference on Hazard Identification and Risk Analysis, Human Factors and Human Reliability in Process Safety, 1992.
- [82] W.E. Baker, J.J. Kulesz, R.E. Richer, P.S. Westine, V.B. Parr, L.M. Vargas, P.K. Moseley, Workbook for Estimating the Effects of Accidental Explosions in Propellant Handling Systems, NASA CR-3023, NASA Scientific and Technical Information Office, Washington, 1978.
- [83] J. Tulacz, R.E. Smith, Assessment of missiles generated by pressure component failure and its application to recent gas-cooled nuclear plant design, Nucl. Energy 19 (1980) 151.
- [84] M. Held, Fragment mass distribution of high energy projectiles, Propellants, High Explosives, Pyrotechnics 15 (1990) 254–260.
- [85] V.J. Clancey, Liquid and vapour emission and dispersion, in: Course on Loss Prevention in the Process Industries, Department of Chemical Engineering, Loughborough University of Technology, 1976.
- [86] Daily Telegraph, 1990, Sydney, 1990, p. 1.
- [87] M.R. Baum, The velocity of missiles generated by the disintegration of pressurised vessels and pipes, J. Pressure Vessel Technol. 106 (1984) 362–375.
- [88] C.V. Moore, The design of barricades for hazardous pressure systems, Nucl. Eng. Design 5 (1967) 81–89.
- [89] M.R. Baum, Failure of a horizontal pressure vessel containing a high temperature liquid: the velocity of end-cap and rocket missiles, J. Loss Prev. Process Ind. 12 (1999) 137–145.
- [90] M.R. Baum, The velocity of large missiles from axial rupture of gas pressurized cylindrical vessels, J. Loss Prev. Process Ind. 14 (2001) 199–203.
- [91] U. Hauptmanns, A Monte Carlo-based procedure for treating the flight of missiles form tank explosions, Probab. Eng. Mech. 16 (2001) 307–312.
- [92] U. Hauptmanns, A procedure for analyzing the flight of missiles from explosions of cylindrical vessels, J. Loss Prev. Process Ind. 14 (2001) 395–402.
- [93] B.G. Cox, G. Saville, High Pressure Safety Code, High Pressure Technol. Assoc. Imperial College, London, 1975.
- [94] R.P. Kennedy, A review of procedures for the analysis and design of concrete structures to resist missile impact effects, Nucl. Eng. Design 37 (1976) 183.
- [95] National Defense Research Committee (NDRC), Effects of impact and explosion, Summary Tech. Rep. of Div. 2, vol. 1, 1946.
- [96] Q.M. Li, S.R. Reid, H.M. Wen, A.R. Telford, Local impact effects of hard missiles on concrete targets, Int. J. Impact Eng. 32 (2005) 224–284.
- [97] R.W. White, N.B. Botsford, Containment of Fragments from a Runaway Reactor, Rep. SRIA-113, Stanford Research Institute, Stanford, CA, 1963
- [98] C.M. Pietersen, Analysis of the LPG Accident in San Juan Ixhuatepec, Mexico City, Report 85-0222, November 19, 1984, TNO, The Hague, 1985
- [99] R.J. Roark, W.C. Young, Formulas for Stress and Stain, McGraw-Hill, New York, 1975.
- [100] G. Gubinelli, S. Zanelli, V. Cozzani, A simplified model for the assessment of the impact probability of fragments, J. Hazard. Mater. A 116 (2004) 175–187.

- [101] G.M. Makhviladze, J.P. Roberts, S.E. Yakush, Combustion of two-phase hydrocarbon fuel clouds released into the atmosphere, Combus. Flame 118 (1999) 583–605.
- [102] F.K. Crawley, The effect of ignition of a major fuel spillage, in: The Assessment of Major Hazards, Institution of Chemical Engineers, Rugby, 1982.
- [103] I.A. Papazoglou, O.N. Aneziris, Uncertainty quantification in the health consequences of boiling liquid expanding vapour explosion phenomenon, J. Hazard. Mater. A 67 (1999) 217–235.
- [104] A.F. Roberts, Thermal radiation hazards from releases of LPG from pressurized storage, Fire Saf. J. 4 (1982) 197–212.
- [105] R.W. Prugh, Quantitative evaluation of fireball hazards, Process Saf. Prog. 13 (1994) 83.
- [106] A.M. Birk, Hazards from propane BLEVEs: an update and proposals for emergency responders, J. Loss Prev. Process Ind. 9 (1996) 173–181.
- [107] A.M. Birk, An experimental investigation of a cylindrical vessel engulfed in fire with a burning relief valve flare present, Chem. Eng. Commun. 80 (1989) 173–191.
- [108] A.J. Pierorazio, A.M. Birk, Dynamic behavior of transportation pressure relief valves under simulated fire impingement conditions, J. Pressure Vessel Technol.: Trans. ASME 122 (2000) 60–65.
- [109] P.K. Raj, Exposure of a liquefied gas container to an external fire, J. Hazard. Mater. A 122 (2005) 37–49.
- [110] L.C. Shirvill, Efficacy of water spray protection against propane and butane jet fires impinging on LPG storage tanks, J. Loss Prev. Process Ind. 17 (2004) 111–118.
- [111] F.N. Nazario, Preventing or surviving explosions, Chem. Eng. 102 (1988) 3–11.
- [112] H. Londiche, R. Guillemet, Comparison of three protective devices for BLEVE prevention, Loss Prev. Saf. Prom. Process Ind. 1 (1991) 551–564.
- [113] C. Young, LPG tank anti-BLEVE and automotive tank safety system. US Patent 4,680,937 (2004).
- [114] H.J. Chen, M.H. Lin, Modeling a BLEVE phenomena with application to relief device design for liquefied ammonia storage, Ind. Eng. Chem. Res. 38 (1999) 479–487.
- [115] A.N. Barator, N.A. Baratova, Y.A. Myshak, D.Y. Myshak, Proceeding of the Third Asia-Oceania Symposium on Fire Science and Technology, Seoul, 1998, pp. 405–416.
- [116] H.C. Hardee, D.O. Lee, Thermal hazard from propane fireballs, Transport Plan. Technol. 2 (1973) 121–133.
- [117] J.A. Fay, D.H. Lewis, Unsteady burning of unconfined fuel vapor clouds, Combustion 16 (1977) 1397–1403.
- [118] K. Hasegawa, K. Sato, Study on the fireball following steam explosion of *n*-pentane, Loss Prev. Saf. Prom. 2 (1977) 297–303.
- [119] K. Hasegawa, K. Sato, Fireballs, 12, Technical Memos of Fire Research Institute of Japan, Tokyo, 1978, pp. 3–9.
- [120] B.R. Williamson, L.R.B. Mann, Thermal hazards from propane (LPG) fireballs, Combus. Sci. Technol. 25 (1981) 141–153.
- [121] D.A. Lihou, J.K. Maund, Thermal radiation hazards from fireballs, in: The Assessment of Major Hazards, Institution of Chemical Engineers, Rugby, 1982.
- [122] J. Moorhouse, M.J. Pritchard, Thermal radiation hazards from large pool fires and fireballs—a literature review, in: The Assessment of Major Hazards, Institution of Chemical Engineers, Rugby, 1982.
- [123] J.A. Duiser, Escape of liquefied gases from broken pipes, in: The Protection of Exothermic Reactors and Pressurised Storage Vessels, Institution of Chemical Engineers, Rugby, 1984.
- [124] J.B. Gayle, J.W. Bransford, Size and duration of fireballs from propellant explosions, Report NASA TM X-53314. George C. Marshall Space Flight Center, Huntsville, USA, 1965.
- [125] D.F. Bagster, R.M. Pitblado, Thermal hazards in the process industry, Chem. Eng. Prog. 85 (1989) 69-77.
- [126] W.E. Martinsen, J.D. Marx, An improved model for the prediction of radiant heat flux from fireball, in: Proceedings of the International Conference and Workshop on Modeling the Consequences of Accidental Releases of Hazardous Materials, San Francisco, 1999.
- [127] B.E. Bader, A.B. Donaldson, H.C. Hardee, Liquid propellant rocket abort fireball model, J. Spacecraft Rockets 8 (1971) 1216–1222.

- [128] I. Hymes, The Physiological and Pathological Effects of Thermal Radiation, SRD R275, UK Atomic Energy Authority, Culcheth, 1983.
- [129] I. Hymes, The effects on people and structures of explosion, blast, thermal radiation and toxicity, in: J.I. Petts (Ed.), Seminar Proceedings of the Major Hazardous Installation: Planning Implications and Problems, Department of Chemical Engineering, Loughborough University of Technology, 1984.
- [130] G.M. Makhviladze, S.E. Yakush, Proceedings of the Third International Seminar on Fire and Explosion Hazards, 2000, pp. 579– 580
- [131] C.M. Pietersen, S.C. Huerta, Analysis of the LPG Accident in San Juan Ixhuatepec, Mexico City, Report 84-0222, November 19, 1984, Netherlands Organization for Applied Scientific Research, The Netherlands, 1985