

CONSEQUENCES OF JET-FIRE INTERACTION WITH VESSELS CONTAINING PRESSURISED, REACTIVE CHEMICALS

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Current practice for the protection of pressure vessels containing reactive, flammable chemicals is typically based upon liquefied petroleum gas (LPG) standards for protection against hydrocarbon pool fires. However, this may not be appropriate. It is well recognised, that the more challenging incident scenario is a jet-fire, wherever pressurised, or pressure liquefied flammable materials are handled. In particular, a reactive chemical fuelled jet-fire may well be more severe than a hydrocarbon pool fire. Additionally, LPG is not a self-reactive chemical. As such, the level of heat transfer that a vessel containing a reactive chemical may be exposed to without incident, could well be significantly lower than an LPG vessel could withstand.

Chemicals undergoing decomposition or self-reaction (e.g. polymerisation) at elevated temperatures may require additional levels of protection to prevent or control a runaway reaction triggered by the input of energy from an external fire. There is insufficient knowledge of the safe allowable heat input to self-reactive chemicals that are held in pressure vessels. Additionally, the adequacy of pressure relief devices sized using current standards in such circumstances is uncertain.

In this paper, work is described to:

- determine, by calorimetry, the effect of heat on chemicals (1,3-butadiene and propylene oxide) capable of exothermic self reaction;
- assess the feasibility of carrying out calorimetry on pressure liquefied gases, including calorimetric tests which simulate fire situations; and
- compare the jet flame characteristics of 1,3-butadiene with a propane jet in an intermediate scale test.

The results are discussed in terms of the likelihood of thermal runaway, the vent sizing requirements of the pressure relief device and the protective effect of thermal insulation.

Keywords: self-reactive, 1,3-butadiene, propylene oxide, vent sizing, fire protection, jet fires.

INTRODUCTION

Current practice for the protection of pressure vessels containing reactive, flammable chemicals is typically based upon liquefied petroleum gas (LPG) standards for protection against hydrocarbon pool fires. The appropriateness of this may be questioned on two fronts. LPG is not a self-reactive chemical, where the levels of fire protection are intended to prevent the pressure vessel itself from reaching its critical failure temperature ($> 400\text{ }^{\circ}\text{C}$). In the case of a self-reactive chemical, the critical temperature is likely to be the substantially lower one of that leading to the onset ($< 350\text{ }^{\circ}\text{C}$) of exothermic runaway. Further, the more likely incident scenario involving plant containing pressurised flammable materials may well be a jet-fire rather than a pool fire. Jet fires are typically more severe than pool fires because of their high heat fluxes and high mechanical erosive effects. This has been confirmed by numerous workers, including HSL¹.

For chemicals undergoing decomposition or self-reaction (e.g. polymerisation) at elevated temperatures, there is insufficient knowledge of the amount of heating that they may be safely exposed to when held in pressure vessels. Such information is needed to correctly design an adequate fire protection system to be certain that a runaway reaction, which otherwise might be triggered by the heat from an external fire, may be prevented or controlled. Additionally the adequacy of pressure relief sized using current standards in such circumstances is uncertain.

HSE's Technology Division commissioned a feasibility study of methods to assess the effectiveness of pressure relief and fire protection in a jet fire. The work described in this paper concerns the determination of the:

- Effect of heat, using adiabatic calorimetry, on two substances capable of self-reaction viz. 1,3-butadiene and propylene oxide;
- Performance of fire simulation calorimetry on 1,3-butadiene;
- Jet flame characteristics of 1,3-butadiene in comparison with a propane jet fire in an intermediate scale test; and
- Size of pressure relief device required.

ADIABATIC CALORIMETRY

A literature review (Keaney²) confirmed that adiabatic calorimetry on selected reactive chemicals was necessary to determine kinetic parameters and give an indication of the temperatures and pressures likely to be reached. There is particular concern for vessels provided with thermal insulation, including vessels where the fire protection is by a passive fire protection material.

The reactive chemicals selected as being most suitable for the purposes of jet fire testing and calorimetry were propylene oxide and 1,3-butadiene. Adiabatic studies were undertaken using a Phi-Tec 2 (Singh³) and a Columbia Scientific Industries ARCTM accelerating rate calorimeter (Townsend & Tou⁴). Most of the calorimetry was performed with the Phi-Tec but one Accelerating Rate Calorimeter run was performed on propylene oxide where this fell outside of the operating range of the Phi-Tec calorimeter.

In the Phi-tec calorimeter, the sample is held in a thin-walled stainless steel container which is surrounded by electrical heaters, the whole assembly is installed inside a stainless steel pressure vessel. Heat transfer to or from the sample can be controlled by varying the temperature of the electrical heaters. Adiabatic conditions can be achieved by matching the temperature of the heaters to that of the sample. Alternatively, a steady heat input can be obtained by programming the electrical heaters to maintain a temperature a fixed amount above the sample temperature. If the pressure in the test cell increases, rupture of the thin walled container is prevented by automatically increasing the pressure of nitrogen in the external pressure vessel.

When measurements are required on a substance having a low boiling point and therefore a high vapour pressure at the temperature of interest, the effect of the elevated pressure required in the external pressure vessel is to significantly increase heat losses from the sample container. In addition to this effect, additional heat losses may be observed due to refluxing of the sample in the fill line of the sample container.

TEST PROCEDURES FOR THE ADIABATIC CALORIMETRY

PROPYLENE OXIDE

Propylene oxide is a colourless flammable liquid with a boiling point of 34 °C. In large tanks, it is usually stored under ca. 8 bar nitrogen pressure. For the calorimetry, propylene oxide was cooled in a refrigerator to approximately 5 °C and then filled into a pre-weighed test cell using a syringe.

1,3-BUTADIENE

1,3-butadiene is a colourless reactive gas with a boiling point of -4.4 °C. It is stored liquefied under its own vapour pressure. 1,3-butadiene is normally supplied with an added polymerisation inhibitor, in this case t-butyl catechol. Liquid 1,3-butadiene was condensed in a type 1a Phi-Tec test cell (magnetically stirred, low phi factor) using a cooling bath consisting of solid carbon dioxide and 2-propanol.

In order to configure the Phi-Tec calorimeter such that measurements could be made on 1,3-butadiene it was necessary to develop a method to allow for both the heat losses due to operating in a high-pressure regime and also those heat losses due to reflux. This was done by running several calibration tests with a sample vessel filled with butane, a substance with a similar pressure temperature profile to 1,3-butadiene but with no tendency to self-heat. The data obtained for heat losses with butane were then programmed into the calorimeter control and used to obtain self-heating measurements on 1,3-butadiene. With this type of heat loss compensation, care is required as it is possible for self-heating to be detected, when not actually present, due to excessive heat input from the calorimeter heaters.

RESULTS FROM ADIABATIC CALORIMETRY

PROPYLENE OXIDE

Pure propylene oxide was tested in the Phi-Tec and showed no tendency to self-heat up to a temperature of 216 °C. Due to the limiting operating range of the Phi-Tec calorimeter, a single test performed using the ARC. Self heating became detectable at a temperature of 300 °C, at which temperature the pressure of propylene oxide was of the order of 140 bara. It was concluded from these tests that pure propylene oxide was insufficiently reactive to pursue this type of investigation.

Although pure propylene oxide was relatively stable up to temperatures of approximately 300 °C, it should be noted that propylene oxide has a tendency to undergo base catalysed exothermic polymerisation at ambient temperature (Freeder and Snee⁵). Provided that there were no local hot spots on the tank shell and no catalysis, propylene oxide vapour would be vented at temperatures up to 300 °C before thermal runaway would occur.

1,3-BUTADIENE

Initial tests with 1,3-butadiene gave heat losses such that it was impossible to detect an exotherm below 160 °C. The large heat losses and hence the extremely low level of exotherm sensitivity enabled a plot of 1,3-butadiene vapour pressure to be obtained from these tests. In addition to the heat loss problems, it was found that taking a 1,3-butadiene exotherm to conclusion resulted in an explosive decomposition causing significant damage to the calorimeter. In subsequent tests, attempts were made to automatically switch off the calorimeter before violent decomposition occurred. These attempts were unsuccessful due to the calorimeter having no cooling nor quench facility.

The result from a Phi-Tec test on 1,3-butadiene is given in Table 1. The specific heat for 1,3-butadiene (liquid) is taken as $2.055 \text{ J g}^{-1} \text{ K}^{-1}$. In this test the calorimeter heaters were switched off at 190°C , but at this temperature the heat generation from the polymerisation of 1,3-butadiene was sufficient for the reaction to continue to completion. The plots of temperature and pressure versus time are shown in Figure 1. The plots of LOG [dT/dt] versus reciprocal temperature and pressure versus temperature are compared later in Figures 2 and 3 with the corresponding fire simulation data. The measured vapour pressure data for 1,3-butadiene in the Phi-Tec compares well (see Figure 2) with the data derived from the Antoine constants ($\log_{10}[\text{pressure(mm)}] = 6.859 - (935.5/\{\text{temperature}(^\circ\text{C})-239\})$) provided by Braker and Mossman⁶.

Table 1. PHI-TEC EXPT. WITH 1,3-BUTADIENE WITHOUT FIRE SIMULATION

Run No	Sample mass (g)	T _{onset} (°C)	T _{max} (°C)	ΔT _u (K)	P _{max} (bara)	dT/dt _{max} (K min ⁻¹)	φ factor	ΔT _{ad} (K)	ΔH _r (J g ⁻¹)
pa98	44	114	321	207	87.4	83.7	1.14	236	485

1,3-butadiene shows self-heating from around 114°C . At this temperature, the pressure in the container due to 1,3-butadiene vapour is around 25 bara. Significant rates of self-heating are not obtained until the 1,3-butadiene is heated above its critical temperature at which point the pressure is of the order of 40 bara. It would be expected that higher rates of self-heating would be obtained at lower temperatures in the case of external heating or if the inhibitor had been consumed. In the case of jet fire impingement onto a tank of 1,3-butadiene, the local heat input could be so severe as to cause local decomposition, the products from which may catalyse the reaction of the remaining 1,3-butadiene, thereby causing a runaway at lower temperature.

FIRE SIMULATION CALORIMETRY

Singh³ indicates that fire simulation calorimetry may be performed using the Phi-Tec adiabatic calorimeter. It is claimed that the Phi-Tec can achieve rates of external heating which are representative of fire heat inputs from design codes such as API RP 520⁷ to industrial-scale vessels. Typical rates of temperature rise from external heating of 0.5 K min^{-1} are quoted. Fire simulation calorimetry was carried out in the Phi-Tec to:

- Obtain data for validation of calculation methods using adiabatic calorimetric data.
- Gain experience with, and evaluate the use of, the Phi-Tec calorimeter for this purpose.

The method of simulating external heat input using the Phi-Tec, involves increasing the temperature of the calorimeter heaters above that of the sample by an amount appropriate to the heat input required. This method is limited by the operating software since the maximum allowable temperature difference is 30°C . The heat loss compensation system also uses this method and, for a substance like 1,3-butadiene, this effectively limits the additional temperature available for fire simulation to approximately 15°C . This equates to a heat input of 1 W. The calorimeter was first calibrated so that the heat input to the sample as a result of a given heater lead (in degrees above sample temperature) was known. This calibration was performed using a low φ factor magnetically stirred test cell filled with 70g dimethyl phthalate. The calibration indicated a linear relationship having the equation:

$$Q = 0.0713.T_{ad} \quad (1)$$

It can be seen from this calibration that a relatively large temperature difference gives only a small additional heat input.

A single fire simulation run was performed on 1,3-butadiene using the Phi-Tec calorimeter. The conditions and results for the run are given in Table 2. An additional heat input of approximately 1 W was used. Assuming a specific heat for 1,3-butadiene liquid of $2.055 \text{ J g}^{-1} \text{ K}^{-1}$, this gives an additional heating rate for the 40g of 1,3-butadiene in the test cell of 0.78 K min^{-1} (25 W kg^{-1}). The actual heating rate measured in the initial period, before self heating, was approximately 0.8 K min^{-1} . This equates to a total additional heat input of 8370 J over the measured temperature range. Jet fire impingement (Roberts *et al.*^{8 & 9}) onto a two tonne tank of propane results in a heat input of approximately 1000 W kg^{-1} or 24 K min^{-1} . To simulate a heat input of this order in the Phi-Tec is impractical. It is usual, however, to encounter larger tanks, for example a road or rail tanker would be about 20 tonnes and a static storage tank could be around 80 tonnes, in which case the rates of temperature rise would be accordingly lower. A jet fire is a more severe fire than a pool fire that is assumed by current codes in setting fire relief requirements. The heat input from API RP 520 would lead to a heating rate of approximately 2 K min^{-1} .

Table 2. FIRE SIMULATION RESULTS ON 1,3-BUTADIENE

Run No	Sample mass (g)	T _{onset} (°C)	T _{max} (°C)	Δ T _u (K)	P _{max} (bara)	dT/dt _{max} (K min ⁻¹)	φ factor	Δ T _{ad} (K)	ΔH _r (J g ⁻¹)
PA99	40	115	488	448	93	518	1.15	515.2	1059

Note: Less 209 J g⁻¹ additional heat input

In this fire simulation test, the additional heating has the additional effect of precluding any heat losses, and therefore the effect of self-heating becomes evident where the gradient of the temperature trace deviates from the straight line of the additional heating. The onset of self-heating becomes apparent at 115°C. Figures 2 and 3 compare tests PA98 (performed without external heating) and PA99 (performed with external heating). Figure 2 shows that the pressure for PA99 is generally higher at a given temperature than for PA98. This is because of the lower conversion at a given temperature for the externally heated experiment compared to the experiment without external heating. The initial reaction is expected to be dimerisation mainly to 4-vinylcyclohexene, which is less volatile than 1,3-butadiene and therefore a lower conversion results in a higher pressure. Figure 3 shows log [temperature rate] versus temperature data for both experiments. There is also good agreement in onset temperatures between the two experiments (114°C for PA98 and 115°C for PA99) confirming that the external heating does not affect this important parameter.

The results indicated that, with the heat-input method used, small heat flux fires on unprotected vessels or larger fires on protected (deluge or insulation) vessels can be imitated experimentally.

FIRE TRIALS WITH 1,3-BUTADIENE

SAFETY CONSIDERATIONS

1,3-butadiene was selected for the fire trials since it was one of the least toxic of the pressure liquefied reactive chemicals (e.g. carbonyl sulphide, diborane, ethylene, germane, vinyl chloride). However, 1,3-butadiene is a carcinogen and mutagen. Risk assessments, including

gas dispersion modelling, indicated that a continuous release of 0.1 kg s^{-1} was the maximum allowable for the 400 m radius safety distance available on HSL's Buxton site. Hence it was necessary to design the fuel supply system such that it could be shut-off remotely at very short notice and would fail safe (i.e. closed) in the event of failure. With these restrictions, it was considered that six 60 kg cylinders of 1,3-butadiene could be safely handled at one time.

The flammability properties (Braker & Mossman⁶) of 1,3-butadiene are compared with those of propane in Table 3.

Table 3. 1,3-BUTADIENE AND PROPANE FLAMMABILITY PROPERTIES

Property	1,3-Butadiene	Propane
Boiling point	-4.4 °C	-42.1 °C
Vapour pressure (21.1 °C)	2.49 bar	8.53 bar
Relative vapour density	1.88	1.55
Flash point	-76 °C	-104 °C
Auto-ignition temperature	420 °C	468 °C
Lower flammability limit (by volume)	2%	2.2 %
Upper flammability (by volume)	11.5%	9.5%
Heat of combustion (liquid)	44.2 MJ kg ⁻¹	46.0 MJ kg ⁻¹

1,3-Butadiene may undergo exothermic decomposition. If a runaway reaction is initiated, the cylinder could explode causing burns from the resulting fireball or missile damage. The calorimetry suggested that a runaway reaction is not likely to occur in a cylinder at temperatures below 100 °C. However, verbal advice from the supplier suggested that the cylinders may be safely heated to no more than 30 °C although the safety data sheet indicated 50 °C. Approximately 30 °C was used for the experiments.

JET FIRE SCENARIOS

There are two basic jet fire scenarios:

- (a) A vapour jet fire resulting from puncture, weld, flange or valve failure of a tank above the liquid level or failure of vapour take-off pipework.
- (b) A flashing liquid jet fire resulting from puncture, weld, flange or valve failure of a tank below the liquid level or failure of liquid take-off pipework.

FIRE TEST PROCEDURE

The properties of vapour only and flashing liquid propane jets have previously been investigated¹⁰ and determination made of acceptable scaling between the two. It was therefore decided to use a version of the jet-fire resistance test (JFRT)¹¹ of passive fire protection materials with the flame recirculation chamber modified to incorporate a copper pipe calorimeter (28 mm o.d., 7.3 m exposed length and 0.642 m² exposed area). This was located at the known position of maximum heat flux within the open-fronted box used to give a recirculating fireball in front of the test specimen. Heat flux to the calorimeter could then be measured for jet flames produced by different fuels and for a range of flow rates. The assembled test piece was supported on two steel stands bolted to a pair of concrete blocks, which were positioned on the 15 m x 15 m test pad (see Figure 4). For the fire tests, two fuels were used:

- 1,3-Butadiene vapour supplied from cylinders, immersed in a hot water bath to aid vaporisation, providing a vapour rate of 0.05 kg s^{-1} ;
- Liquid 1,3-butadiene, supplied from cylinders pressurised to 3.45 barg with nitrogen, providing a liquid flow rate of 0.844 kg s^{-1} ; and
- Propane vapour supplied from a 10 tonne storage facility via a hot water vaporiser.

As vapour flow is at a much lower flow rate than liquid flow, 1,3-butadiene vapour fire trials were performed first. Liquid 1,3-butadiene fire trials were then performed until the cylinders were nearly empty. Finally, the propane vapour fire trials were performed to provide a comparison.

In each test, a steady flow of water was established through the pipe calorimeter. The fuel was then released and ignited and the water from the calorimeter collected over a timed period. The 1,3-butadiene flow rate was estimated by weighing the cylinders before and after the tests and the propane vapour flow by a calibrated flow meter. The in and out water temperatures and the flame temperatures along the vertical centre line were measured with type K, stainless steel sheathed thermocouples.

RESULTS FROM FIRE TRIALS

1,3-BUTADIENE VAPOUR

Two successful 1,3-butadiene vapour trials (BD03 and BD04) were performed. In each trial, the 1,3-butadiene burnt with bright orange flames in the flame re-circulation chamber (see Figure 5), with duller orange flames above the flame re-circulation chamber and black smoke was produced at the tips of the flames. The measurements from 1,3-butadiene vapour fire trials BD03 and BD04 are summarised in Table 4.

LIQUID 1,3-BUTADIENE

One liquid 1,3-butadiene fire trial (BD05) was performed. In this trial the liquid 1,3-butadiene burnt producing copious quantities of black smoke (see Figure 6). After the jet was extinguished, a considerable amount of liquid 1,3-butadiene remained burning within the flame re-circulation chamber. A summary of the measurements taken is given in Table 5.

Table 4. 1,3-BUTADIENE VAPOUR TRIAL DATA

Parameter	Trial	
	BD03	BD04
Jet duration (s)	324	237
Mass of fuel used (kg)	15.6	11.4
Vapour mass flow rate (kg s^{-1})	0.048	0.048
Water flow rate (kg s^{-1})	1.42	0.80
Mean temperature difference (K)	18.6	22.9
Beginning and end time for mean (s)	100 -250	60 - 180

Table 5. 1,3-BUTADIENE LIQUID FIRE TRIAL DATA

Parameter	Trial BD05
Jet duration (s)	288
Mass of fuel used (kg)	243
Liquid mass flow rate (kg s^{-1})	0.844
Water flow rate (kg s^{-1})	0.82
Mean temperature difference (K)	2.54
Beginning and end time for mean (s)	90 - 240

PROPANE VAPOUR

Two propane vapour trials (BD07 and BD08) were performed in order to determine the heat flux at the jet fire resistance test rate of 0.3 kg s^{-1} and the equivalent 1,3-butadiene vapour rate of 0.05 kg s^{-1} . The flames observed (BD07) at 0.3 kg s^{-1} were typical of those observed in a jet fire resistance test (see Figure 7) whereas the flames from a 0.05 kg s^{-1} propane vapour jet fire (BD08) were smaller in size (see Figure 8), particularly in regard to the depth of the fireball formed in front of the flame re-circulation chamber. However, the flames appeared brighter in colour and slightly larger than those from the corresponding 1,3-butadiene vapour jet fire (see Figure 5). Measurements from propane vapour fire trials BD07 and BD08 are summarised in Table 6.

Table 6. PROPANE VAPOUR TRIAL DATA

Parameter	Trial	
	BD07	BD08
Jet duration (s)	175	780
Mass of fuel used (kg)	52.5	39
Vapour mass flow rate (kg s^{-1})	0.300	0.050
Water flow rate (kg s^{-1})	2.01	1.39
Mean temperature difference (K)	9.1	14.1
Beginning and end time for mean (s)	50 - 170	140 - 800

DISCUSSION OF FIRE TRIAL RESULTS

The main aim of this phase of the project was to determine if the fires obtained from 1,3-butadiene were more severe than the fires used to assess the fire resistance of passive fire protection materials. A discussion of the various parameters is given as follows.

FLAME TEMPERATURES

The flame temperatures, measured at 0.3 m intervals (from the bottom) up the centre line of the re-circulation chamber by shielded thermocouples ca. 12 cm proud of the surface, are summarised in Table 7.

Table 7. FLAME TEMPERATURE RANGES

Trial	Description	Flame temperatures (Celsius)			
		TC07 (0.3 m)	TC08 (0.6 m)	TC09 (0.9 m)	TC10 (1.2 m)
BD03	1,3-butadiene vapour (0.05 kg s ⁻¹)	900 - 1100	1100 to 1150	1200 to 1250	1200 to 1250
BD04	1,3-butadiene vapour (0.05 kg s ⁻¹)	1050 to 1100	1100 to 1150	1150 to 1200	1200 to 1250
BD05	1,3-butadiene liquid (0.84 kg s ⁻¹)	-13 to 0	-13 to 0	300 to 400	500 to 600
BD05	Burning 1,3-butadiene liquid	600 to 900	800 to 900	850 to 1020	900 to 1050
BD07	Propane vapour (0.30 kg s ⁻¹)	500 to 600	700 to 800	800 to 900	900 to 1000
BD08	Propane vapour (0.05 kg s ⁻¹)	600 to 750	830 to 970	1000 to 1100	1100 to 1200

In each trial, the maximum temperature always occurred at the top position (0.3 m from the top of the flame re-circulation chamber). The results are discussed as follows:

1,3-butadiene vapour flames: The flame temperatures were similar at equivalent positions for the 1,3-butadiene vapour trials and were consistent with the very similar flames observed in each trial.

Flashing liquid 1,3-butadiene flames: At the lowest two positions, the temperatures measured during the jet phase of the liquid 1,3-butadiene trial indicated that these thermocouples were being engulfed in a two phase mixture of flashing liquid and vapour at or below the boiling point of -4 °C. The burning liquid left after the jet was extinguished gave temperatures about 200 °C lower than the 1,3-butadiene vapour jets. The results indicate that a release of liquid 1,3-butadiene close to a vessel is likely to result in the surface being cooled at the impact point and burning liquid forming a pool fire underneath, if there is no drainage.

Propane vapour flames: The results from the propane vapour trials were somewhat surprising in that the temperatures measured at a flow rate of 0.3 kg s⁻¹ were nearly 200 °C below those measured at a flow rate of 0.05 kg s⁻¹. This suggests that, at the higher flow rate, incomplete combustion is occurring at the thermocouples positioned 12 cm from the rear surface of the flame re-circulation chamber.

1,3-butadiene versus propane: The flame temperatures from the 0.05 kg s⁻¹ propane jet were slightly below those from the corresponding 1,3-butadiene jets. This may be due to the particular combination of gas velocity (the 1,3-butadiene pressure was 1.2 barg and the propane pressure 1.6 barg) and release distance used.

HEAT FLUXES

The mean heat fluxes were calculated using the expression:

$$I = (dm/dt \cdot C_w \cdot \Delta T_w) / (S \cdot \sigma) \quad (2)$$

The calculated heat fluxes are summarised in Table 8.

Table 8. HEAT FLUXES

Trial	Description	Mean water flow rate (kg s⁻¹)	Mean temperature rise (K)	Mean heat flux (kW m⁻²)
BD03	1,3-butadiene vapour (0.05 kg s ⁻¹)	1.42	18.6	181
BD04	1,3-butadiene vapour (0.05 kg s ⁻¹)	0.8	22.9	126
BD05	1,3-butadiene liquid ^a (0.84 kg s ⁻¹)	0.82	2.54	14
BD05	Mean burning liquid 1,3-butadiene ^c	0.82 ^b	6.63	37
BD05	Maximum burning liquid 1,3-butadiene ^c	0.82 ^b	17.42	98
BD07	Propane vapour (0.30 kg s ⁻¹)	2.01	9.1	125
BD08	Propane vapour (0.05 kg s ⁻¹)	1.39	14.1	134

Notes: a Measured during jet impingement.
 b Assuming no changes to water flow after the measurement period.
 c Measured after impingement had ceased.

The mean heat fluxes (125 and 134 kW m⁻²) measured from burning propane vapour were similar to the 126 kW m⁻² measured during the second 1,3-butadiene vapour trial (BD04) but were below the 181 kW m⁻² measured during the first 1,3-butadiene vapour trial (BD03), performed when the cylinders were full. The liquid impingement result was very low indicating that the calorimeter was being cooled by unburnt liquid. After impingement had ceased, the mean burning liquid heat flux was only 37 kW m⁻² and the maximum 98 kW m⁻². The heat fluxes measured should be treated with caution as the results are clearly influenced by the cooling effect of unburnt gas on the calorimeter. If the jet had been at a greater stand-off distance (e.g. 1.5 m instead of the JFRT 1.0 m) then the cooling effects may have been much lower and the mean measured heat fluxes higher.

The heat fluxes measured with a pipe calorimeter impinged by a 1.7 kg s⁻¹ flashing liquid propane fire (Roberts et al.^{8 & 9}) and by a kerosene pool fire (Moodie et al.¹²), were in the ranges 180 - 200 kW m⁻² and 75 - 85 kW m⁻² respectively. In an early version of the Jet Fire Resistance Test, Shirvill and Wighus¹³ measured (using heat flux meters) heat fluxes in the range 190 (near the jet impingement point) to 280 kW m⁻². In general (apart from the mean burning liquid 1,3-butadiene heat flux) the measured heat fluxes were higher than the values measured by Moodie et al. in a kerosene pool fire and the value assumed by API for pool-fire pressure relief calculations.

FIRE PROTECTION

Even though the unburnt gas effects probably indicate an underestimate of the heat fluxes, visual observation and measured flame temperatures suggest that the flames and heat fluxes are less severe than those achieved in the jet fire resistance test¹¹ for passive fire protection (PFP) materials. Hence, unless the reactive chemical actually reacts with the PFP, the JFRT should be adequate for assessing the fire performance of material used to protect vessels containing pressurised reactive chemicals. For reactive chemicals, the PFP needs to:

- Protect the wall of the vessel from reaching a temperature where weakening can occur;
- If possible, prevent a runaway reaction from being initiated; and

- Reduce the heat transfer to the vessel so that a relief device with a practical vent size can be used.

The vent sizing requirements are discussed in the next section.

VENT SIZING

The rate of a chemical reaction increases with temperature and many reactions of commercial interest are exothermic. A runaway reaction occurs when the rate of heat generation due to the reaction exceeds the rate of heat loss from the vessel. The rate of heat generation is an exponential function of temperature whereas the rate of heat loss is a linear function of temperature. The major heat loss from a tank will be by convection and radiation to the atmosphere. The runaway reaction will also rapidly increase the pressure of a closed system: the vapour pressure will increase with temperature; this is a vapour pressure system. To avoid the design pressure of the vessel being exceeded, vessels are normally fitted with a pressure relief valve, which will be activated at a set pressure. The diameter of the relief system must be carefully selected. Two-phase flow often occurs from runaway reaction systems. This is because the liquid level in the vessel rises, particularly after vent opening due to the amount of vapour being produced in the reaction liquid. Hence liquid as well as vapour leave the reactor via the vent. A vent sized for vapour flow alone will be inadequate. The calculation of the vent area is a two-stage process: the vent mass flux is first calculated and secondly the vent area calculated from the mass flux, rate of heat generation and any permitted overpressure. The vessel pressure is allowed to exceed the set pressure and rise to a maximum pressure, which is not higher than the design pressure plus permitted accumulation. In this way the required vent area may be reduced from that if no overpressure above the set pressure was allowed.

For a system where the pressure is due to vapour, the simplest mass flux equation (which neglects friction) is the Equilibrium Rate Model (ERM) (Fauske¹⁴):

$$G = (dP/dT)_m (T_m / C_{pm})^{1/2} \quad (3)$$

The subscript, m, refers to mean conditions between the set pressure and the maximum pressure. The commonly used vent sizing equation for a vapour pressure exothermic reaction system is the Leung Equation (Leung¹⁵):

$$A = m_o q_m / G [\{(V/m_o)(h_{fgm}/v_{fgm})\}^{1/2} + \{C_{pm} \Delta T\}^{1/2}]^2 \quad (4)$$

The heat release rate per unit mass is calculated using the following equation:

$$q = C_p (dT/dt) \quad (5)$$

The Leung equation was developed for chemical reactors where the heat input is primarily from the exothermic reaction and there is no external heating. For a vessel containing reactive chemical exposed to fire, the would be the dominant heat source and therefore the Leung equation has been modified (Wilday & Daskalakis¹⁶) to include the effect of external heating on the heat release rate per unit mass. This modified Leung equation again is only for vapour pressure systems and can be used where the external heating is due to fire. The modified value of the heat release rate per unit mass is given by:

$$q_{\text{modified}} = q + 2Q / m_o \quad (6)$$

The rate of temperature rise due to external heating which needs to be applied in the small-scale test is given by:

$$(dT/dt)_{\text{external}} = Q / m_o C_p \quad (7)$$

After a small-scale test has been performed with the additional heat input, it is necessary to calculate the rate of temperature rise due to the reaction, in order to calculate the reaction heat release rate per unit mass:

$$(dT/dt)_{\text{reaction}} = (dT/dt)_{\text{measured}} - (dT/dt)_{\text{external}} \quad (8)$$

$$q = C_p (dT/dt)_{\text{reaction}} \quad (9)$$

The above equations have been used to calculate vent sizes for an example vessel. These calculations have been performed, with the data from a Phi Tec experiments on 1,3-butadiene. Vent sizing calculations were performed for a small vessel of 2 m³ capacity containing 800 kg of 1,3-butadiene (80% filling). The heat input from the fire was assumed to be 33.2 kW. This requires an external temperature rise rate of 0.8°C min⁻¹ calculated using equation (7). The vent sizing calculations use a vent opening pressure of 25 bara with a maximum allowable pressure of 27.5 bara.

API 520⁷ / Parry¹⁷ can be used to calculate the heat flux for the small vessel. Taking the vessel to be a vertical cylinder of equal height and diameter of 1.37 m. The wetted surface area can be calculated as 6.19 m². API 520⁶ / Parry¹⁷ give the following equation to calculate the heat input assuming prompt fire fighting and good drainage:

$$Q \text{ (kW)} = 43.2 F S_w^{0.82} \quad (10)$$

The heat input for the small vessel can thus be calculated as (193 kW x F). The API codes allow the environmental factor (F) to take account of insulation. To achieve a heat input of 33.2 kW as used in the vent sizing calculation would require an insulation thickness of about 2 inches (F = 0.15).

The required vent size for the small vessel can then be calculated using API 520⁷ and BSI¹⁸ if it is assumed that:

- Vapour-only flow occurs instead of the two-phase flow assumed by the ERM; and
- The vapour is produced purely by the effect of the external heating at 33.2 kW and not by the runaway reaction.

The required relief rate is calculated as:

$$W = Q / h_{fg} \quad (11)$$

The vent mass flux for vapour only flow can be calculated as:

$$G = C_d C_{sv} P (M_w/Z_o T)^{1/2} F_B \quad (12)$$

The required vent area A is finally obtained as:

$$A = W/G \quad (13)$$

The calculated vent diameters for runaway reaction alone, runaway and external heating and external heating alone are shown in Table 9. For this size of vessel the vapour-only vent size for fire relief alone (external heating) is more than the required relief area for runaway reaction alone (two-phase relief) but less than the required relief area for fire (external heating) and runaway reaction (two-phase relief). However, for larger vessel sizes, the required vent size for runaway reaction could exceed that for external fire alone.

Table 9. SUMMARY OF VENT SIZING CALCULATIONS

External heating (kW)	Runaway reaction (kW)	Vent diameter (mm)	External Heating
None	7	2.62	None
33	5	8.16	Experimental
33	None	5.47	Calculated

DISCUSSION ON VENT SIZING

VENT SIZING

The vent sizing calculations shown in Table 9 confirm that larger vent sizes are needed if an external fire initiates a runaway reaction than for external fire alone. It is therefore important to take account of the possibility of thermal runaway when sizing vents on vessel containing reactive chemicals. As well as increasing the necessary size of the vent, it will be necessary to design the vent system for the two-phase flow that is to be expected. This will include venting to a safe place, which does not feed the fire, and the possibility of a catch tank or quench tank for the vented liquid.

Vent sizing calculations for runaway reaction with external heating require data from fire simulation calorimetry. Simulation of large storage vessels, with lower surface areas per unit mass, will require lower heat input rates to the calorimeter than simulation of smaller vessels.

The vent sizing calculations in Table 9 assume the API 520 fire heat input into a small, 2 m³, vessel with a 2 inch thickness of insulation. For this case, the fire heat input rate is significant compared with the rate of heat evolved by the runaway reaction and the external heat input can be simulated using fire simulation calorimetry. This size of vessel was chosen as being typical of processing equipment whilst large enough that fire simulation calorimetry is possible; for smaller vessels the higher heat input rates required in such calorimetry may not be feasible.

For typical storage vessels of up to about 80 tonnes capacity, the rate of heat input from an external fire will be very low compared with the heat evolved by a runaway reaction and is probably negligible in terms of carrying out vent sizing for a runaway. However, if the external fire had a long enough duration to initiate a runaway reaction, a larger vent would be required for the runaway reaction than for external fire.

If external heating was from a jet fire, rather than a pool fire, higher heating rates (e.g. by approximately an order of magnitude for a 2 m³ vessel) would result. Fire simulation calorimetry would not be always be feasible, either because simulation of a small process vessel would necessitate a very high rate of external heating or because a large storage vessel would necessitate an infeasibly low rate. In such cases, it may be possible to correct

calorimetric data to add the effects of external heating using a method analogous to that to correct for thermal inertia (sample heat loss) (Townsend & Tou⁴). However, any such data correction procedures would require development, validation and definition of their conditions of applicability.

CONCLUSIONS

The following conclusions are made:

- (a) The flames and heat fluxes from 1,3-butadiene jet fires are less severe than those use in the jet fire resistance test for passive fire protection materials. Hence, unless the reactive chemical actual reacts with the fire protection, the jet fire test should be adequate for assessing the fire performance of material used to protect vessels containing pressurised reactive chemicals providing they have similar burning rates and heats of combustion to 1,3-butadiene.
- (b) For reactive chemicals, the passive fire protection needs to:
 - protect the wall of the vessel from reaching a temperature where weakening can occur;
 - if possible, prevent a runaway reaction from being initiated; and
 - reduce the heat transfer to the vessel so that a relief device with a practical vent size can be used.
- (c) For reactive chemicals, vent sizing for external fire needs to consider whether the fire will give rise to a runaway reaction. If so, two-phase venting will be expected and larger required vent sizes will result.
- (d) Fire simulation calorimetry may be required to obtain data for vent sizing but will not be feasible for all sizes of process equipment and storage vessels. A methodology needs to be developed and validated for correcting calorimeter data for the heat input from an external fire.
- (e) Whilst API 520 provides a link between insulation and the vent size required, it does not take account of specific fire protection methods such as water deluge or intumescent passive fire protection.

NOMENCLATURE

A	Vent area, m ²
C _d	Discharge coefficient
C _{sv}	Flow correction factor, function of isentropic coefficient
C _w	Specific heat of water, 4.180 kJ kg ⁻¹ K ⁻¹
C _p	Reaction mixture specific heat capacity, J kg ⁻¹ K ⁻¹
dm/dt	Water mass flow rate, kg s ⁻¹
dP/dT	Rate of change of pressure with temperature, Pa K ⁻¹
(dT/dt) _{external}	Rate of temperature rise due to external heating, K s ⁻¹
dT/dt _{max}	Maximum rate of temperature rise, K min ⁻¹

ΔH_r	Heat of reaction, J g ⁻¹
ΔT	Temperature difference between temperatures at the relief set pressure and the maximum accumulated pressure, K
ΔT_u	Uncorrected adiabatic temperature rise, K
ΔT_{ad}	Corrected adiabatic temperature rise, K
ρT_w	Water temperature rise, K
F	Environmental factor
F_B	Back pressure correction factor
G	Mass flux, kg m ⁻² s ⁻¹
h_{fg}	Latent heat of reaction mixture, J kg ⁻¹
I	Heat flux, kW m ⁻²
m_o	Reactant mass, kg
M_W	Molecular weight, 54.092 gmol g ⁻¹ kmol kg ⁻¹
P	Vessel pressure, Pa
P_{max}	Maximum pressure, bara
ϕ factor	1 + (heat capacity of test cell/heat capacity of sample)
q	Heat release rate per unit mass of reactant, W kg ⁻¹
$q_{modified}$	Heat released from reactant plus external heat, W kg ⁻¹
Q	Heat input, W
S	Surface area exposed to flame, 0.642 m ² experiment;
S_W	Effective wetted surface area of vessel, 6.19 m ² vent sizing
σ	Absorptivity of copper surface (surface blackened), 0.95
T	Reactant temperature, K,
T_{ad}	Difference between the sample temperature and the calorimeter heater temperature, K
T_{max}	Maximum temperature, °C
T_{onset}	Onset temperature, °C
V	Vessel volume, m ³
v_{fg}	Difference between vapour specific volume and liquid specific volume, m ³ kg ⁻¹
W	required relief rate, kg s ⁻¹
Z_o	Compressibility factor

REFERENCES

1. Roberts, T. A., Gosse, A. and Hawksworth, S., 2000, Thermal radiation from fireballs on failure of liquefied petroleum gas storage vessels, *Trans. IChemE Hazards*, Vol. 78, Part B: 184 – 192.
2. Keaney A. and Roberts T. A., 1996, Hazard consequences of jet-fire interactions with vessels containing pressurised reactive chemicals, HSL Internal Report, PS/96/12.
3. Singh J., 1992, Phi-Tec: Enhanced vent sizing calorimeter - application and comparison with existing devices, International Symposium on Runaway Reactions, p313-330, AIChE, New York.
4. Townsend D. I. and Tou J. C., 1980, Thermal hazard evaluation by an accelerating rate calorimeter, *Thermochemica Acta*, Vol 37: 1.
5. Freeder B. G. and Snee T. J., 1988, Alkali-catalysed polymerisation of ethylene oxide and propylene oxide - hazard evaluation using accelerating rate calorimetry, *J.Loss Prev. Process Ind.*, 1988, Vol 1: 164-168.

6. Braker W. and Mossman A. L., 1980, Matheson Gas Data Book, 6th edition, Matheson Gas Products, Secaucus, New Jersey, 1980.
7. American Petroleum Institute, 2000, Sizing, selection, and installation of pressure - relieving devices in refineries. Part 1 - Sizing and Selection, Recommended Practice 520, Washington DC, January 2000.
8. Roberts T. A. and Beckett H., 1996, Hazard consequences of jet-fire interactions with vessels containing pressurised liquids: Project R04.029 final report, HSL Internal Report PS/96/03.
9. Roberts T. A., Medonos S. and Shirvill L. C., 2000, Review of the response of pressurised process vessels and equipment to fire attack, HSE Offshore Safety Report OTO 2000 051.
10. Roberts T. A., Brown D., Beckett H. and Buckland I., 1995, Comparison of the effects of different fire test regimes on passive fire protection material, I.Chem.E. Symp. Series No. 139, pp. 253 - 266.
11. Jet Fire Test Working Group, 1995, Jet Fire Resistance Test of Passive Fire Protection Materials, HSE Offshore Technology Report OTI 95 634.
12. Moodie K., Cowley L. T., *et al.*, 1988, Fire engulfment tests on a 5 tonne LPG tank, *J. Haz. Mats.*, Vol. 20: 55 - 71.
13. Shirvill L. and Wighus L., 1992, A method of testing resistance to jet fires, *Advances in EP Research*, Vol. 2: 12 - 13.
14. Fauske H. K., 1985, Flashing flows – Some practical guidelines for emergency releases, *Plant Operations Progress*, Vol 4, No 3: 132-134.
15. Leung J. C., 1986, Simplified vent sizing equations for emergency relief requirements in reactors and storage vessels, *AIChE Journal*, Vol 32, No 10: 1622-1634.
16. Wilday A.J. and Daskalakis G., 1994, Pressure relief design for chemical reactors exposed to external fire, Paper 53c, AIChE Summer National Meeting, August 1994.
17. Parry C. F., 1994, Relief systems handbook, IChemE, Rugby, 1994 reprint.
18. BSI 1984, BS 6759: part 3: 1984, Specification for safety valves for process fluids.

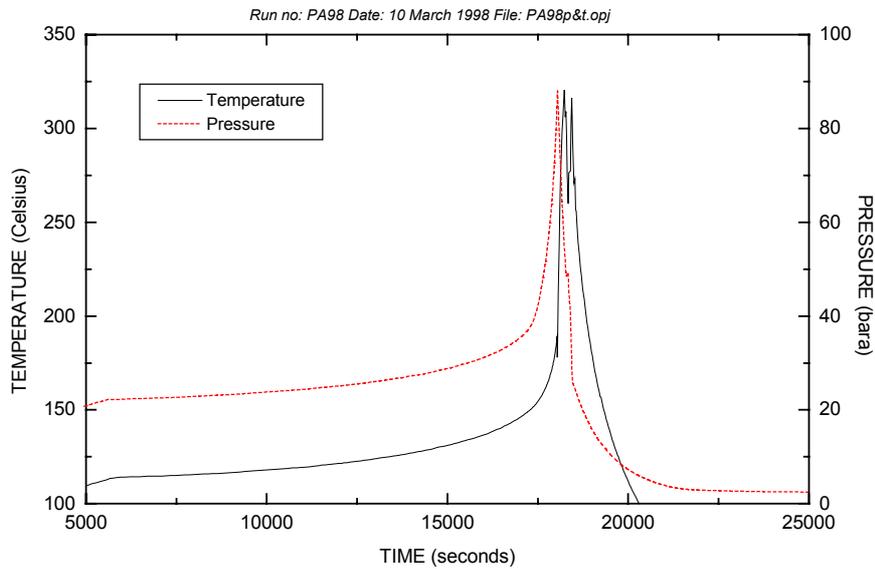


Figure 1. TEMPERATURE AND PRESSURE VERSUS TIME FOR 1,3-BUTADIENE

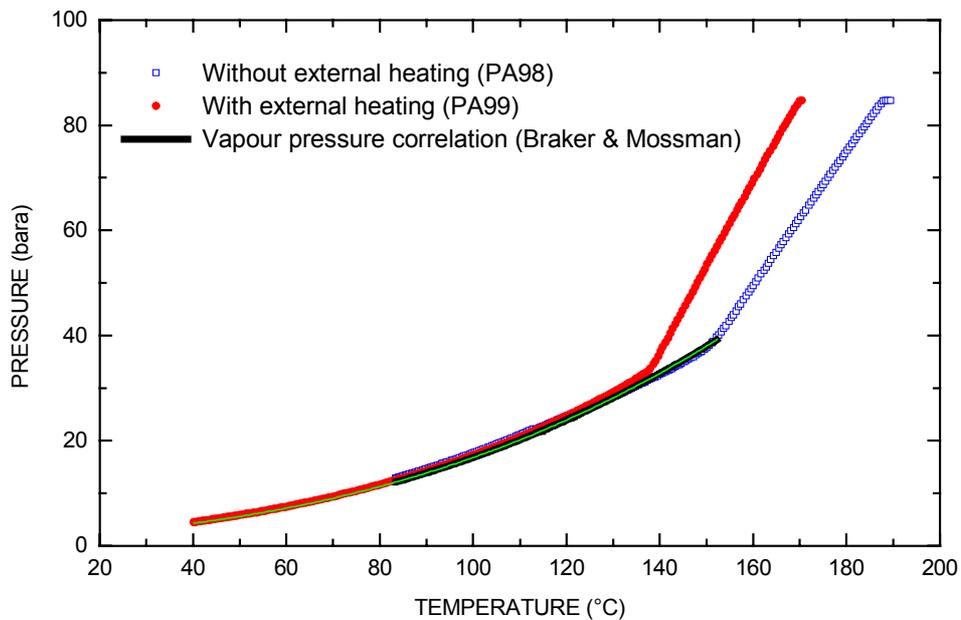


Figure 2. PRESSURE VERSUS TEMPERATURE FOR 1,3-BUATADIENE

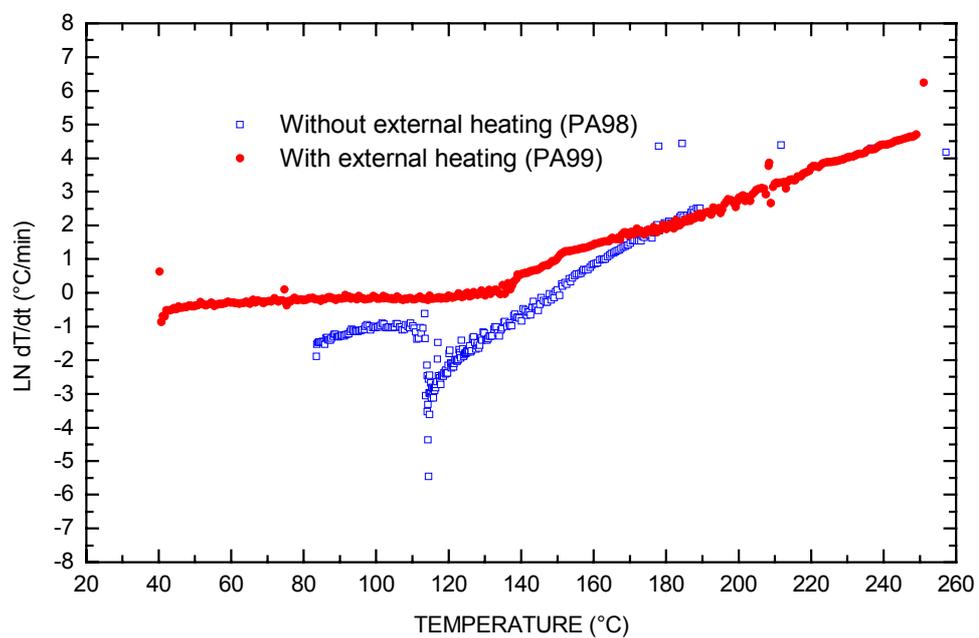


Figure 3. LOG [HEATING RATE] VERSUS TEMPERATURE FOR 1,3-BUTADIENE



Figure 4. PIPE CALORIMETER IN POSITION



Figure 5. FLAMES FROM 1,3-BUTADIENE VAPOUR



Figure 6. FLAMES FROM LIQUID 1,3-BUTADIENE



Figure 7. FLAMES FROM 0.3 KG S⁻¹ PROPANE VAPOUR



Figure 8. FLAMES FROM 0.05 KG S⁻¹ PROPANE VAPOUR