

LATENT SUPERHEAT - A HAZARD OF TWO PHASE LIQUID SYSTEMS

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Superheating readily occurs with two immiscible liquids which are in contact but not in thermal and physico-chemical equilibrium. It may happen at temperatures below the boiling point of either (pure) liquid. Its role in recent disasters is considered, alongside that of other causes of vessel rupture. The destructive force of the energy suddenly released may be many times higher than the rise in static pressure, but little published information has been found on this aspect.

INTRODUCTION

This paper is a sequel to my article (1) written after publication of the report (2) of the Flixborough Inquiry, wherein I showed how a cause which had not been recognised during the Inquiry probably lay at the root of the disaster. The key element lay in the removal six months earlier of a stirrer from one of the reactors. My explanation and the lessons to be learnt from it have since been recognised in a lecture given by B. M. O'Reilly, H.M. Deputy Chief Inspector of Factories in June 1976 (3). Here I try to concentrate on the lessons rather than hold another post-mortem on Flixborough.

Similar mechanisms have caused many accidents and at least one other disaster in oil and petrochemical plants. So my first task was to devise a framework within which they could be classified.

A useful analogy is the fused bomb. Most escapes of inflammable vapour into the air are liable to ignite and/or explode. Thus the container with its contents and the surrounding air constitutes a bomb. Any mechanism which releases inflammable vapour into the air is a fuse or fused detonator. These may be instantaneous or delayed (usually the latter). They may be internal to the plant or external. External fuses often have only a tenuous connection with the plant, eg, a crane or road vehicle which hits a pipe or valve. We, as chemical engineers and plant designers, are concerned mainly with internal fuses. We must and do take pains to ensure that they are absent from the bomb as designed and built, but we have to realise that they may unwittingly be introduced later when something is changed. Such fuses are generally lit as a side effect of some normal action taken in starting up or running the plant.

A fuse may be lit, burn its full course and set off the detonator, which causes a sudden pressure rise in the container. It may even rupture it. But sometimes we are lucky and the vapour fails to explode. This is a misfire. Much of our safety philosophy is aimed at ensuring that our bombs misfire. Perhaps we should be more concerned that they are not fused in the first place.

The larger and faster the escape of vapour, the more likely it is to reach a source of ignition before dissipating harmlessly, and the larger the explosion. Big bombs seldom misfire.

A specially dangerous bomb, as Kletz (4) pointed out, is one where there is a large amount of an inflammable liquid under pressure at a temperature above its atmospheric boiling point. The resulting escape is likely to produce a larger and more persistent explosive mixture with air than a similar escape of gas or non-flashing liquid.

In this paper I concentrate on fuses which can cause release of gas or vapour rather than on the fires and explosions which may follow.

Some of our biggest bombs incorporate large C₃ and C₄ pressurised storage spheres. But it seems they are not easily fused.

A fuse-finder has no easy job. Too often he is hampered by secrecy agreements or finds himself up against a communications barrier. It is as though some people secretly cherish their fuses.

ALL SORTS OF FUSES

An effective fuse for a vented tank containing an inflammable liquid is usually one which causes rapid boiling of the liquid and a sudden evolution of vapour.

Most pressure vessels are protected by relief systems designed and installed to API 520 (5) and 521 (6). These protect the vessels against a number of clearly defined causes of over-pressure. But there are several exclusions, ie, potential fuses for which the relief system alone does not provide adequate protection. These include, 1. water hammer; 2. steam hammer; 3. contact between water and hot oil; 4. internal explosion; 5. other rapid exothermic reactions. This short list provides a general framework for fuse classification. The type dealt with here is a special case of 3.

All engineers are aware of the danger of allowing water to come into contact with very hot oil, but not all are aware of the pitfalls in design which can allow it to happen. These are well described in at least one oil company's design guide (7) which was issued primarily for internal use, and in a paper by Jennings (8). But the danger of allowing water to come into contact with hot hydrocarbon liquid at a temperature below the boiling point of either liquid does not seem to be sufficiently appreciated by Chemical Engineers.

THEORY

Figure 1 is an isobaric temperature composition diagram for two liquid components A and B with boiling points T_A and T_B which are very slightly soluble in each other (solubilities x'_A and X'_B). Over most of the liquid composition from x'_A to (1 - X'_B) there are two liquid phases with a constant boiling point T_{AB} which are in equilibrium with a vapour of constant composition y_A. known as a hetero- or pseudo-azeotrope.

Figure 2 by way of contrast is an isobaric temperature composition diagram for two mutually soluble liquids which form a minimum boiling azeotrope, known as a true or homo-azeotrope.

At least one book on azeotropes (9) tabulates homo- and hetero-azeotropes together indiscriminately, with nothing to indicate which is homo- and which is hetero-. Cremer and Warner's Report No 2 to the Flixborough Court of Inquiry (10) gave the vapour pressure composition relationships at constant pressure of the water-cyclohexane system as calculated both by DSM/Stamicarbon and by Cremer and Warner. Both refer to the immiscibility of water and cyclohexane, but no solubility data are given. Both show the vapour pressure at constant temperature increasing with the water content of the liquid from zero up to the 'azeotropic composition', despite the fact that this is well in the two liquid phase region of Figure 1. (DSM quoted this as 43.47% mol water at 135°C, and show a linear relationship between vapour pressure and composition whereas Cremer and Warner show a curvilinear relationship fitting the van Laar equation. Whilst they are argued hotly, neither party seemed to realise that their theories conflicted with the Phase Rule, and that at constant temperature the total vapour pressure of a system of two components with two liquid phases in equilibrium remains constant over the entire two phase region.) The

argument is reminiscent of the battle between Tweedledum and Tweedledee (11). In this case they seemed to have knocked each other unconscious simultaneously, and as a just punishment for those who violate the Phase Rule, awoke into a world of fantasy. Gulliver-like (12) they found themselves pinned down by an army of little men, led by three eight inch pipers in the pay of King Cole. Eventually after nearly losing the battle with the pipers, their differences now forgotten, they were rescued by Pooh Bah (13) who scattered the pipers with disapproving noises (2).

Returning to Figure 1, we see we can have two partly miscible liquids A and B at the same pressure and at temperatures T'_A and T'_B which are below their boiling points T_A and T_B at that pressure but one of which is above the boiling point T_{AB} of the two phase system. If the liquids are now mixed at that pressure, rapid boiling may occur. The amount of vapour thus formed is given by:

$$M_v = \frac{M_A C_A (T'_A - T_{AB}) + M_B C_B (T'_B - T_{AB})}{y_A L_A + y_B L_B} \dots\dots\dots (1)$$

This is the result of the conversion of sensible heat to latent heat accompanied by a fall in temperature. It is a form of superheating peculiar to two phase liquid systems. No heat of mixing or reaction is involved.

Example

A still used for solvent recovery (Figure 3) consisted of an unstirred steel vessel fitted with a steam coil and a glass condenser. The vessel contained 5 tonnes of cyclohexane (B.P. 80°C) which surrounded the steam coil, and 100 kg of water which had entered accidentally. The steam valve was closed but leaked slightly, so that the temperature of the cyclohexane rose slowly. By the time the bulk of the cyclohexane reached 76°C the temperature of the interface reached the boiling point of the hetero-azeotrope, ie, 69 to 70°C. Bubbles formed at the interface which mixed the liquids, giving a large increase in the interfacial area. The superheat was released rapidly and the vapour formed suddenly within the body of the liquid shot a slug of liquid into the glass condenser and broke it.

It is worth noting that the events described occurred in spite of the fact that both liquid phases were probably mutually saturated when cold before heating started. As the cyclohexane was being heated, the solubility of water in it increased by several hundred per cent. By the time the bulk of the cyclohexane reached 76°C, it was far from saturated.

A similar sudden evolution of vapour could equally well have occurred if the vessel in this example contained initially a larger amount of water covering the steam coil and a smaller amount of cyclohexane above it. The effect would have been enhanced by any sort of barrier to heat and mass transfer such as emulsion or suspended solids at the interface, which would tend to delay the onset of interfacial boiling until a larger degree of superheat had built up.

The second phase did not of course have to be present in the vessel at the start of heating, but could have been introduced at any time during heating.

The phenomenon is one that applies to most combinations of two or more incompletely miscible liquids. Water is not an essential constituent. At higher temperatures for instance, a similar phenomenon could occur with two incompletely miscible molten metals such as zinc and lead.

Stored Energy

The amount of energy stored as latent superheat in two liquid phases waiting to be released when the interface reaches its interfacial boiling point is quite high in relation to the short time ranging from a few milliseconds to a few seconds during which it is released. It is simple enough to calculate the stored superheat. The stored free energy (which is of the same order of magnitude as the superheat) can also be calculated, though this is rather more difficult.

In the example described, the amount of superheat is approximately the difference between the heat contents of 5 tonnes of cyclohexane at 76°C and at 70°C. This amounts to about 75 megajoules, and is roughly the same as that contained in 9 kg of TNT. The damage which it might cause depends on several factors, particularly the time during which it is released. It is probably more akin to a low explosive such as cordite than a high explosive like TNT or nitroglycerine. It would normally be expected to break the glass condenser of the example, while in some cases it might rupture the steel vessel.

Vapour Release in Open Systems (Constant Pressure)

The treatment given above is for an open or constant pressure system, where the amount of vapour formed is easily calculated if the temperatures and quantities of the liquids present immediately before the superheat is released are known, as well as the total pressure. But even in an open or constant pressure system, the generation of vapour will generally be so rapid that some temporary build up of pressure is likely somewhere in the system - usually within the body of the liquid. In the example described, rather more than two kilomoles of vapour would be released, containing approximately 100 kg of cyclohexane. This could carry with it drops and slugs of entrained liquid so that the total amount of cyclohexane escaping is considerably higher.

Vapour Release in Closed Systems

When latent superheat is released in a closed system, so that the vapour formed is unable to escape, the pressure rises and at the same time raises the boiling point of the mutually saturated phases. This reduces the amounts of energy and vapour released. These then depend very much on the gas volume. In a totally liquid filled system there will be a pressure rise only. (Worked examples are given in my earlier article (1) and paper (14) in which the pressure rise and vapour release are calculated for an industrial plant containing cyclohexane, water and inert gas under pressure, where the gas and liquid filled volumes were of the same order of magnitude.)

The maximum working pressure of a process vessel containing one or more liquids under pressure is usually calculated on a basis which includes the vapour pressure of one or more liquid phases plus the partial pressure of any non-condensibles present. A vessel containing one liquid phase (hydrocarbon) plus inert gas might be designed to withstand the higher pressure that would arise if a second liquid phase (water) were also present, yet operated at a lower pressure.

In this case superheating and formation of vapour inside the vessel could occur after a second liquid phase (eg water) had been introduced. The static pressure thereby created would still lie within the design pressure of the vessel. But the dynamic pressure resulting from the impact of slugs of liquid thrown up by the vapour onto the walls of the vessel might possibly destroy it.

Speed of Release - Impulsive Forces

Unfortunately I can only plead ignorance on these important topics, and this ignorance seems general. To quote reference (6) "the speed of vapour generation is generally instantaneous and it is questionable whether the (relief) valve could open fast enough to be of much value". Some related research (15) by Ogisco and others in Japan has been done on the speed and magnitude of pressure surges in containers with a single liquid phase which was suddenly superheated. (This is more difficult to achieve than superheat in a system with two liquid phases.) The magnitude of the pressures reached convinced the authors that this phenomenon may well have been responsible for the unexplained rupture of a pressure vessel in a Japanese petrochemical plant disaster. I hope that this paper will help to convince those responsible for research on chemical process hazards of the need for work in this field. Until proper information is available, it is best to admit that we have little idea how much damage can be caused to a pressure vessel by the sudden release of latent superheat which has built up between two liquid phases within it.

PRACTICAL EXAMPLES AND PREVENTION

Apart from Flixborough, I believe the most serious accident attributable to this fuse was the big Pernis explosion (16) early in 1968. Here there was a vented crude oil storage tank with a steam coil in the bottom. The tank contained a layer of water and aqueous emulsion which covered the steam coil. The aqueous phase was heated to a temperature probably above the initial boiling point of the crude oil. The supernatant oil layer appears to have been insulated by oil in water and water in oil emulsion layers at the interface. Several tons of mixed hydrocarbon-water vapour were rapidly released when the two phases mixed, and the cloud of vapour ignited, probably on reaching a furnace. I have witnessed several accidents caused by this fuse including one on a pilot plant in which a friend and colleague was badly burned. He died a few years later in the prime of life, probably as a result.

The design guide (7) and Jennings' article (8) referred to earlier contain several examples.

Regarding prevention, the most general rule that emerges is:

"Take care when heating a liquid in an unstirred vessel that a second liquid phase is not present initially or introduced into it during heating."

In my earlier paper (10) I listed four conditions required to create this fuse in a cyclohexane oxidation plant such as that operated at Flixborough. I repeat them again here:-

- 1 Hot circulation before start up.
- 2 An unstirred reactor.
- 3 Presence of water in the system.
- 4 System pressure less than sums of vapour pressure of water and cyclohexane at the operating temperature.

All four conditions are essential to the fuse, so provided one is alert to the hazard, it should not be difficult to eliminate it.

Having identified situations in other plants where the same hazard could arise, the conditions required to create it should be listed and positive steps taken to ensure that this fatal combination cannot arise under any circumstances.

COMPARISON WITH OTHER CAUSES OF RAPID VAPOUR RELEASE

In my own experience only chemical explosions inside vessels are as hazardous as the release of latent superheat in two phase liquid systems. Most other exothermic chemical reactions allow time for the pressure to be released. A year ago a batch polymerization in a large works where I happened to be present 'took off', blowing the relief valves and discharging much of

the reactor contents to the flare. Although the reaction was out of control, the operating personnel had at least 10 minutes warning before the relief valves lifted. While the results were spectacular, the safety of plant and personnel were never in much doubt. Earlier on another works I saw a tank of cracked hydrocarbons with a high cyclopentadiene content boil as a result of spontaneous exothermic polymerisation. This continued for several hours, and a large quantity of vapour escaped. Time, however, allowed precautions to be taken to minimise risk of ignition and possible damage (neither of which occurred).

A very serious situation which one can envisage would arise if a quantity of an active polymerisation catalyst were allowed to enter a large storage sphere containing pure propylene. Unless the relief system were designed to deal with this contingency (which seems unlikely) the pressure could continue to rise until the sphere split, releasing several hundred tons of flashing propylene rapidly into the atmosphere. This is the sort of doom-watch situation which I hope has been studied by our Major Hazards Committee.

SYMBOLS USED (any consistent set of units may be used)

C_A, C_B	= molar specific heats of liquids A and B
L_A, L_B	= molar latent heats of liquids A and B
M_A, M_B	= moles of liquids A and B present initially.
M_V	= moles of vapour formed
T_A, T_B	= boiling points of pure liquids A and B at pressure specified.
T_{AB}	= boiling point of two liquid phase system A and B at same pressure.
T'_A	= average temperature reached by liquid A at same pressure before superheat is released.
T'_B	= average temperature reached by liquid B at same pressure before superheat is released.
x_A, x_B	= mol fraction of component A or B in one or both liquid phases.
x'_A	= mol fraction of A in a saturated solution of A in B.
x'_B	= mol fraction of B in a saturated solution of B in A.
y_A, y_B	= mol fractions of components A and B in the vapour.
y'_A, y'_B	= mol fractions of components A and B in the heteroazeotropic vapour.

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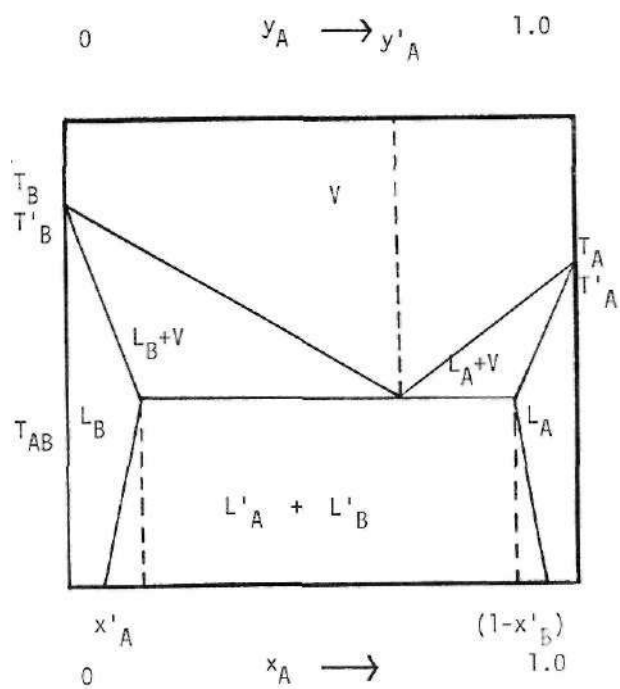


Figure 1 Isobaric Temperature-Composition Diagram for two incompletely miscible liquids

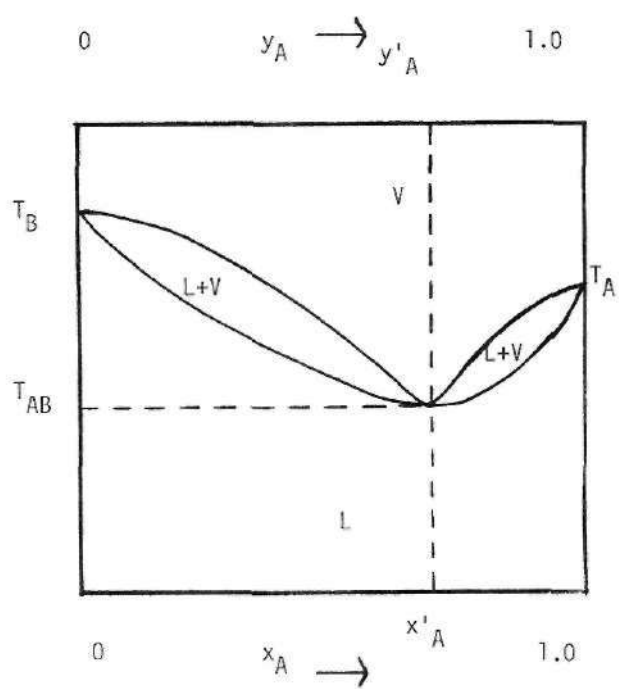


Figure 2 Isobaric Temperature-Composition Diagram for two completely miscible liquids forming minimum BP azeotrope.

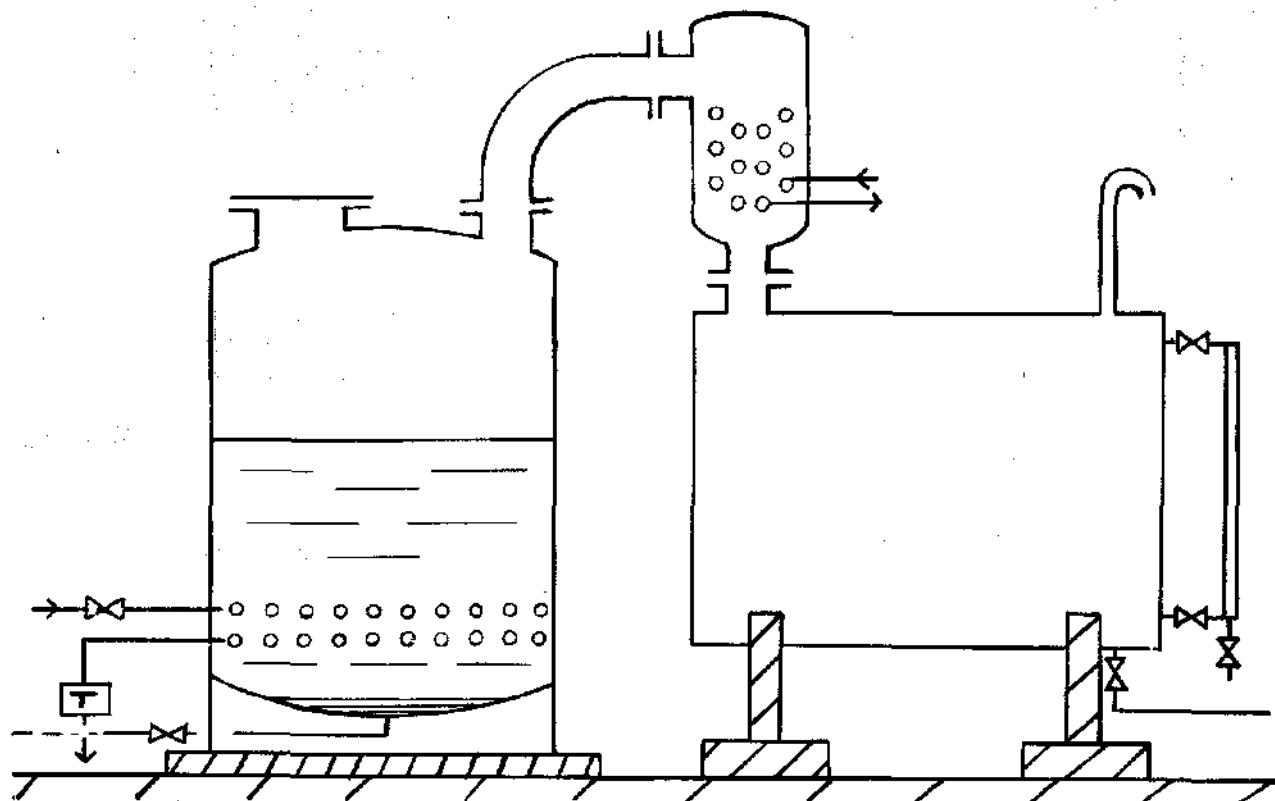


Figure 3 Solvent Recovery Still referred to in example.