

## HAZARDS OF HEATING IMMISCIBLE LIQUIDS

R.B. Keey

Department of Chemical Engineering, University of Canterbury, Christchurch, New Zealand.

A recent incident at an oil re-refining plant in New Zealand highlighted the hazards involved when aqueous layers can separate from a two-phase dispersion on being heated. While the hazards are well-known in the oil industry, and precautions to avoid the separation of water are routinely made, the heating of immiscible liquids is not infrequently done in other industries which may be less aware of the hazards involved. The particular incident illustrates where preventative measures could be taken in operation and design to minimise the risks.

INTRODUCTION

The dangers inherent in the separation of water in tanks storing hot petroleum liquids are well known and documented by Hughes (1). Water may enter a tank through open vents, through condensation as the tank is being pumped out, or by leakages from steam pipes and tracing. Often the temperature of the main body of the oil is much higher than the oil adjacent to the settled water. Severe eruptions within tanks have taken place when hot oil at a temperature above 100 C has suddenly come into contact with this settled water, which then flashes violently off.

Jennings (2) describes incidents of a similar kind which derive from the very large change in specific volume on vaporization. (At atmospheric pressure a given quantity of water transforms into a vapour 1600 times greater in volume.) In each of the two cases described, consequent on a departure from normal working arrangements, the sudden mixing of a hot immiscible liquid with a separated aqueous layer caused a violent ebullition which ejected hot oil through open manholes.

Such an evolution of vapour, if restrained through inadequate means of vapour release, will quickly generate an internal pressure of intolerable dimensions within the process vessel. As previously pointed out (2), the associated phenomenon of a sudden condensation of a vapour due to shock cooling can induce the inverse effect of a dangerously low vacuum in a process vessel.

THEORY

By means of a highly simplified analysis one may get a measure of the magnitude of the foregoing effects. Let us consider a perfectly insulated vessel in which a separated aqueous layer at temperature  $T_w$  resides below a much larger volume of oil at temperature  $T_o$  (Fig.1). The vessel is supposed to have a uniform cross-sectional area  $A$ , so that the volumetric fraction of water in the tank is equal to the fractional depth of the aqueous layer, that is  $f = z/Z$ .

1. Minimum Temperature Excess

The required heat to boil off the aqueous layer entirely is given by

$$Q = Az\rho_w\Delta H_{vw} \quad (1)$$

which is supplied from the overlying oil, the temperature of which will fall from  $T_o$  to  $T_f$  as a consequence. Thus,

$$Q = s_o(T_o - T_f)A(Z - z)\rho_o \quad (2)$$

The temperature  $T_f$  will take its minimum value when  $T_f$  reaches the boiling point of water  $T_{wb}$  under the conditions in the vessel. We find, therefore, from equations (1) and (2) the minimum temperature excess  $(T_o - T_{wb})$  to be given by

$$(T_o - T_{WB}) = f \rho_w \Delta H_{vw} / s_o (1-f) \rho_o \quad (3)$$

on substituting  $f = z/Z$ .

### 2. Maximum Pressure

The volume of steam that is produced is equal to

$$V_s = \bar{V}_s z A \rho_w \quad (4)$$

where  $\bar{V}_s$  is the specific volume of steam under the pressure generated on flashing. If this steam is totally constrained by the vessel, the pressure will rise from the initial value  $P_A$  to a maximum  $P_{max}$  given by

$$P_{max} (V_H + zA) = P_A V_s = P_A \bar{V}_s z A \rho_w \quad (5)$$

where  $V_H$  is the volume of the headspace above the tank contents. Let us suppose that this headspace occupies a fraction of the tank's contents equal to  $f_H / Z A$ . Thus from equation (5) the maximum pressure becomes

$$P_{max} = P_A \bar{V}_s \rho_w f / (f_H + f) \quad (6)$$

The specific volume  $\bar{V}_s$  may be found from the Ideal Gas relationship

$$\bar{V}_s = RT / P_{max} \quad (7)$$

where the gas constant  $R$  is expressed in terms of unit mass (i.e.,  $J \text{ kg}^{-1} \text{ K}^{-1}$ ). Thus, on eliminating  $\bar{V}_s$  from equations 6 and 7, one obtains

$$P_{max} = \sqrt{P_A R T \rho_w f / (f_H + f)} \quad (8)$$

which takes a limiting value of  $\sqrt{P_A R T \rho_w}$  when the tank is full.

### 3. Boiling Time

Consider the case when both the oil and water are at a uniform temperature  $T_A$ , which is less than the boiling point of the water, and the oil is heated. Further, let us suppose that due to poor agitation the water warms up slowly by conduction from the hotter oil above. A heat balance over the aqueous layer for a period  $\delta\tau$  yields

$$hA(T_o - T_w)\delta\tau - 0 = zA\rho_w s_w \frac{dT_w}{d\tau} \delta\tau \quad (9)$$

(input)      (output)      (accumulation)

from which one obtains the differential equation

$$\frac{dT_w}{d\tau} = \frac{h}{z\rho_w s_w} (T_o - T_w) \quad (10)$$

It is convenient to rewrite this expression in terms of the excess temperatures:

$$\theta_w = T_w - T_A \quad (11a)$$

$$\theta_o = T_o - T_A \quad (11b)$$

Also, let us assume that the temperature of the oil is being uniformly heated so that its temperature observes the linear relationship

$$\theta_o = a\tau \quad (12)$$

With these substitutions, equation (8) becomes

$$\frac{d\theta_w}{d\tau} + \left(\frac{h}{z\rho_w s_w}\right) \theta_w = \left(\frac{ha}{z\rho_w s_w}\right) \tau \quad (13)$$

Equation 13 is a linear, first-order differential equation which has the solution

$$\theta_w = e^{-h\tau/z\rho_w s_w} \left[ a\tau e^{h\tau/z\rho_w s_w} - (az\rho_w s_w/h)e^{h\tau/z\rho_w s_w} + C \right] \quad (14)$$

The coefficient  $C$  is determined from the initial conditions,  $\theta = 0$  when  $T = 0$ . Thus equation (14)

simplifies to

$$\theta_W = \frac{az\rho_{W^*}s_W}{h} \left[ \frac{hT}{z\rho_{W^*}s_W} - 1 + e^{-hT/z\rho_{W^*}s_W} \right] \quad (15)$$

The temperature difference between the oil and the water is given by

$$T_O - T_W = \theta_O - \theta_W = \frac{az\rho_{W^*}s_W}{h} \left[ 1 - e^{-hT/z\rho_{W^*}s_W} \right] \quad (16)$$

on noting that  $\theta = aT$ . When the water is about to boil, this temperature difference is also given by equation (3). After some algebraic manipulation, it can be shown that the time needed to reach this condition is equal to

$$\tau = -\frac{z\rho_{W^*}s_W}{h} \ln \left[ 1 - \frac{h \Delta H_{VW}}{as_{W^*}s_O Z(1-f)\rho_O} \right] \quad (17)$$

Worked Example. Consider the following set of circumstances. The water layer fills the tank to a fractional depth  $f = 0.03$  and the headspace occupies a fraction  $f_H = 0.07$ . Let us suppose that heat transfer takes place sluggishly across the oil-water interface, and  $h = 10 \text{ W m}^{-2} \text{ K}^{-1}$ . The specific heat of the oil is taken as  $2.2 \text{ kJ kg}^{-1} \text{ K}^{-1}$ , and the oil density  $700 \text{ kg m}^{-3}$ .

From equation (3) the minimum excess temperature of the oil over the water to cause boiling is

$$(T_O - T_{WB}) = 0.03 \times 958 \times 2257/2.2 \times 0.97 \times 700$$

The maximum pressure that could be developed is found from equation (8) for  $P_A = 10 \text{ Pa}$ .

$$\begin{aligned} P_{\max} &= \sqrt{10^5 \times 4.615 \times 10^2 \times 373 \times 958 \times 0.03/(0.03 + 0.07)} \\ &= 2.22 \times 10^6 \text{ Pa} \end{aligned}$$

If the oil behaves like an incompressible piston, which is feasible if the flashing is rapid and means of vapour escape limited, then such a pressure could be closely attained.

The time to reach the critical flashing condition from ambient temperature is given by equation (17) for  $a = 0.01 \text{ K s}^{-1}$  and  $Z = 2 \text{ m}$ .

$$\begin{aligned} \theta &= -\frac{0.03 \times 2 \times 958 \times 4.17 \times 10^3}{10} \ln \left[ 1 - \frac{10 \times 2257 \times 10^{-3}}{0.01 \times 2.2 \times 4.17 \times 2 \times 0.97 \times 700} \right] \\ &= 4791 \text{ s or about } \underline{80 \text{ min.}} \end{aligned}$$

Although these calculations are very rough, the estimates demonstrate it is possible to heat an unmixed (or poorly mixed) immiscible liquid above a separated aqueous layer to reach a critical condition in which a sudden rise in pressure occurs as the water vaporizes rapidly. The following incident illustrates what is considered to be such a case.

#### INCIDENT

Key (3) describes an incident at a New Zealand works engaged in greasemaking, the re-refining of used oils and allied operations. An explosion occurred in one of the vessels used for drying waste oils and, almost immediately, an intense fire broke out which resulted in the virtual destruction of the factory and its contents. Five men, all process workers in the factory, were killed instantly. A report (4) of the Commission of Inquiry set up to investigate the cause of the incident has been published.

The process of re-refining waste oil consists of heating the oil to  $220^\circ\text{C}$  to drive off water and light hydrocarbon fractions which derive principally from petrol and kerosene. The dried oil is then treated with concentrated sulphuric acid to remove, as a sludge, oxidation products and some additive residues. The remaining solid and other residues are adsorbed on to fuller's earth in a subsequent processing stage. Both the drying and clay-contact processes give off emissions which are subject to legislative control. The vapour-offtake pipes from both process vessels were connected to a common line to a condenser, from which the wet vapours containing liquid hydrocarbons were to be scrubbed and the light hydrocarbons separated, as shown in Fig.2.

At the time of the incident this vapour-scrubbing system was being tested. About 7500 litres of wet waste oil were charged to the vessel used for drying the oil, and heating started the following day. After two heating cycles, with the temperature of the contents finally reaching  $102^\circ\text{C}$ , the plant was

shut down owing to faults developing in the circulating pump of the scrubbing system. The contents of the vessel were left to stand for 5 days during which time the temperature fell to ambient. On the sixth day, the repairs completed, the drying process was restarted. Shortly before the incident, when the indicated temperature was 177 C, a chemist inspecting the plant found nothing abnormal in the operation of either the scrubbing system or the drying vessel.

Considerable insight into the probable cause of events was obtained by laboratory simulations of the heating-cooling cycles in the plant. Normally about 5 vol. per cent of water is held in fine suspension in the waste oil, but on standing a thick sludge of poor thermal conductivity would have deposited above a pool of water of some 60 litres. The oil-water interface would initially have been about 75 mm below the level of the lower agitator (Fig.3), which because of its design would have left the separated layer relatively undisturbed. For  $h \sim 30 \text{ W m}^{-2} \text{ K}^{-1}$ , corresponding say to a 5 mm thick layer of sludge, the critical flashing condition would have been reached at the time of the incident. Further, if the water layer had slowly evaporated by some 5 litres by this time, then an outlet standpipe would have broken the interface to provide, perhaps, enough eddying for the water to mix with the overlying oil and begin to flash off.

Since the excess temperature of oil would be at least 80 C at this stage, this ebullition would have been very rapid and the rise in pressure with the generation of steam almost totally constrained by the incompressible oil and the narrow vapour outlet (only 38 mm diameter). (The maximum pressure from equation (8) is about 4 MPa.) When the pressure reached between 1.5 to 2.0 MPa, a circumferential crack would have appeared at the toe of a fillet weld at the base of the vessel, which then ruptured to throw the upper section skywards. At the same time, hot oil would have been ejected into the factory, initially as a foam under pressure which then would break into a mist of fine droplets.

The emergent pressure wave was strong enough to dislodge heavy items of process equipment and strip pipes carrying heating oil bare of lagging. These pipes were the most probable incendiary sources for the fierce fire that broke out a few seconds after the explosion. There was ample combustible and flammable material in the factory to sustain the fire which took 3 hours to put out.

#### DISCUSSION

This disastrous incident demonstrates the severe consequences of a so-called "steam explosion", the rapid flashing of water when suddenly brought into contact with hot oil. Theoretically, very large pressures can be generated which can exceed the design working pressures of the vessel concerned. There is always a risk of such an event whenever two immiscible liquids are being heated. Clearly there is no danger as long as the aqueous phase is uniformly dispersed throughout the mixture by adequate agitation of the vessel's contents. One sensible precaution would be to cut off the heating system by an appropriate interlocking device should the agitator motor not be running for any reason. Heating with steam should be avoided, if the process fluid is immiscible with water. Should steam heating be unavoidable in such circumstances, then the equipment should be regularly checked for leaks. Provision should be made for draining any separated water. When phase-separation risks are high, there should be the facility for dumping the tank contents into an appropriate, safe receptacle. Finally, the example cited illustrates how the severity of an incident can be magnified by the presence within a single fire-area of a number of operations involving hazardous materials. In this particular instance, however, the fierce fire did not spread beyond a concrete block fire-wall separating the factory from the dangerous goods store which remained intact.

#### NOTATION

$a$  = heating-rate coefficient ( $\text{K s}^{-1}$ )  
 $A$  = cross-sectional area (m)  
 $C$  = integration coefficient (1)  
 $f$  = volumetric fraction, aqueous layer (1)  
 $f_H$  = volumetric fraction, headspace (1)  
 $h$  = heat-transfer coefficient ( $\text{W m}^{-2} \text{K}^{-1}$ )  
 $Q$  = quantity of heat (J)  
 $R$  = gas constant ( $\text{J kg}^{-1} \text{K}^{-1}$ )  
 $s_o$  = heat capacity of oil ( $\text{J kg}^{-1} \text{K}^{-1}$ )  
 $s_w$  = heat capacity of water ( $\text{J kg}^{-1} \text{K}^{-1}$ )  
 $T$  = temperature (K)  
 $T_A$  = ambient temperature (K)  
 $T_O$  = oil temperature (K)  
 $T_W$  = water temperature (K)  
 $V_H$  = headspace volume ( $\text{m}^3$ )  
 $V_S$  = steam volume ( $\text{m}^3$ )  
 $\bar{V}_S$  = specific volume of steam ( $\text{m}^3 \text{kg}^{-1}$ )  
 $z$  = depth of aqueous layer (m)  
 $Z$  = depth of tank contents (m)

$\Delta H_{vW}$  = heat of vaporization of water ( $J\ kg^{-1}$ )  
 $\rho_o$  = oil density ( $kg\ m^{-3}$ )  
 $\rho_w$  = water density ( $kg\ m^{-3}$ )  
 $\theta_o$  = oil excess temperature (K)  
 $\theta_w$  = water excess temperature (K)  
 $\tau$  = time (s)

REFERENCES

1. Hughes, J.R., "The Storage and Handling of Petroleum Liquids Practice and Law", 2 edn, 1970, Griffin, London.
2. Jennings, A.J.D. 1974, Chem. Engr., No. 290, 637.
3. Keey, R.B., 1976, N.Z. Engng 31, No. 11
4. Report Commission of Inquiry into the Explosion and Fire which Occurred at the Factory of Chemical Manufacturing Co. Ltd on 26 September 1974, 1975, Govt. Printer, Wellington, N.Z.

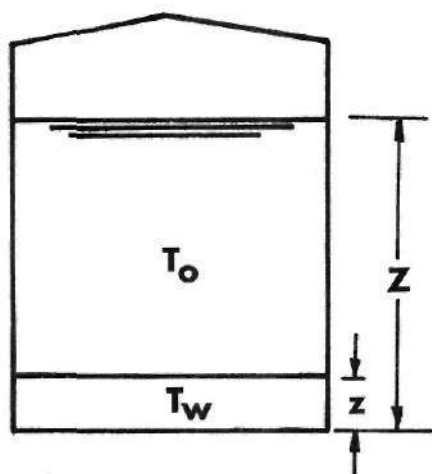


Figure 1 Tank with two-phase mixture

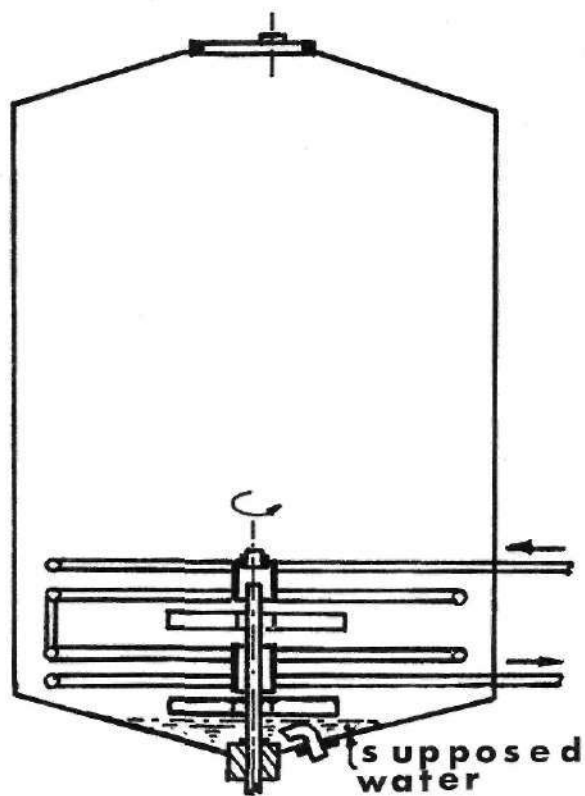


Figure 3 Waste oil drying vessel

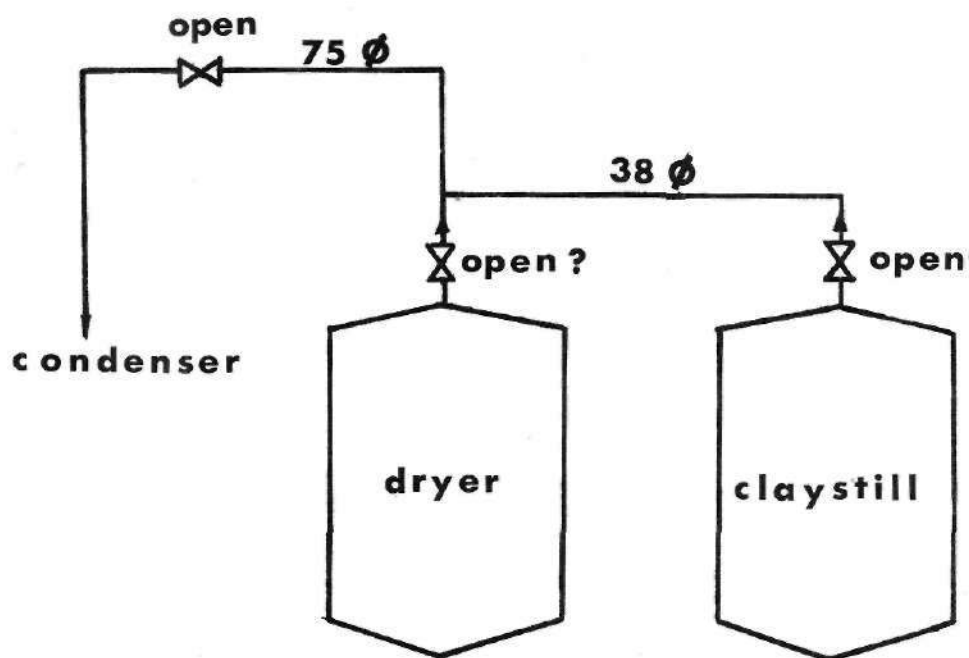


Figure 2 Vapour-offtake lines for oil re-refining plant