



# HYDROCARBON VAPOUR SAFETY PROBLEMS AND SOLUTIONS

## INTRODUCTION

Hydrocarbons and Hydrocarbon Vapours obey some pretty basic but not necessarily intuitive thermodynamic laws. These laws can be used to predict how a particular liquid will respond to changes in temperature and pressure and the resulting hazards inherent in that result. The effect of temperature is particularly a problem in winter as large swings in temperature can occur.

## THERMODYNAMICS

The basic gas law is pretty simple.

The equation is:

$$PV=nRT$$

Where P is the pressure, V is the volume, n is the amount of gas in moles, T is the temperature in °K and R is the gas constant. So for a system with a fixed volume the pressure increases proportionally to the temperature. In heating a vessel with a fixed amount of gas (that is a constant volume) the calculation becomes  $P_2 = T_2 / (T_1 \times P_1)$

This calculation only works for a gas where there is no phase change. That is there is no evaporation of the gas from a liquid phase. We are still dealing with JUST the pressure change, (I will get to the evaporation thing in a second). For a change of from say -20 C to +20 C and the initial pressure was atmospheric (1 atm.) the final pressure increase = 1.15 atmospheres. (The temperature has to be converted to °K before the calculations work) using psi as the units this is pressure increase of 1.2 psi. You would notice some gas being pushed out of the vessel as it is warmed up.

What if you have a phase change?

## CASE 1 BOILING

n-butane has a boiling point of  $-0.5^{\circ}\text{C}$  so a condensate at  $-20^{\circ}\text{C}$  would contain liquid butane. Again, assuming a fixed total volume; 1 litre of n-butane raised from  $-20$  to  $+20^{\circ}$  will vaporize completely. (this may not be entirely true but for the purposes of this discussion I will pretend it is).

1 litre of n-butane liquid has a density of 1.018 and contains 17 moles of butane. Assuming a constant volume of 1000 litres, flashing 1 litre of butane into an air filled vessel at 1 atmosphere pressure will increase the pressure to 1.4 atmospheres. 14 psi to 20 psi. The more liquid we evaporate the more the pressure will increase. The resulting concentration of butane in the air would be 38%. That's one litre of butane evaporated in to  $1\text{m}^3$  of air. This is actually **OVER** the upper explosion limit for butane. (UEL of butane is 8.41%)

## CASE 2 EVAPORATION.

Let's look at n-hexane

The boiling point at atmospheric pressure is  $68.742^{\circ}\text{C}$  and heat of vaporization (which is the important part for this calculation) is 6.896 kcal/mole

The vapour pressure of n-hexane at  $-20^{\circ}\text{C}$  is approximately 0.39 psi

When you heat it up to  $20^{\circ}\text{C}$  the vapour pressure is 2.54 psi

This results in an increase in the pressure due to the presence of hexane of more than 650%.

The interesting part of this is that the liquid wants to be in equilibrium with a gas that has a partial pressure of about 0.18 atmospheres. If you have a large volume of gas total and a small volume of liquid, the liquid will evaporate to try and approach the equilibrium pressure. So, as in the case of a litre of butane, a litre n-hexane in a  $1\text{m}^3$  volume will completely evaporate.

There is no way to calculate actual changes in pressure when the composition of the liquid phase is unknown. And in fact to calculate for complex mixtures you have to use what is called a "cubic equation of state", which is far beyond anything we really need to know.

The important thing to note is that the combination of vaporization and evaporation, along with expansion, can lead to a SUBSTANTIAL increase in the internal pressure of a vessel. These effects occur whether we have an enclosed space, such as a vacuum truck or tanker, or a room. The vapour created doesn't mix well because hydrocarbon vapour is heavier than air, so it tends to make an enriched layer of hydrocarbon close to the floor.

So much for the thermodynamics lesson

## LOWERING RISKS

What can we do to lower our risks?

1. Allow the vessel to be vented while warming up. This will keep the buildup of hazardous vapours to a minimum and prevent RAPID pressurized release of gasses. This has to occur in such a way that the vent is **AWAY** from any sources of ignition.
2. Before allowing the vessel to warm up. Clean the equipment with a 10% Paratene D734-OC solution. The water used should be at room temperature 15-20° C. The D734-OC was designed for exactly this sort of problem, and will contain the vapours that can be handled at room temperatures and capture them in the cleaning solution. It WILL NOT control vapours where the liquid is below its boiling point but it will prevent the others from filling the vapour space. ( I would recommend a gamma jet cleaning nozzle through a port in the tanks) to apply the chemical. The system may still need venting to remove hydrocarbons that were below their boiling point.
3. Rapid depressurization of vessels must be avoided. The presence of vapour close to the ground can migrate to any point source of ignition.
4. Eliminate sources of ignition – these can be anything from a idling vehicle to the pilot light on a furnace or hot water heater. An object does not actually have to be a flame to be a source of ignition.

Straight wash water has little chance in suppressing vapour release. We performed tests on crude oil vapour by testing 2 – 5% solutions of various chemicals against crude oil vapour. (the amounts were determined by the reduction of total peak area by GC headspace analysis.)



% controlled compared to water

Oil Type	Water	EcoSorb	ZymeFlo	Carbonil XT	D-734
Viking Crude	0%	10%	-2%	10%	28%
Gibson Frac Oil	0%	-17%	25%	30%	40%

This table is from a report development of Paratene D734-OC. As you can see the amount of vapour suppression by using the soap in washing out hydrocarbons is much better than straight water. This comparison is for water at room temperature.

It should be well noted that washing a confined space with high temperature water will generate 4 – 8 times as much vapour. D734-OC was designed to work at room temperature to avoid this problem.

## SUMMARY

Changing Temperatures combined with a source of ignition is a recurring theme in many reported fires and explosion related to the handling and transportation of hydrocarbons. Whether the hydrocarbon is a produced fluid or a refined product, the behaviour is the same – an increase in temperature can lead to an unexpected change in the pressure and concentration of a hydrocarbon in the gas phase. This when combined with sources of ignition can result in serious fires and explosions.

The risk can be substantially reduced by using a vapour controlling soap in washing out such vessels and cleaning the vessel with water that is at temperature high enough to promote cleaning but still cold enough to reduce the generation of large amounts of vapour. Adequate venting will also reduce but not eliminate the threat of this sort of problem. Paratene® D734OC was specifically designed for this application and should give superior reduction of the risks from hydrocarbon vapours while simultaneously making the cleaning of vessels and tanks more efficient.