PART 1

GENERAL INFORMATION

Chapter 1

BASIC PROPERTIES
OF BULK LIQUIDS

This Chapter describes the physical and chemical properties that have the greatest bearing on the hazards arising from handling bulk liquids. These properties are vapour pressure, the flammability of the gases evolved from the liquids, and the density.

1.1 Vapour Pressure

1.1.1 True Vapour Pressure

All crude oils, petroleum products and chemical products are essentially mixtures of a wide range of different compounds. The boiling points of these compounds range from -162°C (methane) to well in excess of +400°C, and the volatility of any particular mixture of compounds depends primarily on the quantities of the more volatile constituents (i.e. those with a lower boiling point).

The volatility (i.e. the tendency of a product to produce gas) is characterised by the vapour pressure. When a product is transferred to a gas free tank or container, it starts to vaporise, that is it liberates gas into the space above it.

There is also a tendency for this gas to re-dissolve in the liquid, and equilibrium is ultimately reached with a certain amount of gas evenly distributed throughout the space. The pressure exerted by this gas is called the equilibrium vapour pressure of the liquid, usually referred to simply as the vapour pressure.

The vapour pressure of a pure compound depends only upon its temperature. The vapour pressure of a mixture depends on its temperature, constituents and the volume of the gas space in which vaporisation occurs; that is, it depends upon the ratio of gas to liquid by volume.

The True Vapour Pressure (TVP), or bubble point vapour pressure, is the pressure exerted by the gas produced from a mixture when the gas and liquid are in equilibrium at the prevailing temperature. It is the highest vapour pressure that is possible at any specified temperature.

As the temperature of a product increases, its TVP also increases. If the TVP exceeds atmospheric pressure, the liquid starts to boil.

The TVP of a product provides a good indication of its ability to give rise to gas. Unfortunately, this is a property that is extremely difficult to measure, although it can be calculated from a detailed knowledge of the composition of the liquid. Reliable correlations exist for deriving TVP from the more readily measured Reid Vapour Pressure and temperature.

1.1.2   Reid Vapour Pressure

The Reid Vapour Pressure (RVP) test is a simple, and for petroleum products, generally used method for measuring the volatility of bulk liquids. It is conducted in a standard apparatus and in a closely defined way. A sample of the liquid is introduced into the test container at atmospheric pressure, so that the volume of the liquid is one fifth of the total internal volume of the container. The container is sealed and immersed in a water bath where it is heated to 37.8°C. After the container has been shaken to bring about equilibrium conditions rapidly, the rise in pressure due to vaporisation is read on an attached pressure gauge. This pressure gauge reading gives a close approximation, in bars, to the vapour pressure of the liquid at 37.8°C.

RVP is useful for comparing the volatilities of a wide range of products in a general way. It is, however, of little value in itself as a means of estimating the likely gas evolution in specific situations, mainly because the measurement is made at the standard temperature of 37.8°C and at a fixed gas/liquid ratio. For this purpose, TVP is much more useful and, as already mentioned, in some cases correlations exist between TVP, RVP and temperature.

1.2   Flammability

1.2.1   General

In the process of burning, product gases react with the oxygen in the air. The reaction gives sufficient heat to form a flame, which travels through the mixture of product gas and air. When the gas above the liquid is ignited, the heat produced is usually enough to evaporate sufficient fresh gas to maintain the flame, and the liquid is said to burn. In fact, it is the gas that is burning and is being continuously replenished from the liquid.

1.2.2   Explosive Limits

A mixture of product gas and air cannot be ignited and burned unless its composition lies within a range of gas in air concentrations known as the flammable range. The lower limit of this range, known as the Lower Explosive Limit (LEL), is that product concentration below which there is insufficient product gas to support and propagate combustion. The upper limit of the range, known as the Upper Explosive Limit (UEL), is that product concentration above which there is insufficient air to support and propagate combustion.

The explosive limits vary for different products.

1.2.3   Effect of Inert Gas on Flammability

When an inert gas, for example, nitrogen, CO_2 or flue gas, is added to a product gas/air mixture, the result is to increase the Lower Explosive Limit concentration and to decrease the Upper Explosive Limit concentration. These effects are illustrated in Figure 1.1, which should be regarded only as a guide to the principles involved.

Every point on the diagram represents a hydrocarbon gas/air/inert gas mixture, specified in terms of its hydrocarbon and oxygen content. Hydrocarbon gas/air mixtures without inert gas lie on the line AB, the slope of which reflects the reduction in oxygen content as the hydrocarbon content increases. Points to the left of the line AB represent mixtures with their oxygen content further reduced by the addition of inert gas.

The lower and upper flammability limit mixtures for hydrocarbon gas in air are represented by the points C and D. As the inert gas content increases, the explosive limit mixtures change as indicated by the lines CE and DE, which finally converge at the point E. Only those mixtures represented by points in the shaded area within the loop CED are capable of burning.

On this diagram, changes of composition due to the addition of either air or inert gas are represented by movements along straight lines directed either towards the point A (pure air), or towards a point on the oxygen content axis corresponding to the composition of the added inert gas. Such lines are shown for the gas mixture represented by the point F.

It is evident from Figure 1.1 that, as inert gas is added to product gas/air mixtures, the flammable range progressively decreases until the oxygen content reaches a level, generally taken to be about 11% by volume, when no mixture can burn. The figure of 8% by volume of oxygen, specified in this Guide for a safely inerted gas mixture, allows a margin beyond this value.

When an inerted mixture, such as that represented by the point F is diluted by air, its composition moves along the line FA and therefore enters the shaded area of flammable mixtures. This means that all inerted mixtures in the region above the line GA go through a flammable condition as they are mixed with air, for example, during a gas freeing operation.

Those mixtures below the line GA, such as that represented by point H, do not become flammable on dilution. It should be noted that it is possible to move from a mixture such as F to one such as H by dilution with additional inert gas (i.e. purging to remove hydrocarbon gas).
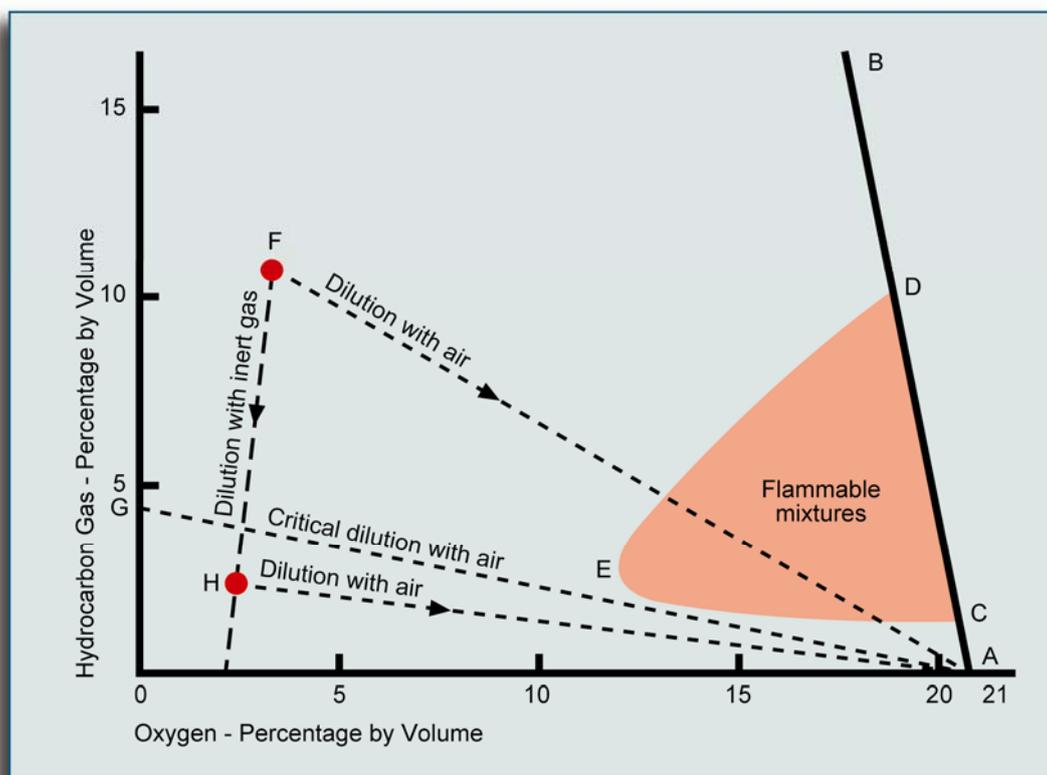
Insert Figure 1.1 – Flammability composition diagram

1.2.4   Tests for Flammability

Since product gas/air mixtures are flammable within a comparatively narrow range of concentrations of product gas in air, and concentration in air is dependent upon vapour pressure, in principle, it should be possible to evolve a test for flammability by measuring vapour pressure. In practice, the very wide range of petroleum products, and the range of temperatures over which they are handled, has prevented the development of one simple test for this purpose.

Instead, the oil industry makes use of two standard methods. One is the Reid Vapour Pressure test (see Section 1.1.2) and the other is the flashpoint test, which measures flammability directly. However, with some residual fuel oils, it has been shown that the flashpoint test will not always provide a direct indication of flammability (see Section 2.7).

1.2.5   Flashpoint

In this test, a sample of the liquid is gradually heated in a special pot and a small flame is repeatedly and momentarily applied to the surface of the liquid. The flashpoint is the lowest liquid temperature at which the small flame initiates a flash of flame across the surface of the liquid, thereby indicating the presence of a flammable gas/air mixture above the liquid.

For all oils, except some residual fuel oils, this gas/air mixture corresponds closely to the Lower Explosive Limit mixture.

There are many different forms of flashpoint apparatus but they fall into two classes. In one, the surface of the liquid is permanently open to the atmosphere as the liquid is heated and the result of such a test is known as an 'open cup flashpoint'. In the other class, the space above the liquid is kept closed except for brief moments when the initiating flame is introduced through a small port. The result of this class of test is termed a 'closed cup flashpoint'.

Because of the greater loss of gas to atmosphere in the open cup test, the open cup flashpoint of a petroleum liquid is always a little higher (by about 6°C) than its closed cup flashpoint. The restricted loss of gas in the closed cup apparatus also leads to a much more consistent result than can be obtained in open cup testing. For this reason, the closed cup method is now more generally favoured and is used in this Guide when considering the classification of petroleum. However, open cup test figures may still be found in the legislation of various national administrations, in classification society rules and other such documents.

1.2.6   Flammability Classification

There are many schemes for dividing the complete range of bulk liquids into different flammability classes based on flashpoint and vapour pressure and there is a considerable variation in these schemes between countries. Usually, the basic principle is to consider whether or not a flammable equilibrium gas/air mixture can be formed in the space above the liquid when the liquid is at ambient temperature.

Generally, in this Guide, it has been sufficient to group bulk liquids into two categories entitled non-volatile and volatile, defined in terms of flashpoint as follows:

Non-volatile

Flashpoint of 60°C or above, as determined by the closed cup method of testing. These liquids produce, when at any normal ambient temperature, equilibrium gas concentrations below the Lower Explosive Limit. They include distillate fuel oils, heavy gas oils and diesel oils. Their RVPs are below 0.007 bar and are not usually measured.

Volatile

Flashpoint below 60°C, as determined by the closed cup method of testing. Some petroleum liquids in this category are capable of producing an equilibrium gas/air mixture within the flammable range when in some part of the normal ambient temperature range, while most of the rest give equilibrium gas/air mixtures above the Upper Explosive Limit at all normal ambient temperatures.

The choice of 60°C as the flashpoint criterion for the division between non-volatile and volatile liquids is to some extent arbitrary. Since less stringent precautions are appropriate for non-volatile liquids, it is essential that under no circumstances is a liquid capable of giving a flammable gas/air mixture ever inadvertently included in the non-volatile category. Therefore, the dividing line must be chosen to make allowance for such factors as the misjudging of the temperature, inaccuracy in the flashpoint measurement and the possibility of minor contamination by more volatile materials. The closed cup flashpoint figure of 60°C makes ample allowances for these factors and is also compatible with the definitions adopted internationally by IMO and by a number of regulatory bodies throughout the world.

1.3   Density of Hydrocarbon Gases

It is important to know if the density of a gas is greater or smaller than the density of air. If the gas density is higher than the density of air, the gas will spread over the bottom of a compartment or, in a terminal, stay close to the ground. In cargo handling operations, layering effects can be encountered and may give rise to hazardous situations.

Table 1.1 gives gas densities relative to air for a few products.

Gas	Density relative to air		
	Pure hydrocarbon	50% by volume hydrocarbon/ 50% by volume air	Lower Explosive Limit mixture
Propane	1.55	1.25	1.0
Butane	2.0	1.5	1.0
Pentane	2.5	1.8	1.0

Table 1.1 – Propane, butane and pentane; densities relative to air:

High densities, higher than air, and the layering effects that result from them, are only significant while the gas remains concentrated. As it is diluted with air, the density of the gas/air mixture from all three types of cargo approaches that of air and, at the Lower Explosive Limit, is indistinguishable from it.

1.4   Corrosiveness

Tanks, pipelines, hoses and associated equipment, such as pumps, gaskets, instruments and fittings, must be made of materials which either:

- have good mechanical and chemical resistance against the bulk cargo, or
- have a suitable coating to protect against the properties of the bulk cargo.