Issued under the authority of the Home Office
(Fire and Emergency Planning Directorate)

Fire Service Manual
Volume 2
Fire Service Operations

Petrochemical Incidents
Preface


The guidance provided in this book replaces and updates, as appropriate, information previously published on Petrochemicals and provides additional information regarding Liquefied Natural Gas.

Safety is of paramount importance. The need for the consideration and implementation of suitable measures, as outlined in the 'Fire Service Guides to Health and Safety' (see 'Further Reading'), should always be borne in mind by all personnel when attending operational incidents.
# Petrochemical Incidents

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## 8.3 How Explosions Develop from Initial Low Velocity Flames

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Oil refining in Britain is a major industry. It is a development of the post war era, mainly as a direct result of the economic situation in which Britain found itself after the Second World War and of the enormously increased use of oil which the war itself and the years of reconstruction after it brought about. Up to that time, over three quarters of the oil used in Britain was imported and stored in the form of finished refined products. It was refined mainly in the United States of America and oil companies in Britain shipped in the products the market needed, the petrol, lubricating oils, diesel fuel, aviation fuel, fuel oil and so on.

By the middle forties, however, shortage of dollars, shortage of refining capacity in the western hemisphere, and the fact that the main supplier, America, was becoming a net importer of oil had made it necessary to change this pattern. One further factor was important; the great oilfields of the middle east were then opening up. This was crude oil which could be obtained predominantly for sterling. The decision was therefore taken for Britain to have its own refineries, drawing their supplies of crude oil mainly from the middle east. The refineries were built by the major oil companies operating in Britain at the time.

Early in the 1960s came the discovery of rich oil and gas reservoirs in the North Sea, with oil companies pooling their financial, technical and managerial resources, in the United Kingdom sector of the North Sea. The first major United Kingdom oil find came in November 1970 in the central North Sea when British Petroleum discovered the Forties Field. This was a major field by world standards. The United Kingdom had suddenly arrived as an oil producer. It was the Shell/Exxon joint operation which in 1971 pioneered the search for oil into the northern North Sea. The emerging North Sea oil industry offered a secure source of supply and a vision of some improvement in economic conditions. The United Kingdom was not only fortunate in the abundance of its new found oil wealth but it was also fortunate in the type of oil discovered. Crude oils from the North Sea generally yield a higher proportion of light oils and hence command premium prices in the world crude oil markets. With such a price outlook, massive investments were necessary to bring the oil and gas ashore with the building of large oil production platforms and receiving terminals at Sullom Voe and separation plant at St Fergus on the Scottish mainland.

The function of a refinery is to convert crude oil into a series of oil products in amounts that keep pace with the demands of society. These demands have varied over the years, reflecting changes brought about by a variety of factors such as the relative costs of fuels, a heightened awareness of the need to protect the environment and the adoption of new technologies. For example, in recent years there has been a decline in the demand for heating and fuel oils caused by a move away from oil fired power stations, industrial boilers and domestic oil heating. At the same time there has been an increase in demand for petrol, diesel and aviation fuels.

Refineries have responded to these changes by modifying existing processes and developing new ones, in order to produce less heating and fuel oils and more petrol, diesel and aviation fuels, thus refinery outputs match the market demands.

Oil has many uses: it is an illuminant which is how it started to be used, a lubricant or the raw materials of thousands of chemicals, plastics, man made fibres and detergents. Its greatest importance however is that it is a source of energy.
In the oil producing countries, crude oil is brought by pipeline from the oil wells, to the coast and stored in huge storage tanks. The oil is then pumped aboard oil tankers and transported to oil refineries at destinations round the globe. Powerful ships pumps often unload the crude oil at a rate of 12,000 tons (tonnes) per hour into storage tanks, usually external floating roof tanks, some capable of receiving in excess of 20 million gallons (90,000 cubic metres) or in some cases, large tankers (VLCCS) lying offshore may have to transfer crude oils into smaller tankers first. Once received in the refinery the oil is now ready to be processed.

1.1 General Characteristics

1.1.1 Vapour Formation

Petroleum oils at temperatures below their boiling point vaporise only at the surface and in the presence of a vapour space. If the liquid is contained in a closed vessel, vaporisation will occur until the vapour space is saturated at that particular temperature, i.e., until the space contains such a concentration of the vapour that condensation occurs at the same rate as vaporisation. When this condition obtains, the liquid and the vapour are said to be in equilibrium. The vapours produced tend to mix more or less readily with air or other gases in the vapour space, and if they are left alone, the space will eventually contain a homogeneous mixture of all the gases contained in it. This tendency of gases to mix is called diffusion. The tendency of liquids to vapourise takes place more quickly with some liquids than others. For instance, a small quantity of ether will vapourise almost immediately when exposed to air; petrol requires a longer time, whilst water will take longer still. This tendency of a liquid to vapourise is called its volatility.

A gas (or vapour) with wide limits of flammability is potentially more dangerous than one which has a narrow flammable range.

1.1.2 Flammable Limits

It is the vapour which is given off from a flammable liquid that burns when combined with oxygen from the air, and oil which is not vaporising, or has no vapour space above it, cannot burn. Moreover, the air and vapour must be in certain proportions in order to burn. The concentration varies for different vapours; for instance the flammability range of petrol vapour in air is between 1.4 - the lower limit - and 5.9 - the upper limit, per cent of petrol vapour by volume; i.e., petrol vapour requires a maximum of 98.6 per cent and a minimum of 94.1 per cent of air to support combustion. The flammable limits of some hydrocarbon compounds and petroleum liquids, i.e., mixtures of hydrocarbon compounds are given in Table 1.1. Hydrogen is included, as it is a regular by-product and is present in refineries and chemical plants in large quantities and is particularly hazardous, together with one or two other extremely dangerous substances.

A gas (or vapour) with wide limits of flammability is potentially more dangerous than one which has a narrow flammable range.

It is interesting to compare the flammable limits of the compounds in Table 1.1 with those of hydrogen - which are 4.1 to 74 per cent by volume.
The temperature at which this will occur is called the auto-ignition temperature (sometimes it is called the self-ignition temperature). This is the lowest temperature to which a solid, liquid or gas requires to be raised to cause self-sustained combustion without initiation by a spark or flame.

If, for example, some petrol vapour which is leaking and is diluted with air to within its flammable range, comes into contact with a source of heat such as hot brickwork or pipes which are above 246°C then ignition will occur automatically.

This is why if a non-cooling extinguishing, such as chemical dry powder, is used on a petrol fire, the flame may be quenched; but if there is an incandescent source of ignition or sufficient residual heat build-up, the vapour will almost immediately reignite if application of extingushant is discontinued, before cooling by water spray or blanketing with foam is commenced.

The approximate self-ignition temperature of some hydrocarbon compounds is given in Table 1.2. Hydrogen is again included for comparison.

1.1.4 Safe Dilution Point

Most petroleum vapours are heavier than air and will travel considerable distances following contours of the ground, depending on wind strength and direction. The further the vapours travel from the point of escape, the more the vapours will be diluted with air until the volume of air will cause the mixture to become outside the flammable limit. The safe dilution point for petroleum vapour is generally accepted as 50ft (15m) from the source of emission, but in assessing the safety margin, the wind and prevailing conditions MUST be considered. Any heavy emission of vapour could, in favourable downwind circumstances, dilute at a greater distance than this, spreading over a wide area to a vapour to air ratio within the flammable range. If such a vapour cloud flashes over, the flame will propagate very rapidly over the whole of the vapour trail back towards the source of leak, and may cause a number of fires in its path.

1.1.6 Toxicity

Apart from the flammability of petroleum oils, another important hazard is toxicity. The nature of the toxic hazards arising from hydrocarbons depends on the composition of the fraction, and the important fractions are hydrocarbon gases containing benzene and heavy aromatic oils. Air containing only 0.1 per cent by volume of hydrocarbon vapour can cause irritation to the nose, ears and throat; heavier concentrations can cause dizziness and unconsciousness. A 0.5 per cent concentration could prove fatal.

Petroleum fractions containing benzene are those present in petrol. Benzene has a destructive effect on blood-forming organs, which occurs on repeated exposures to low concentration. Vapour inhalation should be prevented altogether. Heavy aromatic oils, which are encountered in the catalytic cracking plant, hydroformer and chemical plants, are dangerous, especially in contact with the skin. As a method of identification, lines and equipment containing aromatic products are sometimes marked with coloured bands.

Hydrogen sulphide (or sulphur pungent hydrogen), which is to be found in fresh crude oil, sulphur plants and polymerisation processes, is extremely toxic and is highly corrosive in contact with metals. It can be easily recognised by its offensive smell of rotten eggs, and will tend to paralyse the olfactory nerves.

It is important to realise that this gas can create a false sense of security through the effect of paralysing the sense of smell. Sulphur dioxide is another extremely toxic gas produced in the sulphur plants.

### Table 1.1

<table>
<thead>
<tr>
<th>Flammable limits in air.</th>
<th>Explosive limits* (per cent in air)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower</td>
</tr>
<tr>
<td>Methane (gas)</td>
<td>5.0</td>
</tr>
<tr>
<td>Ethane (gas)</td>
<td>3.0</td>
</tr>
<tr>
<td>Propane (gas)</td>
<td>2.4</td>
</tr>
<tr>
<td>Butane (gas)</td>
<td>1.5</td>
</tr>
<tr>
<td>Pentane (liquid)</td>
<td>1.4</td>
</tr>
<tr>
<td>Hexane (liquid)</td>
<td>1.2</td>
</tr>
<tr>
<td>Heptane (liquid)</td>
<td>1.2</td>
</tr>
<tr>
<td>Petrol</td>
<td>1.4</td>
</tr>
<tr>
<td>Petroleum naphtha</td>
<td>1.1</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.7</td>
</tr>
<tr>
<td>Hydrogen (gas)</td>
<td>4.1</td>
</tr>
<tr>
<td>Methyl ethyl ketone (solvent)</td>
<td>1.8</td>
</tr>
<tr>
<td>Acetone (solvent)</td>
<td>2.5</td>
</tr>
<tr>
<td>Forfin (solvent)</td>
<td>2.1†</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2.7</td>
</tr>
<tr>
<td>Acrylne (gas)</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* Slight variations in these limits may be found according to the grade of the particular petrol, naphtha or kerosene.
† Decomposes rapidly above this limit.

### Table 1.2

<table>
<thead>
<tr>
<th>Self-ignition temperatures.</th>
<th>Degrees centigrade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, CH₄</td>
<td>538</td>
</tr>
<tr>
<td>Ethane, C₂H₆</td>
<td>514</td>
</tr>
<tr>
<td>Propane, C₃H₈</td>
<td>466</td>
</tr>
<tr>
<td>Butane, C₄H₁₀</td>
<td>450</td>
</tr>
<tr>
<td>Pentane, C₅H₁₂</td>
<td>309</td>
</tr>
<tr>
<td>Hexane, C₆H₁₄</td>
<td>234</td>
</tr>
<tr>
<td>Heptane, C₇H₁₄</td>
<td>223</td>
</tr>
<tr>
<td>Octane, C₈H₁₈</td>
<td>212</td>
</tr>
<tr>
<td>Nonane, C₉H₂₀</td>
<td>206</td>
</tr>
<tr>
<td>Petrol</td>
<td>246</td>
</tr>
<tr>
<td>Kerosene</td>
<td>254</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>378/416</td>
</tr>
<tr>
<td>Fuel oil (Nos. 3 to 6)</td>
<td>269/407</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>245</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>585</td>
</tr>
</tbody>
</table>

Petrochemical Incidents


1.2 Classification of Crude Oil and its Derivatives

Crude oil and its derivatives are potentially hazardous materials. The degree of the hazard is characterised essentially by volatility and flash point.

Classification of these materials by the Institute of Petroleum, based (except for liquefied petroleum gases: L.P.G.) on closed cup flash points, is as follows:

CLASS 0 Liquefied Petroleum Gases.

CLASS 1 Liquids which have flash points below 21°C.

CLASS 2 (a) Liquids which have flash points from 21°C up to and including 55°C handled below flash point.

CLASS 2 (b) Liquids which have flash points from 21°C up to and including 55°C handled at or above flash point.

CLASS 3 (a) Liquids which have flash points above 55°C up to and including 100°C handled below flash point.

CLASS 3 (b) Liquids which have flash points above 55°C up to and including 100°C handled at or above flash point.

Unclassified: Liquids which have flash points above 100°C.

1.2.1 Class 1 Liquids

Liquids which have flash points below 21°C.

Included in this classification are the following petroleum spirits:

- L.N.G. (methane and ethane)
- Heptane
- Aviation spirit
- Benzene
- Coal tar naphtha
- Crude petroleum
- Heptane
- Liquefied natural gas (L.N.G.) and liquefied petroleum gas (L.P.G.)

Liquefied petroleum gases are completely unrelated to other natural petroleum liquids. Special care should be taken with L.N.G. and L.P.G. as, within their explosive limits in the presence of air, they will flash whenever there is any source of ignition present. There are many other flammable liquids, especially solvents such as acetone, methyl ethyl ketone, which should be included in any CLASS 1 listing.

Liquids in Class 1 have very low but varying flash points and the greatest caution should be exercised when they are in the presence of air.

1.2.2 Class 2 Liquids

Liquids which have a flash point from 21°C up to and including 55°C referred to as medium oils; they always present an element of danger, especially in hot weather. Jet fuel (kerosene), white spirit (turpentine) substitute and tractor vaporising oils are included in this class.

1.2.3 Class 3 Liquids

Liquids which have flash points above 55°C include gas oils, diesel oils, heavy fuel oils and bitumen. These oils will not give rise to a flammable vapour mixture unless they are heated and brought to a temperature above their flash point, which in some cases may be as high as 260°C. However, the difference between flash point and auto-ignition is much less with the heavier oils than with lighter oils. Under normal conditions, a dangerous vapour atmosphere will not exist inside a tank holding a CLASS 3 liquid, and it is only when such tanks are subjected to heat from some external source, such as radiated heat or direct flame impingement that they can present a fire hazard.

Crude oils vary greatly in their characteristics, as the term ‘crude’ is used to define petroleum in its natural state as taken from the earth. Crude oil can range from an extremely light liquid to a very heavy product. Accordingly they are hard to classify and require further refining. Secondly, the proportions of the different fractions produced by primary distillation do not match the demand for them.

2.1 Crude Oil

The exact composition of crude oil varies depending on its source. Samples from different locations may vary in colour and in physical properties such as density. The thousands of different hydrocarbons which are found together in crude oil can conveniently be classified into three groups:

- ALKANES
- NAPHTHENES
- AROMATICS

2.1.1 Other compounds

Crude oil may contain anything from one per cent to seven per cent of sulphur compounds. These compounds include hydrogen sulphide (H₂S), thials, disulphides and thionepine. Compounds of nitrogen and oxygen are present in much smaller but still significant quantities, around 0.1 per cent would be typical for nitrogen compounds.

Salt water and sand are two of the most commonly encountered impurities found in crude oil. They get into the crude oil during its formation.

2.2 The Refiner’s Task

The petroleum refiner has two aims. He must make products which meet the high quality specifications of today’s markets, and he must produce the right proportion of each product from the crude oil so that nothing is left over or wasted. To achieve these objectives the refiner uses four main types of process. A separation process can be used, such as ‘distillation’ to split the crude oil into groups of compounds, or even to separate one particular compound from another. It may, however, be necessary to change one sort of compound into another in order to obtain the correct balance of production. This the refiner can do with conversion processes, breaking large molecules into smaller ones by ‘cracking’, building small molecules into larger ones by ‘polymerisation’, or converting low grade raw petrol into high quality motor spirit by ‘polymerisation’, or converting low grade raw petrol into high quality motor spirit by ‘reforming’.

The refiner may have to remove product impurities or render them harmless: examples of the type of processes used are ‘hydrofining’ and chemical sweetening. Finally, there are many other processes, such as the blending of products, the manufacture of special products, such as bitumen, and the production of lubricating oils by solvent extraction.

The first stage of refining is primary distillation. Crude oil is heated to a temperature at which most of it is vaporised. The vapour rises up a tall tower within which there is a temperature gradient. The temperature decreases towards the top allowing different components to condense and be collected at different levels.

Primary distillation separates hydrocarbons into a series of fractions. These are groups of hydrocarbons which have similar boiling points. Although the process provides an initial separation, there are two shortcomings associated with the fractions produced. Firstly, most of the fractions which are destined to become products are not at the level of quality which is needed and require further refining. Secondly, the proportions of the different fractions produced by primary distillation do not match the demand for them.
In general there is an excess of fuel oil and a shortage of the naphtha fraction required for petrol and chemical feedstocks.

2.3 The Refining Processes

2.3.1 Primary distillation

Crude oil is a mixture of hydrocarbons which have boiling points ranging from around 20°C to well above 350°C.

At the start of primary distillation crude oil is heated to around 360°C in a furnace. At this temperature most of the hydrocarbons are converted to gases. The resulting mixture of liquid and gas passes from the furnace into the bottom of a fractionating tower operating near atmosphere pressure, (atmospheric pipestill Figure 2.1). The tower has about 40 trays over which liquid flows and descends, passing from tray to tray since there is a temperature gradient through the tower. The boiling point range of the liquid in the trays becomes progressively higher, and thus the liquid is progressively hotter, passing down the tower.

As hydrocarbon gases rise up the tower they flow through devices which cause them to be thoroughly mixed with the down-flowing liquid. Both bubble caps and jet trays are used along with other mixing devices. Each tray in the tower contains 2–3in (51–76mm) of liquid. The fractionating tower is heated at the bottom by the hot oil vapour and liquid which enter. By removing some of the liquid from the top of the tower, cooling it and then re-introducing it, the upper part of the tower is cooled to about 93°C. In this way the temperature gradient is obtained.

The intimate mixing of gas and liquid means that when a hydrocarbon reaches a tray where the liquid is below its boiling point, the gas condenses. In condensing, the gas heats the liquid which is already close to its boiling point. This causes some of the more volatile constituents of the liquid to evaporate and join the remaining gases rising up the tower. This process goes on in each tray. The result is that each tray holds a "close cut" of product: a mixture which has a comparatively narrow range of boiling points.

By adjusting such variables as the temperature of the crude oil feed and the temperature range in the fractionating tower, and by altering the amount and temperature of the liquid fed back down the tower, the distillation conditions can be controlled to give optimum "cuts" of each product.

The major fractions produced from primary distillation are:

- **Gases** from the top of the tower. Some are used as fuel in the refinery while the remainder are liquefied.
- **Naphthas** used for blending into petrol or as chemical feed stock.
- **Kerosenes** which are the basis of aviation fuel.
- **Gas oils** for diesel fuel production.
- **Heavy gas oils** which provide the feedstock for catalytic cracking.

At the bottom of the fractionating tower, the less volatile liquid passes out of the lowest tray and combines with the liquid remainder from the crude oil to form a residue of high boiling point (>400°C) hydrocarbons. The atmospheric residue passes through a furnace, where it is heated to 400°C, and into a second fractionating tower where distillation is carried out under a partial vacuum (Vacuum pipestill Figure 2.2). Lowering the pressure reduces the boiling points of the hydrocarbons in the liquid, which allows them to be distilled below the temperature at which thermal decomposition would occur. Fractions obtained from vacuum distillation provide the feedstock for catalytic cracking and lubricating oil production.
2.3.2 Catalytic Cracking

Cracking is a conversion process which breaks large oil molecules into smaller ones. One such process is in "cracking" a heavy gas oil feed to form high grade petrol and gas. One process used is known as "fluid catalytic cracking". "Catalytic" because a chemical substance called a catalyst is used (this helps the cracking reaction without being changed itself) and 'fluid' because the catalyst in powder form can be made to behave like a liquid when it is blown with air or hydrocarbon.

Heavy gas oil feedstock is sprayed in to meet a stream of red hot catalyst from the regenerator; the hot catalyst vaporises the oil and the vapourised oil fluidises the catalyst. Both flow into the reactor where cracking takes place at a temperature of 500°C. The cracked oil vapours pass to a fractionating tower in which the small molecules of petrol and gas formed by cracking are separated from the heavier and unconverted products and in the distillation process.

Further fractionation separates the petrol from the light gases which are used for refinery fuel, fed to a polymerisation plant, or used to make chemical feedstocks.

During cracking, catalyst particles become coated with a layer of carbon which prevents them from taking any further part in the reaction. Carbon-coated catalyst particles are circulated from the reactor to the regenerator where the carbon coating is burned off in an air blast at around 725°C.

The clean catalyst which is recycled to the reactor vessel carries sufficient heat to vaporise the hydrocarbon feedstock and sustain the cracking process.

2.3.3 Polymerisation

Cracking produces an excess of some small hydrocarbon molecules. Polymerisation is the reverse of cracking; building up small molecules into larger ones. Feedstock for the polymerisation plant contains mostly propenes and butenes, the light gases produced by the catalytic cracking plant are combined to produce heavier materials like butane and a further supply of high quality petrol.

Before polymerisation takes place the level of sulphur compounds in the feedstock must be reduced to avoid damaging the chemical catalyst used in the process. Polymerisation takes place at a temperature of 200°C under a high pressure of around seven megapascals in the presence of phosphorous V acid catalyst. A polymerisation plant may produce as much as 1000 tons (1016 tonnes) a day producing:

- Liquefied petroleum gas (L.P.G.) – which is sold
- Heptenes – which are used to make plasticisers

Fuel oil – which is blended into other fuel oils
A mixture of C₃ and C₄ hydrocarbons – which is further separated in the recovery plant on the chemical sites.

2.3.4 Reforming

A high quality petrol is one which burns smoothly without 'knocking'. This is determined not just by the size of the hydrocarbon molecules present but also by their shape.

Reforming is concerned with increasing the anti-knock value of petrol components. It is a process by which the shape rather than the size of an oil molecule is changed in order to improve product quality. The feedstock for reforming is heavy naphtha obtained from primary distillation. The naphtha feedstock is first treated in a hydrofiner to remove any sulphur compounds. After hydrofining, a mixture of hydrogen, hydrogen sulphide and any light products formed during hydrofining is separated from the naphtha. This mixture still contains 70 per cent hydrogen and is called treat gas which is used on other process plants. The hydrofinned naphtha feedstock is then preheated to around 500°C before being fed into a series of reactors operating at high pressure and in the presence of...
2.3.5 Sulphur Recovery

Crude oil contains a variable, but significant proportion of sulphur compounds. These tend to be concentrated in the heavy fractions such as fuel oils. Sulphur compounds must be removed before certain processes, such as reforming and isomerisation take place, if left, such compounds would damage the catalysts used in these processes causing a decrease in efficiency. From an environmental point of view, any such compounds present in a fuel would be converted to sulphur dioxide during combustion, this acid gas causes damage to steel engine parts and when released in exhaust gas dissolves readily in moisture thus contributing to increased acidity in the atmosphere.

The main sulphur treatment processes involves three separate stages:

- **Liquefied petroleum gas (L.P.G.)** – which is sold.
- **High grade heavy naphtha** – for petrol blending.
- **Sulphur recovery** – where hydrogen sulphide is oxidised to sulphur.

The poisonous hydrogen sulphide from the hydrofiners is burned in a controlled reaction furnace with a limited amount of air to form sulphur. Some refineries may produce as much as 100 tonnes of pure elemental sulphur per day. This is a valuable by-product sold on in liquid form to industries for use in vulcanisation of rubber and the manufacture of sulphuric acid.

2.3.6 Residfining

Residfining is a new process development to remove impurities from fuel oil so that it can provide more feedstock for catalytic cracking. The value of fuel oil is relatively low since the amounts obtained from other refining processes exceed demand. Its value can be increased by cracking the fuel oil to produce smaller molecules such as those found in petrol.
However, fuel oil cannot be fed directly from vacuum distillation into a cracking plant because it contains impurities which would damage the catalyst. These impurities include compounds containing sulphur, nitrogen or metals (such as nickel and vanadium) and large unsaturated hydrocarbon molecules which tend to form coke when cracked.

In a residfiner these impurities are reduced and large coke forming molecules are hydrogenated to reduce the degree of unsaturation. This is achieved by forcing hydrogen gas, at high pressure into the fuel oil in the presence of a catalyst at temperatures up to 400°C. Sulphur compounds are converted to hydrogen sulphide and nitrogen compounds to ammonia, while heavy metal impurities are held on the catalyst.

Hydrogen sulphide and ammonia are separated from the reaction mixture and passed on to the sulphur treatment plant. The remaining mixture of hydrocarbons passes into a fractionating column for separation to yield gases, which are fed into the refinery fuel gas system, naphtha is used in petrol blending, and gas oil which is blended with gas oil from the primary distillation process. The final product 'Residolate' which remains, passes to the catalytic cracking plant.

### 2.3.7 Isomerisation

Isomerisation, like reforming, is concerned with improving the quality of petrol by changing the shape of the hydrocarbon molecules. The quality of petrol is indicated by the smoothness with which it burns in an engine. Prior to the development of unleaded petrols, chemical 'anti-knock' agents such as tetraethyl lead were added to all petrols to ensure efficient burning. Isomerisation provides an alternative way of improving the quality of petrol which avoids the use of potentially harmful LEAD compounds.

Feedstock for isomerisation is light naphtha obtained from primary distillation. Hydrofining is required to convert sulphur compounds into hydrogen sulphide to avoid damaging the chemical catalyst. Following hydrofining more hydrogen is added and the reaction mixture is heated to 260°C and fed into a reactor at a pressure of around 1.87 million pascals.

After reaction, the product mixture is separated into two streams, one of hydrocarbons and the other of hydrogen. Further processes and separation result in the production of:

- Liquefied petroleum gas (L.P.G.) – which is sold
- High grade light naphtha – which is used for petrol blending.

### 2.3.8 Lubricating Oil Treating

The lubricants plant is concerned with the manufacture of base stocks which are used in the production of a range of lubricants. Feedstocks for basestock manufacture are obtained from the vacuum distillation of the primary distillation residue. Careful control of the vacuum distillation produces a series of fractions of differing viscosity which, after further treatment provide a complete range of high and low viscosity lubricant basestocks.

The viscosity index is a measure of the viscosity/temperature properties and oxidation stability of an oil; the higher the viscosity index (V.I.) the less the viscosity changes with temperature. This is a particularly important characteristic since oils which have a high viscosity index thin out less when heated to the running temperature of internal combustion engines, and thicken less when cold under starting conditions. Each feedstock contains a mixture of alkanic, naphthenic and aromatic components which
Coloured unsaturated hydrocarbons are reduced to their sulphur compounds present. Dark to the catalytic cracking plant. After solvent stripping, this product stream passes to a hydrofiner where it is mixed with hydrogen at high pressure. This improves the colour and stability of aromatic compounds passes to another solution of aromatic compounds passes to another recovery unit where ketone is removed and recycled, while the aromatic compounds are fed to the catalytic cracking plant.

If left in the feedstocks would adversely affect the viscosity temperature properties and oxidation stability of oil products, so they are removed by solvent extraction. The feedstock is mixed with solvent in a countercurrent extraction tower. The solution of aromatic compounds passes to another section of the plant where the solvent is recovered and recycled, while the aromatic compounds are fed to the catalytic cracking plant.

After solvent stripping, this product stream passes to a hydrofiner where it is mixed with hydrogen at high pressure. This improves the colour and stability of the final lubricant basestock. The wax content is reduced by mixing the stream with ketone solvent and gradually reducing the temperature of the resulting solution by passing it through a series of heat-exchangers and chillers. More and more wax crystallises out as the temperature is lowered. The cold slurry is fed into large rotary filters where the wax is separated from the ketone solution. Oil and ketone pass to a recovery unit where ketone is removed and recycled.

It is necessary to reduce the wax content of the product stream in order to improve the low-temperature properties of the final lubricant basestock. The wax content is reduced by mixing the stream with ketone solvent and gradually reducing the temperature of the resulting solution by passing it through a series of heat-exchangers and chillers. More and more wax crystallises out as the temperature is lowered. The cold slurry is fed into large rotary filters where the wax is separated from the ketone solution. Oil and ketone pass to a recovery unit where ketone is removed and recycled.

More saturated ones which are lighter in colour. Sulphur compounds are reduced to hydrogen sulphide and recovered.

Sulphur compounds are reduced to hydrogen sulphide and recovered.

The process is carried out in a cracking furnace at high pressure and high temperature (770°C) in the presence of steam. Naphtha or gas oil feedstock is used for the regular grade. In both cases, feedstream is fed through a bubble tower and heated by means of a furnace coil passing into the coke drums. A solid coke which is formed by polymerisation and condensation reaction, settles out and has to be removed from the drums by pumps using a conventional high pressure water drilling rig at a pressure of approximately 3,000 psi (207 bars).

The coke lumps are then mechanically crushed and fed into a calciner kiln. These kilns are brick lined, sloping steel cylinders, 230ft (70m) long and 12ft (3.8m) in diameter, and rotate at three revolutions per minute. They are fired by fuel gas at the end opposite the coke fed-in. All volatiles contained within the coke are burned off as the product passes through the kiln. After the coke leaves the kiln it is water cooled and mechanically handled for loading into specially designed road or rail transportation to customers.

Fire hazards regarding the end product are negligible, but due to the very high temperatures involved during production, a potential fire hazard always exists.

2.4 Calcined Coke

Calcined coke, commonly known as petroleum coke, was once a small by-product of petroleum refining. Because of present day demands, and the product's versatility for use in the manufacturing of electrodes in the production of aluminium and steel, one major refinery in Britain has a large coking plant.

This coke must not be confused with coke produced as a by-product of coal. There are two types of calcined coke; 'regular' and 'premium'. The 'regular' coke is produced primarily for the manufacture of electrodes in the production of aluminium, and 'premium' for the manufacture of electrodes in the production of steel in electric arc furnaces. Two separate but similar units are used, the difference being in the initial liquid feedstock to the coke drums.

A liquid stream consisting primarily of 'thermal tar' is used for premium coke and a liquid stream of 'topped crude' is used for the regular grade. In both cases, the feedstream is fed through a bubble tower and heated by means of a furnace coil passing into the coke drums. A solid coke which is formed by polymerisation and condensation reaction, settles out and has to be removed from the drums by pumps using a conventional high pressure water drilling rig at a pressure of approximately 3,000 psi (207 bars).

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Fire hazards regarding the end product are negligible, but due to the very high temperatures involved during production, a potential fire hazard always exists.

Water should only be used as a last resort, steam normally being utilised in all cases of fire.

2.5 Manufacture of Chemicals

The manufacture of chemicals is an important aspect of the oil business and continues to grow. More than 70 per cent of all the organic chemicals made in this country have an oil base. Polythene, detergents, man made fibres for house furnishings and clothing, synthetic rubbers, building materials, tyres, paints, stockings, anti-freeze; these are just some of the innumerable every day products which emanate from petroleum chemicals. At most refineries, chemical feedstocks such as ethylene and butadiene are produced, from which many of these end products are derived.

2.5.1 Steam Cracking

The steam cracking plant is concerned with breaking large hydrocarbon molecules, from the naphtha or gas oil feedstocks, into smaller alkene and diene molecules for the use in the manufacture of plastics, rubbers and other chemicals. The choice between the use of naphtha or gas oil as a feed stock depends on cost and availability.

The process is carried out in a cracking furnace at low pressure and high temperature (770°C) in the presence of steam. Naphtha or gas oil feedstock, is preheated and mixed with steam before passing into the cracking furnace. In the furnace, the long chain hydrocarbon molecules are cracked into shorter chain molecules from which many of these end products are derived.

- A mixture of hydrocarbons of low molecular mass. Although the main product is ethene, the mixture also contains large amounts of propene and smaller amounts of C-4 hydrocarbons, (butane-butenes, 2-methyl-propene, buta-1,3-diene) hydrogen, methane, ethane and alkylnes.

Water should only be used as a last resort, steam normally being utilised in all cases of fire.
The ethane feedstock contains carbon dioxide which must be removed before ethane is cracked, so that it does not remain in the ethene product. If it was not removed at this stage it would solidify at the low temperatures at which ethane is stored.

At Mossmorran, ethene is produced from the steam cracking of ethane. The source of the ethane feedstock is natural gas liquids (N.G.L.) from the North Sea. Following the removal of methane, the remaining gas liquids pass to an N.G.L. separation plant. From here, purified ethane feedstock (sometimes propane if ethane is in short supply) is piped into the ethene plant.

Cracked naphtha, a mixture of hydrocarbons rich in aromatics.

A tarry residue containing hydrocarbons of high molecular mass.

As the steam-cracked reaction products leave the cracking furnace they are quenched with oil. This causes rapid cooling which prevents alkenes from recombining. After quenching, the product stream passes into the primary fractionating tower where the quench oil is recovered and cooled in a heat exchanger before being recycled to the process. The heat removed from it is used to generate steam in a waste-heat boiler. Tarry residue is stored in storage tanks and further used in blending with heavy gas oil.

Materials of lower boiling points pass out of the top of the fractionating tower to the process-gas compressor. After compression the feed is washed to remove any sulphur compounds which may be present. The desulphurised stream passes into the depropaniser where ethene and propene, together with other hydrocarbons of low molecular mass are separated and fed into the ethene recovery plant.

2.5.2 Ethene Recovery

The ethene recovery plant is concerned with the separation of pure (99.90 per cent) ethene from the mixture of hydrocarbon gases produced by the steam cracking plant. Ethene is used in the manufacture of the plastics, polythene and P.V.C. and exoxyethane products such as ethane, 1,2 diol, which is commonly used as anti-freeze.

2.5.3 Fife Ethylene Plant

Ethene (known commercially as ethylene) production is not confined to an ethene recovery unit as found at Exxon Fawley. Exxon Chemical has one of the largest ethene production plants in the world at Mossmorran in Fife, Scotland. The plant has an annual production capacity of 650,000 tonnes.

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The ethene feedstock contains carbon dioxide which must be removed before ethane is cracked, so that it does not remain in the ethene product. If it was not removed at this stage it would solidify at the low temperatures at which ethane is stored.

Treated ethane is fed into preheated cracking furnaces and mixed with steam at around 800°C. Under these conditions ethane is converted mainly to ethene and hydrogen. When the ethene concentration has reached an optimum value, the cracking reaction is stopped by rapid cooling of the reaction mixture with water in two stages, producing first high pressure steam and then low pressure steam.
mainly straight chain butenes and 2-methylpropene is passed on to the 2-methylpropene extraction plant. Butan-2-one is an important organic solvent used in a variety of pharmaceutical and industrial processes.

2.5.5 Methylpropene Extraction and M.T.B.E. Production

2-Methylpropene is an important feedstock used in the manufacture of halobutyl rubbers. The extraction process involves the formation of another important chemical, methyltert-butyl-ether (M.T.B.E.) as an intermediate. When added to petrol this compound improves engine performance. It is widely used in unleaded petrols.

Following extraction and after washing, the feedstock is mixed with methanol and passed into a reactor. Methylpropene reacts with methanol to form M.T.B.E. which is separated from the unreacted straight chain butenes. Some M.T.B.E. passes out of the extraction process to be used as an additive for petrol blending. The remainder is decomposed back to ethylpropene and methanol.

Methanol is separated from both product streams by washing with water.

The reaction conditions are particularly important since the process must selectively hydrogenate buta 1-3 diene to butenes, but not the butanes.
2.5.6 Halobutyl Rubber Production

On the halobutyl rubber production plant the polymers plant is concerned with the production of halobutyl rubber by the co-polymerisation and subsequent halogenation of 2-methylpropene (from the 2-methylpropene extraction plant) and 2-methylbuta-1-3-diene (which is imported from other chemical sites). These rubbers are principally used in the manufacture of the inner liners of tubeless tyres. Due to their relative inertness and impermeability to gases, halobutyl rubbers are also used in the manufacture of pharmaceutical stoppers. A mixture of feedstocks and chloromethane diluted chilled to approximately -100°C, is fed into a reactor cooled to the same temperature by an ethylene refrigeration system. The reaction product is a slurry of rubber particles and unreacted monomer in chloromethane diluent. This slurry is fed into a dissolving drum where it is mixed with hot solvent in order to dissolve the rubber particles. The rapid increase in temperature causes unreacted monomers and chloromethane to flash off on gases. These pass to a chloromethane recovery unit where they are separated and recycled back to the process. The remaining rubber solution is reacted with chlorine (or bromine) to produce halobutyl rubber product. The halobutyl rubber solution passes into a flash drum and stripper, where the solvent is flashed off by direct heating with steam, leaving a watery slurry of rubber. The solvent is recovered and recycled to the process. The slurry is fed through a de-watering unit, which removes the free water present, and finally to a two-stage drier. Dry rubber product is baled and packaged ready for sale.
2.6 Principal Products of an Oil Refinery

(1) Gas, which is converted by Gas Boards for use as town gas, or is used for fuel in the refinery's own furnaces.

(2) Propane, for heating, metal cutting and flame welding, lighting for caravans etc.

(3) Butane, a liquefied petroleum gas used as a fuel for heating and cooking, air conditioning on farms etc.

(4) Naphtha, used in its raw state in the manufacture of plastics such as PVC.

(5) Petrol, a fuel for motor cars and other spark-ignition internal combustion engines.

(6) Heptanes, for use in the manufacture of plastics such as PVC.

(7) Ethylene, used in the manufacture of polyethylene, and an essential chemical for ethylene glycol, which is used in the manufacture of terylene and anti-freeze.

(8) Butadiene, used in the manufacture of synthetic rubber.

(9) Butyl rubber, for car inner tubes, shock absorbers and cable insulation.

(10) Turbo-jet fuels for civil and military jet aircraft.

(11) Kerosene (paraffin) a fuel for portable domestic heaters.

(12) Tractor vaporising oil, a kerosene fuel for all types of commercial tractor.

(13) White Spirit, a solvent used in the manufacture of paints, varnishes, enamels and polishes, also used for dry cleaning.

(14) Auto diesel, a fuel used in automotive diesel engines on roads and railways.

(15) Marine diesel, a fuel for marine diesel engines.

(16) Sulphur, an essential chemical in the manufacture of sulphuric acid and fertilisers.

(17) Lubricating oil, for lubricating all kinds of machinery, motor cars, marine, aviation and industrial machines.

(18) Lubricating oil additives, for the improvement of engine performance and reduction of wear.

(19) Fuel oils, for home heating, industrial furnaces, ship propulsion and electricity generation.

(20) Bitumens, for road construction, roofing and waterproofing materials.

(21) Calcined coke, for the manufacture of electrodes for aluminium production and electrodes in electric arc steel-producing furnaces.
Chapter 3 - Storage Tanks

3.1 Storage Tanks

Storage tanks will be found in a number of shapes and sizes, the majority at oil refineries and petrochemical sites are vertical cylindrical tanks ranging in sizes from 8 metre diameters to tanks of 90 metre diameter holding as much as 21 million gallons (90,000 cubic metres) of oil, but horizontal cylindrical and spherical pressure vessels will also be seen.

Some tanks may be refrigerated (containing cryogenic product) some may be heated and enclosed with insulation (containing heavy oil e.g. bitumen/asphalt). Primarily crude oil tanks and those for volatile refined products, such as gasoline have roofs in the form of a pontoon so designed to float on the surface of the liquid to alleviate any ullage (or outage) space and are provided with a seal round the periphery to prevent flammable vapour escaping. These seals reduce the risk of fire, help to avoid loss of product through evaporation, and minimise the unpleasant odour of the oil in its natural state.

The firefighter may find the various terms indicating capacity as used in the oil industry, somewhat confusing, but the change to metrication will provide clarification. At the present time in the USA the capacity of oil storage tanks is generally quoted in gallons or barrels, (1 barrel = 35 imperial gallons = 5.61 cubic feet) although the size of a tank may be stated in cubic feet. Under metrification, tank capacities will be reckoned in cubic metres, or indeed small quantities may be given in litres (1 cubic metre = 1000 litres). On the other hand, because dues for shipping which are imposed by the Department of Trade and Industry (Marine Division) are rated on tonnage (under the regulation 1 ton = 100 cubic feet), oil tanker capacities are invariably quoted in tons. Under metrification, tanker capacities will be given in metric tonnes, and these are in fact almost equal to imperial tons. (1 ton = 1.016 tonnes).

3.2 Types of Tank

The types of cylindrical tank recommended for the storage of hydrocarbon oil having regard to volatility are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Class 'A' (flash point below 22.8°C)</th>
<th>(a) Floating Roof</th>
<th>(b) Non-Pressure fixed roof with internal floating deck</th>
<th>(c) Pressure fixed roof.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 'B' (flash point between 22.8 and 65.6°C)</td>
<td>(a) Floating roof</td>
<td>(b) Non-pressure fixed roof with internal floating deck</td>
<td>(c) Non-pressure fixed roof with atmospheric vents.</td>
</tr>
<tr>
<td>Class 'C' (flash point above 65.6°C)</td>
<td>'Non-pressure' fixed roof with atmospheric vents (Tanks which contain heavy fuel oils or bitumens are insulated and heated.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Because the pressure fixed roof tank is limited in size, larger tanks require a different construction. The floating roof tank provides economical storage of volatile liquids with a high degree of safety and floating roof tanks of 300ft (91m) in diameter and 70ft (22m) high are becoming commonplace in refineries; these are capable of holding the full cargo of a Y.L.C.C.

The steel roof floats on the oil and rises or falls as the liquid is pumped in and out of the tank. The essential feature of this type of roof is a vapour-tight seal between the periphery of the roof and the tank shell.

3.5 Floating Roof Tanks

Pressure roof tanks, however, are provided with special breather vents which minimise the losses of vapour from volatile liquids that would result if the normal free-flow atmospheric vent was fitted. They also protect the tank from excessive pressure. The breather vent helps to maintain an over-rich vapour in the ullage space of the tank and thereby prevents possible ignition.

Atmospheric and breather vents are sometimes fitted with flame arresters to prevent the propagation of flame into the tank. These take the form of perforated plates, non-corrodible wire gauze, fine slots in a metal block, crimped metal or bunches of narrow metal tubes. It has been found, however, that flame arresters which have become clogged with paint, dust, scale or other waxy deposits may interfere with the normal working of the vents, and so regular maintenance is essential. This can be a problem in a refinery where there are hundreds of tanks. In addition, when the breather vents are closed, flame cannot pass through them and in the case of volatile oils, such as petrol, the vapour inside the tank would be too rich to ignite. Consequently some companies have dispensed with flame arresters.

All tanks of this design whilst constructed with a weak roof to shell seam have a P.V. (pressure vacuum) valve or a free vent. Normal venting on a non-pressure fixed roof tank is by an open or free flow atmospheric vent which allows the unimpeded flow of vapour in and out of the tank, but prevents the ingress of rain and airborne dust.

Vertical cylindrical tanks can range in size up to 300ft (90m) in diameter, and more than 60ft (18m) in height. Horizontal tanks may be used for specific purposes, especially for underground tanks, and liquefied petroleum gas tanks up to 200ft (60m) in length are not uncommon. Standard metric sizes are now recommended for vertical cylindrical tanks, and Table 3.1 shows the capacity of some random sizes of metric tanks.

### Sizes of Tanks

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### Fixed Roof (Cone) Tanks

Oil storage tanks are generally constructed of a number of courses (or strakes) of mild steel plates, which are generally welded together, but may be riveted, if of older construction. Since the internal pressure on the tank is greater at the bottom, the side (or shell) plates increase in thickness from the top to the bottom. Strakes are usually 6ft (1.8m) in height, and this gives a method of easy calculation of the height of a tank.

Roofs of the non-pressure type of tank are conical or domed in shape and are self-supporting, i.e. there are no internal columns to take the weight of the roof, but the steel plates rest on a supporting steel framework. The roof plates are fixed at the periphery to the top curb angle of the shell by a single fillet weld which is weaker than the shell seams or than the weld attachment of the shell to the base of the tank.

All tanks of this design whilst constructed with a weak roof to shell seam have a P.V. (pressure vacuum) valve or a free vent. Normal venting on a non-pressure fixed roof tank is by an open or free flow atmospheric vent which allows the unimpeded flow of vapour in and out of the tank, but prevents the ingress of rain and airborne dust.

### ‘Pressure’ Roofs

Constructional details of ‘pressure’ roof tanks are similar to those of the ‘non-pressure’ type, but because of the higher internal pressure, they are limited to tanks up to 128ft (39m) in diameter.

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### Floating Roof Tanks

Because the pressure fixed roof tank is limited in size, larger tanks require a different construction. The floating roof tank provides economical storage of volatile liquids with a high degree of safety and floating roof tanks of 300ft (91m) in diameter and 70ft (22m) high are becoming commonplace in refineries; these are capable of holding the full cargo of a V.L.C.C. The steel roof floats on the oil and rises or falls as the liquid is pumped in and out of the tank. The essential feature of this type of roof is a vapour-tight seal between the periphery of the roof and the tank shell.
3.5.1 Pontoon Floating Roof Tanks

The early type of floating roof consists of a single deck with a vertical rim at the periphery and is known as a pan-type roof. A pan type roof has one deck and is always in contact with the stored liquid. The sun's heat on the deck can cause severe boiling losses from volatile oils, and so the pan roof has been superseded by the pontoon floating roof which has an annular pontoon around the periphery, encircling a single centre deck. In addition to buoyancy, the pontoon provides air-space insulation from the sun's heat, and thus inhibits boiling of the oil in the annular area. The annular space between the floating roof and the shell may be rendered vapour-proof by means of a special fabric seal in tube form, the tube being filled with liquid or by a resilient urethane foam fabric seal. Either seal has the ability to conform to the tank shape so that there should be no vapour in the space between the roof and the shell above the seal, but the liquid-filled seal has the disadvantage that it can be punctured by any sharp protrusion on the shell. Another type of seal for floating roof tanks is the pantagraph hanger with steel shunts. The stainless steel shunts are spaced about 10ft (3.05m) apart and provide a sure electrical bond between the floating roof and the sealing ring which is in contact with the tank shell.

Insulated pantagraph hangers maintain the contact of the shunts with the tank shell. Floating roofs are usually installed in external open top tanks and therefore the top of the shell is generally strengthened by the addition of a wind girder around the shell near the top as a protection against the shell 'blowing-in' during high winds. At some refineries, these wind girders have been provided with hand rails so that personnel can walk safely around the top of the shell for maintenance, inspection and firefighting especially a seal fire at the rim of the roof. Firefighting can then take place safely from the wind girder on the outside of the tank, and men do not need to go down on to the pontoon roof.

Floating roof tanks are also provided with drains to remove rain water and discharge it outside the tank. Four types are normally to be found; open, siphon, pipe with swing wing joints or flexible hose. The first two types of drain discharge the water through the contents of the tank so that it collects at the bottom, where it can be drawn off through a connection at the base of the tank. The other two types convey the rain water to the outside of the tank without it coming into contact with the contents. Roof drains are essential to help prevent roof sinking potential. (See Figure 3.7)

3.5.2 Double-Deck Floating Roof Tanks

A further development of the floating roof to give better buoyancy and stability is the double-deck type of construction. The design of the roof provides sufficient buoyancy to keep the roof floating with any two compartments punctured. Emergency overflow drains are provided to prevent storm water accumulation from exceeding the capacity of the roof. This provides an extension of the insulating air space between the two decks over almost the whole surface area of the liquid, and this has the advantage of shielding the oil from the effect of solar heat, thus significantly reducing the formation of temperature generated condensable vapour under the floating roof.

3.5.3 General

Fittings that will be encountered on an external floating roof tank include:
- Stairway/rolling ladder to give access to the roof
- Windgirder with walkway (may have handrails fitted)
3.5.4 Roof Design

Of the two most common types of roof design, the double deck is preferred to the single deck pontoon roof from a fire management evaluation for the following reasons:

• Vapours trapped under the roof lead to instability. The double deck roof is stiffer and so does not flex so readily causing 'high and low' spots (sometimes referred to as ballooning). Vapours tend not to accumulate under the roof as much as with a single deck type, but are distributed on the rim seal area.

• In single deck roof tanks, the centre of the roof is below the fuel level at the rim seal due to sagging of the roof. Should the drain line fail, product could flow up the drain line and accumulate on the roof if there is no non-return valve or an installed valve is faulty.

• For the very same reasons, open 'emergency' drains cannot be used on single deck roofs thus meaning that should the primary drain fail, product will accumulate on the roof.

• Double deck roofs can be fitted with emergency drains that drain water through the product.

• There is less flexing or distortion of a double deck roof and due to the construction there is less chance of corrosion allowing seepage of product onto the roof.

3.5.5 Internal floating roof tanks

A further development in tank design is a tank which combines the fixed and floating roof type of
construction, generally known as the internal floating roof tank. A steel, fibre-glass, aluminium or plastic floating deck, similar to the pan-type floating roof, but without the elaborate draining system, is protected by a cone or domed roof with open eaves to allow ventilation of the small amount of vapour which may escape past the seals into the space above the floating deck. The roof may be column supported, or the floating deck may be installed in a self supporting fixed roof tank. In recent years it has become the practice to install geodesic dome type roofs over the complete floating roof tank, these are lightweight structures. This type recent years it has become the practice to install geodesic dome type roofs.

3.6 Pressurised Storage Tanks

Standard tanks are not suitable for the storage of liquefied petroleum gases, such as propane or butane, owing to the high pressures required to maintain these gases in a liquid state; they are therefore stored in special pressure vessels. The ideal shape for a pressure vessel is spherical, as the internal pressure is the same at any point, but long, heavily-built small diameter horizontal tanks with rounded ends are also used.

3.6.1 Spheres

Spheres are used at oil refineries for the storage of L.P.G. in bulk, for ammonia or for ethylene under pressure. They are made of steel plates welded together in the same manner as for circular tanks, but they are supported on six or more steel legs, the number depending on the overall size of the vessel. The legs are enclosed in concrete except where they are welded to the sphere. Each vessel may have an individual fire wall or bund enclosure with a retention capacity of about 50 per cent of the contents of the tank, although, as a result of the Feyzin (France) fire, new installations are not bunded and do not hold leaking gas in the area, but arrangements are made to drain away leaking contents to a safer area.

The concrete floor of the area inside the bund (where they exist) is sloped towards a sealed catch basin (or pig trap as they are sometimes called) within the area, as remote as possible for the sphere, so that any spilled liquid, especially underneath the sphere, is directed into the catch basin. A gate valve (kept closed) is generally installed outside the fire walls in the sewer line from the catch basin to prevent any spilled liquid petroleum gas entering the refinery sewer system. Each enclosed area within the fire wall drains separately to the sewer system. Each sphere is protected externally by a water drencher system, and has a water draw-off and anti-freeze internal drain connection at the base to allow water in the tank to be drawn off and run into a catch basin. The water draw-off arrangements are safeguarded by two or more valves so that close down can be achieved despite possible ice formation. Total passive fire protection is also an accepted practice.

3.6.2 Horizontal Pressure Vessels

Horizontal pressure vessels for the storage of volatile oils or gases under pressure are easily recognisable by their rounded ends. They are more stoutly constructed than normal vertical cylindrical tanks and, of course, incorporate suitable pressure relieving devices. Fire walls (or bunds) may be provided, but in newer installations similar arrangements exist for collecting spilled liquid and directing it into safer areas. There is also water draw-off piping at the base of the tank similar to that on spheres.

Safety valves are fitted at the top of L.P.G. spheres as a precaution against possible over-pressurisation, and since the safety valves normally discharge vapour when they blow, it is the general practice for them to vent the atmosphere. L.P.G. spheres always have sufficient vapour space left in the vessel so that the liquid has room to expand as, if the vessel is overfilled, it can result in the safety valve blowing and discharging liquid. A small amount of vented liquid will vaporise into a very large volume of gas. Owing to location problems, it may be unwise to vent to atmosphere, and in these cases the vapour is routed into flare stack lines. Precautions are invariably incorporated to ensure that when a safety valve blows, liquid cannot be discharged directly into the flare stack, as this could lead to burning L.P.G. being vented from the flare stack.

Each sphere is protected externally by a water drencher system, and has a water draw-off and anti-freeze internal drain connection at the base to allow water in the tank to be drawn off and run into a catch basin. The water draw-off arrangements are safeguarded by two or more valves so that close down can be achieved despite possible ice formation. Total passive fire protection is also an accepted practice.

3.7 Refrigerated Tanks

There is an economic advantage in refrigerated storage over pressure storage for very large quantities of liquid, and owing to the increase in the quantities of L.P.G. which are being used in recent years, giant refrigerated tanks of 100ft (30m) in height may now be found at oil refineries. At atmospheric pressure, propane boils at -42°C and...
normal butane at 0.6°C. By cooling to below boiling and maintaining the liquids in a chilled state, it is possible to store them in tanks designed to operate at slightly above atmospheric pressure. Cryogenic storage spheres are also used for the storage of liquefied ethylene gas at a temperature of 104°C enabling it to be stored at atmospheric pressure instead of under pressure as is normally necessary.

3.7.1 Fully Refrigerated Storage

Tanks are either of single or double wall construction, the inner tank is enclosed by an outer tank constructed from low carbon steel and the annular space between the tanks is filled with an insulating material e.g. perlite. As a safety measure the annular space may contain an inert gas, such as nitrogen.

3.7.2 Refrigerated Pressure Storage

Refrigerated pressure storage (sometimes called semi-refrigerated storage) combines partial refrigeration with low or medium pressure. These storage tanks are usually spherical in shape and can be 40ft (12m) or more in diameter.

3.8 Tank Fittings

3.8.1 Access to the Roof

Access to the roof of an oil tank is provided by means of a metal staircase which generally runs spirally from the ground to the top of the tank, or from a point some distance from the ground. On floating roof tanks, a second ladder leads down to the roof from the top of the spiral staircase. The end of this ladder is free to move on rollers on a runway fixed to the roof as the roof moves up and down.

Firefighters should wear breathing apparatus if required to climb on to floating roofs because there is a risk of gassing if vapour is escaping from a seal.

If the roof is low, vapour could collect above the roof, so refinery personnel are then only permitted to descend to the roof if they are wearing breathing apparatus and have a life-line attached to them, the free end of which must be held by another person on the staircase platform.

3.8.2 Inspection Manholes

At least one manhole will be found on the roof, whilst one or more are also fitted round the base. In some cases ladders run from the manholes down the inside of the tank (internal floaters), but generally the interior is reached through the base opening. Manholes are opened when necessary for ventilation purposes, or to give access for internal cleaning and maintenance for which large capacity tanks are fitted with a 4ft (1.22m) D shaped hatchway, built and bolted into the bottom strake.

3.8.3 Dip Hatches

The level of oil in a cylindrical tank is ascertained by dip hatches which are fitted on the roof; on floating roof and 'non-pressure' fixed roof tanks the dip hatch is a hole with a hinged lid, but on pressure roof tanks, a special gastight fitting is installed which allows gauging and sampling to be carried out without loss of the internal pressure. Sampling of the contents of a tank is also done through the dip hatch by lowering a weighted corked can to the required depth, then jerking out the cork fastened to the lowering cord and allowing the can to fill. In modern oil refineries, remote-reading automatic gauging devices are used, but these often supplement rather than replace the older dip hatch.

3.8.4 Vents

Atmospheric and breather vents are fitted to permit air to escape when the tank is being filled and to enter when it is being emptied, otherwise the tank might be damaged by an excessive difference between the external and internal pressure.

3.8.5 Pipeline Connections

On vertical tanks one or more pipeline connections are made through the bottom strake of the shell plate. Generally two such connections are used as it is then possible to use separate pipelines for filling and emptying. This reduces the risk of water contamination when the filling line is cleared with water. Two connections also permit blending to be carried out, and in this case on older refineries, one of the pipeline connections may sometimes be fitted with a 'swing pipe' inside the tank with hoisting gear to enable the free end of the arm to be raised or lowered to any level. A swing pipe was considered useful when blending, since it enabled the contents to be drawn off from the top and returned to the bottom, or vice versa, thus speeding the mixing process. However, except for floating swing arms, the installation of swing pipes is now not generally found. Certain types of oil contain small quantities of water, sludge or other impurities and these tend to settle, so that the oil near the top is virtually free from such contamination, and an automatic water draining device is now generally incorporated instead of a manual drain valve. This prevents spillages of product in case a manual drain valve were to be left open.

3.8.6 Steam Coils

Steam coils are fitted close to the bottom of tanks used to store bitumens and heavy oils in order to keep the contents fluid enough to be pumped. The coils consist of rows of steam pipes connected at alternate ends by hairpin bends. The steam supplied in this way is of no firefighting value and should be cut off in the event of fire as it merely serves to increase the temperature of the oil.
4.1 Layout of Oil Refineries

4.1.1 General

The firefighter entering a modern petrochemical complex is presented with a vast array of process operational hardware comprising furnaces, fractionating/vacuum towers, heat exchangers, large feed drums, pumps, compressors, fin-fan structures, storage tanks, miles of pipelines, valves, administrative, process and maintenance buildings and in many cases huge cooling towers.

Modern day refineries not only have to convert the crude oil into a number of saleable products and produce base feed streams for chemical plants, but have to be capable of receiving the crude oil and finally despatching the refined products to their destination. There must, of necessity, be adequate tankage to receive the crude oil and to provide storage capacity for the intermediate products (i.e. those which are not fully processed) and component products suitable for direct blending into finished product tankage.

Since practically all processes in a petrochemical plant are associated with heating and cooling and products have to be pumped, provision has to be made for utilities in the shape of steam (low-high pressure) electricity, fuel gas, cooling water, refinery air, processing water and compressed air, in some cases oxygen may be supplied from an external source. Facilities must be provided for the receipt of crude oil and other refined products at marine terminals, also for the despatch of refined products to other locations (e.g. Europe) either by sea (tankers, barges, coastal vessels) road and rail transport.

The size of a refinery will vary in accordance with its capacity and diversification of processing, a modern refinery will probably occupy some 30-40 acres (12–16 hectares) for each million tons (tonnes) annual capacity. Modern refineries present a much more compact appearance than the older ones. In the older refinery the design tended to be a segregation of refinery activities into various areas, e.g. process, blending, despatch, tankage, and utilities, each area tending to be autonomous in its own operations. The unity of purpose required in the modern refinery design with its integrated operations, from crude oil processing to despatch, leads to a situation where the capabilities of each individual in the operating team can develop to the highest degree.

To firefighters the layout of most refineries can be broadly divided into five sections:

- the marine installations
- the storage areas
- the processing plants
- the maintenance areas
- the administration areas

In some refineries there may also be chemical plants.

4.1.2 Marine Terminals

The marine terminal or jetty can be considered as the start of refinery operations where the tankers discharge their cargoes of crude oil. Normally, with the larger refineries jetties are constructed well out
to sea or water-way, in order that they can accommodate deep draft loaded tankers including in many cases the largest V.L.C.C.s (very large crude carriers) i.e. 350,000 tonnes. Besides loading and unloading facilities, full provision has to be made for bunkering tankers with fuel oil and for receiving their ballast water. Ballast water is normally obtained from the sea or river and this accounts for the muddy/sludge residue which accumulates in some storage tanks. Fresh water provided at the jetty is normally for re-filling ships' clean water pipelines, such valves are designed to be fail safe against product leakage or other emergency on the end of all jetty pipelines carrying flammable materials. Many such valves will be power operated and capable of manual operation in an emergency. Provision will be provided for remote 'stop' facilities at the jetty head for shore loading pumps.

Fire protection at jetties will vary from site to site, each petrochemical company will have its own design basic practices, therefore the firefighter may well find fixed fire water monitors at each berth, the loading arms may be protected with a water curtain drencher system, portable wheeled type fire monitors and in many locations tower mounted dual purpose water/foam remote operated monitors may be installed, these may be direct or indirect systems.

4.1.3 Conventional Jetties

The conventional type of jetty installation is built alongside the shore, or is connected to the shore by a single or double approachway (trestle). In many cases several tankers can often be moored at the same time discharging or receiving cargo, i.e. crude oil, gasoline, aviation fuels and LPG. Crude oil cargos are discharged from the tankers by pumps on board in the cargo pump rooms, a V.L.C.C. may be discharging at a pump rate of 12,000 tonnes per hour, discharging into crude lines with a 36 inch diameter. In most of the modern tankers which are designed with a free flow pipeline system between shore pipeline and vessels may consist of hoses or metal retractable swing arms. As a precaution against product leakage or other emergency on the jetty, shut off valves are provided at or near the shore end of all jetty pipelines carrying flammable materials. Many such valves will be power operated from a remote location, the valves so designed to ensure that surge pressures are not produced in the pipelines, such valves are designed to be fail safe and capable of manual operation in an emergency. Provision will be provided for remote 'stop' facilities at the jetty head for shore loading pumps.

Fire protection at jetties will vary from site to site, each petrochemical company will have its own design basic practices, therefore the firefighter may well find fixed fire water monitors at each berth, the loading arms may be protected with a water curtain drencher system, portable wheeled type fire monitors and in many locations tower mounted dual purpose water/foam remote operated monitors may be installed, these may be direct or indirect systems.

However, in many cases flexible cargo hoses are still in use. As product is removed from the cargo tanks, air enters the tank ullage space through the vapour lines and dilutes the hydrocarbon vapours present at the commencement of discharging.

Some tankers may be fitted with an inerting system which can be produced by one of two main processes. Ships with main or auxiliary boilers may then be used to produce gas by burning diesel or light fuel oil. (See Fire Service Manual – Marine Incidents.)

The gas produced is then scrubbed and then used the same way as boiler fluegas. Where fitted and capable of manual operation in an emergency. Provision will be provided for remote 'stop' facilities at the jetty head for shore loading pumps.

Fire protection at jetties will vary from site to site, each petrochemical company will have its own design basic practices, therefore the firefighter may well find fixed fire water monitors at each berth, the loading arms may be protected with a water curtain drencher system, portable wheeled type fire monitors and in many locations tower mounted dual purpose water/foam remote operated monitors may be installed, these may be direct or indirect systems.

4.1.4 Monobuoy Mooring

A totally different type of marine installation is the monobuoy mooring and floating buoy usually referred to as the "monobuoy". With this type of floating buoy, V.L.C.C.s can remain in deep water and discharge their cargo direct through a pipeline on the ocean bed to storage tanks. The monobuoy is a single floating buoy about 30ft (9m) in diameter, which is secured to the seabed by chains and heavy anchors. Built into the centre of the buoy is a swivel that can rotate 360° around a pipe assembly which runs down to the seabed and then to storage tanks inshore. Two flexible hose lines which will float on the surface of the sea are connected to the pipe assembly. When the tanker is ready to discharge its cargo of crude oil, it moors to the buoy, and this can
be safely achieved in any direction according to wind, tide and weather conditions. The floating hoses are then picked up and connected to the ships discharge manifold. The ships pumps are used to pump the oil through the pipeline to the storage tanks onshore. This type of deep sea mooring has been adopted world wide.

4.1.5 Hydrocarbon Storage

As crude oil is discharged ashore from the tanker it is received in crude oil tanks which invariably will be external or covered (internal) floating roof type. Where it is possible these tanks will be conveniently sited together near the jetty. With construction of high tensile steel, storage tanks are now available in larger diameters (100m) and greater capacity is allowed in single bunds; some tanks are capable of receiving the total cargo of a VLCC which from a refining company's point of view is cost effective (refer to I.P. code, refining safety code 1981). The main hazards from the storage of flammable liquids are fire and explosion involving either bulk liquid or escaping liquid or vapour. Such incidents may be the result of inadequate design, manufacture, installation or maintenance, equipment failure, incorrect operation or exposure to heat from a nearby fire. Tanks must be built to design criteria that ensure physical integrity of the tank against all reasonable expected forces, such as tank contents, ground settlement or movement, wind, snow. Suitable codes relating to the design and construction of storage tanks and associated fittings are B.S.2654 and A.P.I. standard 650.

Spacing of Tanks For Petroleum Stocks.
(Ref I.P. refining safety code 1981)
Guidance on the minimum tank spacing for classes I, II & III(2)

(a) Tanks of diameter up to 10m are classed as small tanks.

(b) Small tanks may be sited together in group, no group having an aggregate capacity of more than 8000m³. Such a group may be regarded as one tank.

(c) Where future changes of service of a storage tank are anticipated the layout and spacing should be designed for the most stringent case.

(d) For reasons of firefighting access there should be no more than two rows of tanks between adjacent access roads.

(e) Fixed roof tanks with internal floating covers should be treated for spacing purposes as fixed roof tanks.

(f) Where fixed roof and floating roof tanks are adjacent, spacing should be on the basis of the tank(s) with the most stringent conditions.

(g) Where tanks are erected on compressible soils, the distance between adjacent tanks should be sufficient to avoid excessive distortion. This can be caused by additional settlements of the ground where the stressed soil zone of one tank overlaps that of the adjacent tank.

A distinction is clearly made between large fixed roof tanks and large external and internal floating roof tanks. The recommended safety distances between storage tanks and between storage tanks and filling points are less for floating roof tanks than for fixed roof tanks due to the excellent safety record of floating roof tanks. Previously to the introduction of electrical bonding from floating roof to tank shell a number of rimseals fires had occurred that in the event were successfully extinguished with portable equipment.

4.1.6 Bunds

Bunds (product retention basins) (refer to H.S.E. the storage of flammable liquids in fixed tanks exceeding 10,000m³ total capacity 1991).

Storage tanks should be surrounded by a bund (dike) to limit the spread of spillage or leakage. Alternatively, liquid may be directed to a separate evaporation/collection area, using diversion walls as necessary. Bunds may contain more than one tank and should be designed to hold at least 100 per cent of the capacity of the largest tank within the bund, after making allowances for the space occupied by other tanks. In exceptional cases where there is no risk of pollution or of hazard to the public this figure may be reduced to 75 per cent.

The total capacity of tanks in a bund should not exceed 60,000m³ (120,000m³) for floating roof tanks.

| Table 4.1 Spacing tanks for petroleum stocks of classes I, II & III(2) |
|-----------------------------|------------------|------------------|
| Factor                      | Type of tank roof| Recommended minimum distance |
| (1) Within a group of Small Tanks. | Fixed or floating | Determined solely by construction/ maintenance/operational convenience. |
| (2) Between a group of Small Tanks and another group of Small Tanks or other large tanks. | Fixed or floating | 10 m minimum, otherwise determined by the size of the larger tanks (see 3 below). |
| (3) Between adjacent individual tanks (other than Small Tanks). | (a) Fixed | Half the diameter of the larger tank, but not less than 10 m and need not be more than 15 m. |
|                              | (b) Floating | 0.3 times the diameter of the larger tank, but not less than 10 m and need not be more than 15 m. |
| (4) Between a tank and the top of the inside of the wall of its compound. | Fixed or floating | Distance equal to not less than half the height of the tank. (Access around the tank at the compound grade must be maintained.) |
| (5) Between any tank in a group of tanks and the inside top of the adjacent compound wall. | Fixed or floating | Not less than 30 m. |
| (6) Between a tank and a public boundary fence. | Fixed or floating | Not less than 15 m. |
| (7) Between the top of the inside of the wall of a tank compound and a public boundary fence or to any fixed ignition source. | — | Not less than 30 m. |
| (8) Between a tank and the battery limit of a process plant. | Fixed or floating | Not less than 15 m. |
| (9) Between the top of the inside of the wall of a tank compound and the battery limit of a process plant. | — | Not less than 15 m. |

* In the case of Crude Oil Tankage this 15 m option does not apply.
Intermediate lower bunds may be used to divide tanks into groups to contain small spillages and to minimise the surface area of any spillage as this affects the maximum size of a bund fire. Recommended height of a bund (primary retention) 1.5m to 2m.

4.1.7 Process Units

It is in the numerous process units that there is the greatest diversification between the older and the modern refinery. Because all processes rely on vast quantities of cooling water (or air) which has to be circulated by pumps or fan-fans, the less space there is between process units the better use can be made of cooling water. After use much cooling water is reclaimed and treated to remove contaminants before being recycled for use.

In other cases where there is an abundance of water (i.e. seawater) new water is used continuously and once used is passed through clean water separators before return to its source. Cooling water can account for a large proportion of the total water effluent of a refinery with flow rates up to 250,000 litres per minute.

From about 1960 onwards, most refineries have been constructed as integrated processing complexes. Up to this time processing units in the older refineries were operated independently, the product from each unit being fed to tankage, the next unit in the processing line would then draw its feed from this tankage as the need required, hence on the older sites tankage would be scattered over a wider area.

It was the accepted practice on the older refineries for each operating unit to have its own control room. On the larger sites there could be up to twenty or more control rooms each manned with operators specific to that processing operation. Control rooms now are more centralised with automatic control of processes achieved by computers, inevitably this has led to a reduction in manpower. E.S.D. (emergency shut down systems) are provided so that in the event of an emergency the operating processes can be shut down safely from within the control room with minimum risk to operators. To protect process operating personnel, control rooms are now being constructed to withstand blast (i.e. vapour cloud explosion) and closed circuit television cameras are utilised around operating units, marine terminals and other high risk areas.

4.2 Distribution Areas and Pipelines

The final function of the oil refinery is the distribution of the finished products, to their destinations. Bulk distribution would be by sea going tanker, especially for overseas markets, where local refineries do not exist.

Water transportation is comparatively cheap and where geographical conditions permit is widely used for distribution purposes. Small tankers will operate in coastal waters supplying parts which are inaccessible to larger vessels. On inland waterways and estuarial waters, barges are also used, being either self propelled or towed.

Coastal tankers and barges are loaded at the marine terminal or jetties where the same stringent precautions against spillage etc. are enforced as when unloading crude oil from larger crude carriers (V.L.C.C.s).

A large proportion of refined products are distributed to installations direct by trunk pipelines, a network jointly used by a number of oil companies.

Road and rail transportation makes up the remainder of product distribution.

4.3 Road Tankers and Rail Cars

Both road tankers and rail cars are used for distributing bulk supplies of finished products from the refinery to installations and depots. Rail cars with a capacity of up to 100 tons (101 tonnes) are usually cylindrical tanks mounted on bogies, with transverse baffles designed to prevent surging of the contents when the tank car is in motion.

The design of road tankers has altered over the years and, although cylindrical tankers are still used, the more modern ones are more or less rectangular in cross-section. Their capacity is generally about 7,300 gallons (33,000 litres) or less. Filling methods depend on the design of the vehicle compartment which may be fitted with a permanent perforated fill-pipe extending into a small well at the bottom of the tank, or filling maybe through open-dome hatches.

Filling via open-dome hatches has now almost completely superseded closed filling through fixed pipe connections owing to the need to meet faster filling rates, this is especially the case for low flash products. Many companies top load high flash products. Bottom filling may still be found but this method is rarely adopted as there are few loading racks which are suitable for this method.

Although many thousands of tons (tonnes) of highly flammable petroleum products are transferred daily by road tankers and rail cars, few accidents occur, due to the prohibition or indeed strict control over the use of naked lights and other sources of ignition. Strict company operational procedures ensure compliance with statutory regulations.

The design of the fill-pipe is such that when the end of the pipe is at the bottom of the tank, liquid is directed smoothly along the tank bottom with the minimum of splashing. This method of loading helps to prevent the generation of static charges caused by splash filling. Electrical bonding of the metal fill-pipe also prevents a static discharge between the pipe and tank hatch during filling or when withdrawing the fillpipe after loading operations are complete. Earthing of the tank vehicle also ensures electrical continuity and has the same effect as
Stringent precautions are always enforced to prevent fires occurring: strict "permit" to work procedures adopted, smoking is forbidden other than in clearly designated areas and only safety-type torches and equipment are permitted in flammable atmospheres.

High Pressure - A sudden release of energy, failure of a pipeline or vessel under pressure releasing large volumes of liquid giving rapid vaporisation and producing an excessive vapour cloud. The principal objective is to eliminate the possibility of a minor incident developing into one of catastrophic proportions. It is generally accepted that the philosophy of effective control of hydrocarbon fires recognises the need for massive cooling in the shortest possible time with limited risk to personnel.

Plant operatives are required to take every precaution when working on plant or storage tanks to prevent accidents or danger to life, on high risk units (i.e. toxic gas environment) personal gas monitoring equipment will be worn. The basis of a safe plant design is to eliminate foreseeable risks of fires and explosions.

However it is recognised that such incidents may still occur, because of equipment failure or operating error and therefore design features must be included to minimise the resulting damage. Of these design features, passive protection (fire proofing) and blast protection are of major importance. Passive protection of certain critical

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**Figure 4.7 Road loading stand fire**

**Figure 4.8 Road loading stand, foam system under test**

Bonding. Rail cars can be considered as adequately earthed via the rail lines, but isolation of the section of track on which the rail car rests is necessary if the system is electrified.

Fire protection and firefighting equipment for the protection of road/rail loading racks will be dependent on the products being handled. Automatic fixed foam systems will normally be found protecting road/rail loading racks handling low flash products, i.e. gasoline, whereas L.P.G. rail/road loading stands will be protected by fixed water deluge systems with manual or automatic operation. Fixed oscillating foam monitors may also be found in some locations.
equipment and supporting structures enables a degree of fire exposure to be tolerated whilst a fire is being brought under control and finally extinguished, without major collapse or further failures.

When examining design requirements for fire protection, the balance of fixed protection must be evaluated with the availability of portable equipment. It is clear that one vapour cloud explosion or detonation can damage beyond repair high cost fixed fire protection equipment, recent major incidents within the petrochemical industry have proven this. As a consequence there is an immediate need for thousands of gallons (litres) of water a minute to be instantly available for firefighting at an acceptable pressure to meet the high demand required to deal with a major process unit or tank fire, so that pumps, deluge systems and monitors can be brought into use immediately.

5.1.2 Single Fire Concept Water Supplies

The extent and capacity of the firefighting, fire protection equipment in a petrochemical plant is based on the assumption that only one major fire will occur at any one time. Thus the requirements of the largest single fire contingency determine the design of the major firefighting facilities. However, the sizing of the firefighting system components may not be set by the same single contingency, since different firefighting techniques are required on the various plant and offshore facilities. For example, the capacity of the foam system is usually determined by tankage requirements where as fire water capacity is usually a function of process unit requirements.

5.1.3 Major Fire Risks

Process units, marine terminals loading stands, tankage and pressurised storage facilities are the areas of major risk. In process areas, fire water application is the most effective firefighting method, with water being applied to exposed structures and equipment for effective cooling, to prevent further failures and possible escalation, minimising damage until the fire is extinguished invariably by product isolation. It is fortunate that refineries are frequently situated where there are unlimited supplies of water, either by the sea or large rivers, although direct access to this water is sometimes difficult. In many cases pump-houses are provided at marine terminals to pump large volumes of water on shore to large water storage tanks that may have a capacity of 3.5 million gallons, this water supply may play a dual role providing process cooling and firefighting needs.

Fire water systems, where possible should be of a ring main recirculation principle, with sufficient block isolating valves provided so that no more than 1000ft (300m) of firemain can be lost in the vest of main failure through ageing, pressure surge, or as a result of a vapour cloud explosion. The fire water source will normally be specified to be an unlimited supply, however, where the fire water supply from a given source is limited, fire water storage shall be with a capacity equal to an 8 hour supply at specified design rates independent of other plant process water usage. Fire-water mains within process plants must be installed below ground. This will provide some protection against blast damage caused through the pressure wave produced by a vapour cloud explosion.

At one major refinery, for example, the ring main is fed by seven fixed fire water pumps located in two areas to ensure security of supply (these pumps, three electric, two steam and two diesel driven) feeding from water storage tanks with a combined capacity totalling over 8 million gallons at a pressure of 150 psi (10 bars) is constantly available. It may be in some cases that supplies are often interconnected and shared between companies fed by either fresh or salt water. Fire hydrants are provided at strategic points around the plant, they are usually spaced no further than 300ft (90m) apart. Hydrants may be the pillar type with three or four standard 2 1/2 inch (70mm) diameter outlets plus in many cases a 4 inch (102mm) outlet. A number of refineries are now installing new hydrants that incorporate one 6 inch (150mm) outlet in conjunction with the move to large diameter fire hose.

At the Fawley refinery an additional water resource is provided by utilising the high volume process cooling water mains 60 inch (1500mm) 48 inch (1200mm) 24 inch (600mm) on which are installed 8 inch (200mm) diameter manifolds with six 70mm (2.5 inch) and one 6 inch (150mm) storz outlets. In addition to ring mains other water supplies are usually provided, either in the form of static tanks with a hard standing for pumping appliances or direct access to the open water.

5.1.4 Fixed Water Protection Systems

There is now a strong trend toward the use of mobile trailer mounted fire monitors for first strike firefighting, however, company basic practices require the installation of fixed monitors around operating plant that can be used to direct large volumes of cooling water on to process equipment and other facilities such as road/rail loading rakes, major pump areas, jetty structures, and will be a great advantage in elevated high risk areas. These monitors can be operated by one operative and should the area become untenable the monitor can be set on jet or spray pattern placed at the most advantageous angle and left unattended. Operating valves to the monitors can, if required, be located in a safe remote area.

On many petrochemical plants elevated remote operated monitors will be found, these may be driven electrically, air operated or water driven hydraulically. A good practice is to fit a valve fire service booster connection to the monitor standpipe at ground level. This can serve two benefits, one to boost pressure during an incident, the other in providing a flushing out facility most essential if the fire water system runs on salt water.

Fixed fire water deluge systems will also be found in petrochemical plants where special and immediate protection is required and such an installation is the only effective solution, e.g. high risk equipment, such as large flammable liquid drums in areas with restricted access for normal firefighting. Such systems may be manually or remotely operated.

Cooling water spray rings may also be found on storage tanks. For pressurised and refrigerated storage vessels the use of a water spray/deluge system is a method of rapid application of protective cooling. The means of distributing of water uniformly may be by the water ring systems which can also include a top mounted deluge nozzle, sometimes referred to as the mushroom discharge orifice.

5.1.5 Mobile Water Monitors

Mobile firefighting equipment is an integral part of the protective equipment in a petrochemical plant. The effectiveness with which such equipment can be used, particularly in the early stages of a fire with...
limited personnel available, depends primarily on the speed with which it can be brought into operation. The design of such a monitor greatly enhances the speed with which it can be utilised if it can be set up by one person, carries its own hose, is fitted with non-return valves in the water inlet and once put into position can be left safely unattended.

5.1.6 Storage Tank Protection

Flammable liquid storage tanks and associated facilities can be protected with a variety of fire protection systems. (Reference document N.F.P.A. 11 low expansion foam extinguishing systems.) This document categorises storage tank fire protection systems as fixed and semi-fixed systems. Fixed systems (direct) are complete installations usually piped from a central foam station that discharges foam through fixed foam delivery outlets onto the hazard protected. The installation will be designed to have its own foam concentrate tank complete with foam concentrate pump (electrically or water driven). These systems may be activated by a fire detection system or be manually operated. Many such installations will have an unlimited water supply utilising the ring main principle. Semi-fixed (indirect) relates to the type of distribution system where the hazard is equipped with foam discharge outlets connected to delivery piping which terminates at a safe distance from the hazard with pumping in connections for Fire Brigade use.

Foam concentrate and water requires transporting to the incident. Installed fixed fire protection for storage tanks will include the following: foam chambers, those are fixed discharge outlets attached to the outside tank shell, so designed to apply foam directly onto the surface of the burning fuel. These systems are commonly used for the protection of both cone roof, open top floating roof and covered (internal) floating roof tanks.

As outlined in N.F.P.A.11, the number of foam chambers required on a tank will depend on the tank diameter. Foam chambers will be installed at equally spaced positions around the tank just below the roof to shell joint. For example an 180 to 200 foot (54m to 60m) diameter tank would require six discharge outlets to provide foam flow uniformly. Foam chambers are connected to a series of piping designed to transport the pre-mix foam water solution from the proportioning source located outside the tank dike wall to the foam chamber. The foam chamber may be supplied from either a fixed or semi-fixed foam system.
On external floating roof tanks foam chambers are designed to protect only the rim seal area. Depending on the diameter of the tank there may be only one foam chamber e.g. 150ft (45m) diameter; in many cases one foam chamber will be provided at the gauger’s platform area. However, on tanks with a diameter greater than 45m, multi-pour foam systems (chambers) may be fitted; this option may vary from oil company to oil company.

On covered internal floating roof tanks with steel or aluminium double deck or pontoon floating roofs, foam chambers are designed to protect only the rim seal area. Depending on the diameter of the tank there may be only one foam chamber e.g. 150ft (45m) diameter; in many cases one foam chamber will be provided at the gauger’s platform area. However, on tanks with a diameter greater than 45m, multi-pour foam systems (chambers) may be fitted; this option may vary from oil company to oil company.

At the foam chamber, sometimes referred to as the vapour seal box, is fitted a frangible seal (very thin glass) this is installed to prevent flammable vapours entering the foam piping. The seals are designed to burst when foam pressure is applied. Built into the piping system close to the foam chamber is a foam making generator. This generator contains an expansion tube and air inlets to aspirate the foam solution. Fitted inside the tank at the point of foam entry is a deflector plate, designed to ensure that foam is deflected onto the side of the tank to run evenly onto the surface of the fuel.

On external floating roof tanks foam chambers are designed to protect only the rim seal area. Depending on the diameter of the tank there may be only one foam chamber e.g. 150ft (45m) diameter; in many cases one foam chamber will be provided at the gauger’s platform area. However, on tanks with a diameter greater than 45m, multi-pour foam systems (chambers) may be fitted; this option may vary from oil company to oil company.

On covered internal floating roof tanks with steel or aluminium double deck or pontoon floating roofs,
One advantage of foam chambers is that each system is engineered specifically for a particular application ensuring that the foam is not wasted and foam is distributed evenly over the surface of the fuel. The primary disadvantage is that foam piping and chambers may be damaged by the internal explosion or dike fire. Foam discharge for rim-seal protection on open top floating roof tanks can be with the discharge systems located on the roof itself. These chambers can be designed for the protection of the seal area only. It is not uncommon for internal floating roof tanks to be protected against a full surface fire. In conjunction with the foam system on floating roof tanks, a foam retention dam is provided on the roof to retain the foam as it is produced, the foam dam normally would be 24 inches (600mm) high and no more than 2ft (0.6m) from the tank wall. Where secondary seals are installed the foam dam should extend at least 2 inches (50mm) above the top of the secondary seal. One advantage of foam chambers is that each system is engineered specifically for a particular application ensuring that the foam is not wasted and foam is distributed evenly over the surface of the fuel. The primary disadvantage is that foam piping and chambers may be damaged by the internal explosion or dike fire. Foam discharge for rim-seal protection on open top floating roof tanks can be with the discharge systems located on the roof itself.
Figure 5.16 Modified catenary foam system

Figure 5.17 High back pressure generators for base injection of cone roof hydrocarbon storage tanks

Figure 5.18 Base injection system typical arrangement

Figure 5.19 Base injection

Figure 5.20 Cojlexip foam system – layout

systems may either provide foam onto the top of the seal or supply foam beneath the seal, and may be either fixed or semi-fixed.

Top of the seal (catenary system) is primarily the same as described for foam chambers located on the tank shell. The principal difference is that the foam pourers and associated pipework are located on the floating roof. The foam solution line either runs up the side of the tank and down the internal ladder or through the inside of the roof. A flexible hose is used near the top of the system to allow for roof movement.

Below the seal protection (cojlexip method) is basically identical in design to that of seal systems. The primary difference is that the foam discharge orifice actually penetrates the seal.

5.1.7 Subsurface Foam Injection

Subsurface injection is where the foam is injected into the base of the tank and allowed to “float” to the top of the fuel where it forms a foam blanket over the surface of the fuel. Foam may be discharged into the tank either through separate foam delivery lines or through the tank’s product fill line. Many subsurface foam injection systems are semi-fixed. If separate foam lines are used they will be spaced equally around the tank to give uniformity of the flow of foam. It is most important that the foam is discharged above the layer of water and sludge commonly found in the bottom of the tank. High back pressure foam makers are required in subsurface injection systems to counteract the amount of hard piping and the head pressure of the fuel in the tank.

5.1.8 Semi-Subsurface Injection System

Equipment designed for these systems is basically the same as that used for regular subsurface
injection, the primary difference being the actual point of delivery of the foam. Semi-subsurface injection discharges the foam through a flexible hose that under pressure rises from the bottom of the tank up through the fuel to the surface. Under normal conditions this flexible hose is housed within a container at the base of the tank. Because semi-subsurface injection systems actually apply foam directly onto the surface of the fuel, the system can be used on tanks containing polar solvents as long as alcohol resistant foams are used.

### 5.2 Foam and other Media

Over the years the size of oil storage tanks has increased dramatically and this means that if a fire occurs (large open top full surface area fire) very large quantities of foam will be required to maintain a successful extinguishment. Although it is possible that chemical foam powders may still be found in some countries, modern methods rely on the use of mechanically produced foams, primarily protein based and synthetic foam concentrates.

Foam concentrates can be stored in bulk quantities, it is easier to transport in 45 gallon (200 litre) drums and bulk foam tanks carrying up to 5000 gallons (22,500 litres). Whilst serious fires in oil storage tanks are not frequent, storage tanks of 300 ft (90m) diameter are now common, marine tankers in excess of 350,000 tons (352,000 tonnes) capacity present a huge demand for foam concentrate should one become involved in fire. It is therefore not practical to use 5 gallon (227 litre) cans.

Each major petrochemical company will make its own decision in conjunction with the local authority fire and rescue service on its approach to pre-planning for a major fire/emergency. Included in those plans will be how best operationally to supply bulk foam concentrate to the emergency scene. It may be desirable to have self-propelled mobile foam tankers carrying up to 9000 gallons (22,500 litres) of foam concentrate, or foam trailer units carrying bulk supplies that require a tractor unit to hitch up and mobilise to the scene. Other means may be the use of flatbed lorries on which are fitted 225 litre containers that are manifolded together, in some cases the flatbed lorry may be equipped with a fork lift truck to ensure ease of movement of foam containers.

For special risks such as marine terminals, fixed pipework may be installed, suitably valved and fitted with pumping in connections whereby foam concentrate can be pumped direct to the area concerned by mobile tanker. One major oil company has a fixed 3 inch (76mm) hard piped foam line installed at the jetty with 2.5 inch (70mm) delivery valves fitted adjacent to each fire hydrant. When required foam concentrate is pumped by bulk tanker down the 3 inch (76mm) line. This type of facility helps to reduce congestion of equipment in such restricted areas.

Bulk storage of foam concentrate in elevated tanks adjacent to each fire hydrant. When required foam concentrate is pumped by bulk tanker down the 3 inch (76mm) line. This type of facility helps to reduce congestion of equipment in such restricted areas.

Bulk storage of foam concentrate in elevated tanks from which tankers can be quickly topped up during an incident can also be found. Whatever the merits of one system as compared to another, bulk foam supplies should be available.

**Local authority fire and rescue personnel who have the responsibility of attending an incident at the petrochemical plant must ensure that they are fully familiar with the resources available and have exercised in the appropriate methods to be used.**

### 5.2.1 Foam Making Equipment

Most petrochemical plants will be equipped with specialist designed first line firefighting vehicles, in many cases these vehicles will carry foam concentrate in varying capacities and may well be fitted with large output foam monitors. Water pumps ranging from 1000 gpm (4,500 litres) to 2,200 gpm (9,900 litres) being accepted as an industry standard. Large foam producing monitors of varying design for dealing with major fires in oil storage tanks and other risks, as well as a vast variety of smaller foam making branches, generators, inductors etc., will form a significant part of the firefighting inventory. (See Fire Service Manuals, Volume 1: Firefighting Foam – Technical and Volume 2: Firefighting Foam – Operational.) Large capacity foam monitors will usually be trailer units that can be towed by a fire appliance or other commercial vehicles.

Similarly a variety of bipod foam monitors will be included in the inventory; these monitors can be transported by hand. Large capacity foam monitors vary considerably in their output capacities 900 gpm (4,000 litres) 1800 gpm (8,000 litres) 3,500 gpm (16,000 litres) 12,500 gpm (56,000 litres) are now available to industry and local authority fire and rescue services. Availability of this equipment would be based on a quantified risk assessment of the plant or refinery to be protected.
5.2.2 Foam Pourers and Towers

Foam pourers (chambers) are fixed foam discharge outlets attached permanently to the outside shell of a storage tank, designed to flow foam directly onto the surface of the burning fuel. Foam pourers are installed on the tank shell just below the shell to roof joint.

5.2.3 Portable Foam Towers

Portable foam towers may still be found at some refineries. These portable towers are large pre-assembled and moved to the scene before foam is fabricated. Towers built mainly of aluminium or light alloy telescopic tubes, which are mechanically or hydraulically elevated, these towers are manually played a significant role in the successful extinguishment of a 100 ft (30.48m) diameter tank which may occur. Details should be agreed of the foreseeable fire, explosion, toxic or other hazard which may occur. Details should be agreed of the initial (pre-determined attendance) and make-up attendances of local authority fire and rescue fire departments. Facilities will also be provided at marine jetties to enable fire boats to be connected into the fire water system and if required pump water in-shore. At a number of refineries 6 inch hose (150mm) will be available to facilitate such a requirement.

5.2.4 Foam Wands

Foam wands based on the concept of the foam tower being smaller are easier to construct and manoeuvre on the fire ground. The wands available commercially have been constructed in the field at specific tank firefighting incidents, indeed they played a significant role in the successful extinguishment of a 100 ft (30.48m) diameter internal floating roof tank. Wands are normally constructed of steel or other fire resistant material. As with foam towers they are designed to hang over the shell of the tank and be supplied by foam lines. Light weight foam wands can be positioned manually whilst the heavier version will require the use of a crane or hydraulic platform.

5.2.5 Steam Lances/Spears

Steam is a valuable agent when dealing with fires involving vapour or gas leaks from seals or flanges of pipework. It is also useful on fires involving hot vapour lines especially where the temperature at the point of emission is above the flash point or auto-ignition temperature of the vapour or gas. Steam has the effect of reducing the temperature at the point of vapour of gas leak without causing excessive contraction of the metal, it also reduces the concentration of oxygen in the fire air surrounding the point of leakage. Many of the process plants require the use of steam and so use can often be made of the immediate availability of the medium in appropriate circumstances.

5.2.6 Steam Snuffing Systems

A dedicated piped steam smothering or “snuffing” system is recommended for control of fires resulting from process furnace tube rupture or failure in a header box. Adequate steam taps should be installed within the system and the steam lines to the furnace should be equipped with valves that can be operated from a protected area located at a safe distance from the furnace.

Fixed steam snuffing systems will also be found within process equipment for the protection of high temperature/pressure heat exchangers, where an unplanned release of hydrocarbon vapour could result in immediate auto-ignition.

5.2.7 Refinery Fire-Fighting Tugs

Some refineries maintain special firefighting tugs (See Fire Service Manual Volume 2 Marine Incidents). The vessels are provided specifically to deal with fires at marine jetties where the greatest risk is involved as tankers are discharging their cargos of crude oil, or are loading refined products. Firefighting tugs provide flexibility for a firefighting response when dealing with marine emergencies. Whilst most jetties are equipped with fixed fire protection, this is very vulnerable to explosion damage, the immediate availability of suitable equipped fire tugs offers a sea-borne firefighting option. A feature of these fire boats is the large capacity fire pumps, many modern vessels with a water output in excess of 10,000 gpm (45,000 lpm) and foam production exceeding 45,000 lpm. Some tugs are fitted with hydraulic platforms which give additional height and manoeuvrability to the monitors. A further feature now incorporated on a number of these vessels is oil pollution equipment, detergent spraying and oil retention booms.

Firefighting tugs provide flexibility for a firefighting response when dealing with marine emergencies. Incidents within the plant will normally be reported to the works fire station and where applicable will be passed on to the local brigade control. In many cases, the plant fire and rescue service may themselves deal with the incident and may only call for assistance from the local fire and rescue service for the more serious incidents. It is imperative that
mobilising arrangements should be clearly agreed so that there can be no possibility of misunderstanding so far as attendance is concerned. Any reduction in manning outside normal working hours should be taken into account when planning the initial attendance (P.D.A.), which may vary to different sections of the plant according to risk, but there must also be a ‘DISSAER’ plan by which mass assistance can be summoned immediately if the situation should warrant such an attendance. Plant ‘onsite’ major disaster plans would encompass such a requirement.

5.3.1 Attendances

Maps should be provided for issue to incoming fire appliances highlighting the various entrances to the petrochemical plant and the route they are required to take. The maps should indicate location of water supplies (emergency water supplies) plant fire station, foam storage area, communication points, holding areas for fire appliances. Incoming fire appliances should in the first instance report to an agreed rendezvous point (generally the plant fire station) and should then be directed on to a carefully selected assembly area.

5.3.2 Control

Overall control at a fire is vested in the senior fire brigade officer present. There should always be complete liaison, and the technical knowledge of processes and plant of the refinery fire officer will be invaluable to the local authority Incident Commander.

Specific arrangements should be made for incident control and allied responsibilities throughout the whole 24 hours and at weekends, including the recall by the refinery management of specialist personnel to incidents occurring outside normal working hours. The main fire control point should be arranged with regard to communication throughout the whole refinery and to the local authority brigade control. In most cases, the refinery fire station will be appropriate as it is generally well sited, constructed and equipped. An important point is that the main control should be usable in any situation which may arise, and where toxic gases may be released, it is essential that a respirable atmosphere should exist within the main control point. A secondary control point should be considered in appropriate circumstances.

Forward controls should be planned as appropriate so that they can report back without difficulty to the main control. These forward controls should preferably be completely mobile so that they can be quickly re-positioned as the situation requires. The guidance provided in the Fire Service Manual, Volume 2 Fires Service Operations – Incident Command should be taken into account when pre-planning operational procedures for dealing with petrochemical incidents. At one refinery the pre-plan includes the issue of a refinery portable radio to the first attending local authority fire appliance, to provide immediate communication with the fire ground. At large fires where a control unit attends, it should be clearly laid down in the pre-planning whether this will be stationed at the main control, or will act as a forward control. Local requirements will dictate the most suitable policy in this respect.

5.3.3 Foam Compound Requirements

At a major fire involving oil storage tanks, the demand for foam concentrate will be excessive. (See Fire Service Manual Fire Service Operations Foam and Foam Technical). Although all petrochemical sites maintain a stock of foam concentrate, a sustained foam attack using a number of large capacity foam monitors will quickly exhaust onsite supplies. It is essential that emergency pre-planning must, of necessity, consider how and from where additional foam supplies can be obtained. Most major suppliers have foam concentrate tankers available for instant mobilisation on a 24 hr call out system, drum stocks are also available but this will inevitably require manpower arrangements onsite and suitable transportation such as fork lift trucks and flat-bed lorries. In most cases local fire and response fire services have made mutual aid arrangements with industrial sites and airports for the supply of foam concentrate. Included in emergency planning will be arrangements for a control to be set up for the mobilisation not only of foam concentrate but in some cases the supply of large capacity foam monitors (e.g. six gun). Foam officers are also appointed both at brigade headquarters and on the fire ground, to co-ordinate these supplies.

5.3.4 Reliefs, Feeding etc.

The pre-planned emergency arrangements should also include the provision of relief crews and, where firefighters are likely to be detained for lengthy periods, for the attendance of canteen vans, or some other form of emergency feeding. Other pre-planned emergency arrangements include such details as:

- Medical aid
- The provision of dry clothing
- Safety officers to protect the safety of personnel
- The provision of a safety launch when men are working on jetties
- Arrangements for dealing with flooding and drainage
- Organisation for fire-fighting at sea
- Liaison with police for signposting, clearance of sightseers etc.
- Liaison with press and television
- Administrative matters for dealing with casualties and fatalities
- Possible arrangements with BT to deal with extra work at exchanges
- Feeding and rehabilitation of emergency response personnel
- Marshalling area for fire appliances.
Chapter 6 – Fighting Petrochemical Fires

6.1 Precautionary Measures

Because of the attention paid to safe working practices, losses due to fires and emergencies are relatively small, but the potential for major incidents exists and therefore the emergency response, if it is to be effective, must be planned and well rehearsed. It is a requirement that all petrochemical staff should receive instruction in the use of "first aid" equipment such as fire extinguishers, steam spears, portable and fixed monitors and breathing apparatus.

6.1.1 Non-ignited Releases

When flammable liquids or vapours escape from tanks, vessels or pipelines, every available means should be used to limit their spread and prevent ignition. Once the extent of the contaminated area has been defined the area should be closed off using suitable signs - road barriers.

Preventative action may include the use of foam for vapour suppression, and use of water curtains for vapour dispersal. Spills should be cleaned up as quickly as possible, this may well involve the use of vacuum trucks to remove liquid spillage. Once liquid spillage has been safely removed common practice is to lightly cover the affected area with sand or other absorbent material.

6.1.2 Oil Leaks

If a leak or line failure occurs in an oil product line, pumps should be shut down and block valves closed as appropriate, to isolate the line, if possible suction should be applied to the line involved to remove residual product and reduce volume flow in area of leak. Should the leak involve a tank or relatively large vessel, operations personnel should attempt to transfer product. Consideration may be given to pump water into the vessel or tank during product removal to raise product level above any leak.

Preventative action may include the use of foam for vapour suppression, and use of water curtains for vapour dispersal. Spills should be cleaned up as quickly as possible, this may well involve the use of vacuum trucks to remove liquid spillage. Once liquid spillage has been safely removed common practice is to lightly cover the affected area with sand or other absorbent material.

NOTE: Crews attempting to disperse a vapour cloud should NEVER enter the vapour area, and must have protection of water fog available at all times. Where possible portable monitors should be used.
6.1.3 Gas Leaks

In the event of a leak in a gas or L.P.G. line or vessel, consideration should be given to shutting down furnaces near the release, where possible the use of steam to provide a positive pressure within the furnace itself should also be considered.

It should be remembered that it is possible for vapours to be ignited from hot metal or refractory lining within the firebox. Every effort must be made to direct vapours away from furnaces by the use of water spray, utilising initially any fixed monitors sited within the vicinity. Petroleum vapours and L.P.G. vapours are heavier than air, any such release will follow low contours of the ground and blanket large areas under still weather conditions.

6.2 Use of Water on Petroleum Fires

Water is the best and most effective agent for controlling oil fires. However compared to the use of water on solid material fires there are differences in the way it should be used, and in the things it can accomplish. Water is cheap, usually comparatively plentiful, and has a higher specific heat than other liquids, which gives it excellent cooling properties.

In the burning of most substances, the actual combustion takes place only after the solid or liquid fuel has been vaporised or decomposed by heat to produce gas or vapour, and the visible flame is the burning gas.

When water is applied to a fire in wood or other similar combustible material, its principal effect is to cool off the unburned wood, stop the evolution of vapour from it and thus starve the flame which feeds upon this vapour. Ultimately it will quench the red hot embers to complete extinguishment. However, if water, preferably in the form of light spray, is applied to the surface, the surface will be cooled down, the release of vapour to feed the flame will cease, and the fire will be extinguished. Thus for fire in some kinds of oil, water is well suited for extinguishment, and a similar situation in much the same way as it does with wood or other ordinary combustible materials. For heavy oils in the 'high flash' category, cooling is a means of reducing the vapours which feed the fire. Use water in the form of fog or a fine spray, never use a jet. In considering the lighter flammable liquids in the 'low flash' category a very different situation prevails. These oils give off sufficient vapour to burn at ambient conditions. Any water reaching the oil surface will not boil; it will probably sink to the bottom without being greatly heated, hence its cooling effect is negligible. The principal effect which it will have will occur within the flame itself, where of course any small drops will be vaporised and will remove heat. But here we are fighting the flame, not the fire. In general water is ineffective as an extinguishing means of fires fed by gases or vapours from volatile oils.

However, there are important functions that water can perform. Consider what will happen if as a result of an accident, a pipe is broken and gasoline leaks out at the rate of say 45 litres per minute. Assume that this gasoline is ignited immediately. The fire area will be small at first, but will speedily enlarge until the area is sufficient to consume all of the fuel just as it escapes. (The burning rate will be approximately 6 litres per min per m²). A leak of 45 litres per minute will produce a fire area of at least 7.5 sq. m. It could grow no larger because the fuel is being burned up as fast as it is supplied; it will not grow smaller because just much this fire area is required for air access, heat transfer and vaporisation, to balance the feed rate.

What will happen if a water stream is applied?

Some of the water will be in small drops even if a straight stream is used. Some of the small drops will be evaporated to absorb heat from the flame, thus slightly decreasing the rate of heat transfer to the oil surface. The water reaching the surface will slightly cool it, decreasing the vapour release. Both effects will be to decrease the burning rate per square metre. Since the fire is being fed, the fire (if not stopped by bund walls, etc.) will expand its area to make up for the decreasing burning rate. The fire will spread. Of course, if it is so restrained that it cannot spread, the level will rise until the enclosing walls cease to be able to contain it. Remember, this is a gasoline fire, most of the water used on such a fire will end up beneath the oil, floating it so as to raise the level; this also will tend to make it overflow any existing restraining walls.

In summary, water is an effective extinguishing agent for 'heavy' oils, but it cannot extinguish a fire involving gas or light oils, except under highly unusual circumstances.

6.2.1 Cooling

Water is used to cool or protect buildings, structures, tanks etc., from heat or flame impingement. Flame contact may heat steel structures so they weaken and ultimately fail. Water properly applied (in the form of fog or spray) and in sufficient quantity (generally estimated at 10.2 litres per min per m²) can absorb the heat and prevent damage. It is important to remember that many of the liquid petroleum products which will be encountered have boiling points well below 100°C. Gasoline and kerosene start to boil below 100°C, the boiling point of water. If a tank or vessel contains such an oil, the part of the shell which is below liquid level will be kept cool by the liquid inside. Even though the liquid contained in the tank is boiling, the steel which it contacts cannot get very hot. Water applied to the lower oil-wetted parts of a tank may run off barely warmed, and thus be largely wasted.

Water does its most effective job of cooling when it is converted into steam. As far as steel tanks and other similar petroleum equipment are concerned, the working rule is that priority cooling must be given to equipment that is being touched by the flames. The parts of the equipment that are invisible because they are in the flame are the parts which need the protection; the equipment which can be seen is less likely to be endangered. For cooling of adjacent tanks one third of the surface area should be used for calculation purposes.

Water is the best and most effective agent for fighting the flame, not the fire. In general water is ineffective as an extinguishing means of fires fed by gases or vapours from volatile oils.

However, if water, preferably in the form of light spray, is applied to the surface, the surface will be cooled down, the release of vapour to feed the flame will cease, and the fire will be extinguished. Thus for fire in some kinds of oil, water is well suited for extinguishment, and a similar situation in much the same way as it does with wood or other ordinary combustible materials. For heavy oils in the 'high flash' category, cooling is a means of reducing the vapours which feed the fire. Use water in the form of fog or a fine spray, never use a jet. In considering the lighter flammable liquids in the 'low flash' category a very different situation prevails. These oils give off sufficient vapour to burn at ambient conditions. Any water reaching the oil surface will not boil; it will probably sink to the bottom without being greatly heated, hence its cooling effect is negligible. The principal effect which it will have will occur within the flame itself, where of course any small drops will be vaporised and will remove heat. But here we are fighting the flame, not the fire. In general water is ineffective as an extinguishing means of fires fed by gases or vapours from volatile oils.

6.2.2 Water Application

Water applied to an oil fire may be used in two principal forms - spray (or fog) and straight stream, and each has its particular advantages, disadvantages, and scope of application. In general the straight stream has the greatest range of driving force, the wide angle spray (or fog) has short range and affords the maximum protection for the firefighter. An in between position, which combines the two, will in most cases be the most desirable. A dense spray of water may be used as a barrier between flame and firefighters, to protect them against radiant heat. Thus permitting closer approach for such important steps as closing a valve to shut off the flow of fuel feeding the fire. The object is to get the water, in the right form, to the place where it will have the most effect as a cooling or extinguishing agent.

Most of what has been previously said relates to the cooling effect of water. The mechanical effects are almost of equal importance. The place where oil burns may be very important. Oil floats on water, and flooding a fire area may cause burning oil to flow over to an area where it could cause further fire escalation and damage to the plant. Or, it might be diverted into an area where it could burn without doing any damage at all. This may be accomplished by the combined effects of floating and the force of hose streams. If a container develops a bottom leak, injecting water may float the oil above the level of the leak. This method has been tried to stop the flow of product feeding an otherwise uncontrollable fire. Water for this purpose can be supplied at any level, but DO NOT overflow the tank. The rate of water addition must match the rate of leakage once the bottom water level has been established. Careful monitoring is essential.

6.2.3 Use of Foam

It is generally accepted that for major fires requiring the use of large volumes of foam concentrate, foam equipment should not be brought into operation until logistics have been met, e.g. water supply – foam concentrate supply, suitable equipment to project foam onto the fire are adequate and assured to extinguish the fire.
A premature attack would not reduce the fire potential, indeed it would only waste valuable and limited foam stocks.

The object in the use of foam is to provide a non-flammable layer between the surface of the fuel and the burning vapour above. The primary purpose of this layer is to cut off the radiant heat emitted by the zone of combustion which heats the surface of the liquid and causes the evolution of vapour - the only source of fuel for the flames.

Secondary effects of the foam layer may also be the restriction of air supply and cooling of the liquid surface.

### 6.2.4 Behaviour of Foam and Application Rates

Chapter 7 of Fire Service Manual, Volume 2 Fire Service Operations - Firefighting Foam, gives details of foam behaviour and application rates when dealing with storage tank fires and various scenarios are discussed.

### 6.2.5 Use of Various Types of Foam Branches/Foam Monitors

Because of the wide divergence of foam-making branches and foam monitors which may be in use at petrochemical plants, it may be helpful to tabulate the requirements of those which are likely to be found.

Table 6.1 shows the type of equipment, pump operating pressures, foam solution flow-rates, 3% foam concentrate demands and Estimated Maximum throw.

<table>
<thead>
<tr>
<th>Foam-making equipment</th>
<th>Inlet pressures (typical)</th>
<th>Foam Solution flow rates (typical)</th>
<th>3% Foam Concentrate demands (typical)</th>
<th>Est. max. throw distances (typical at 37° elevation)</th>
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<td>Imp. Galls/min</td>
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On a large diameter tank fire depending on type of equipment available, it may require four, five or even more foam monitors to provide the required foam application rate, this would entail perhaps 10 to 15 pumping appliances to provide the water supply. When considering the congested areas around tank farms and process plants, the question of marshalling this number of pumps and siting foam monitors around a tank on roads not necessarily designed for such traffic poses quite a problem for the fire officer. The necessity for pre-planning and exercises becomes apparent.

#### 6.2.6 Mounting a Foam Attack

Further detailed guidance on using foam for firefighting is contained within Fire Service Manual, Volume 2 Fire Service Operations - Firefighting Foam and the guidance contained in that manual should be applied as appropriate for petrochemical incidents.

In general, conditions at hydrocarbon fires vary so widely that it becomes difficult to generalise on the methods of applying foam. As has been documented, ample quantities of foam concentrate must be available to enable a foam attack to be mounted and whilst further stocks are being accumulated and equipment positioned, fire exposures should be protected with cooling streams (preference for oscillating monitors) reducing the risk to personnel.

### 6.3 Extinguishing Petroleum Fires

Many fires at large refineries are often successfully dealt with by the refinery firefighting personnel, and the role of the local authority fire brigade is generally one of reinforcing refinery firefighters when larger fires occur. The technical knowledge of refinery fire officers can be invaluable to a local authority fire officer if, by virtue of his rank, he will have to take command of a large fire at a refinery; good liaison is therefore essential.

Firefighting, to be effective, involves both fire control and fire extinguishment. Prevention of fire spread often determines the success of extinguishing efforts. This involves the protection of tanks, other structures and pipelines that are affected by radiant heat or by direct flame impingement. Cooling streams of water should be directed so as to give adequate water coverage without waste. The maintenance of adequate drainage of a fire area will prevent floating blazing oil igniting unfired areas, and often provides a means of removing fuel with consequent salvage of product and plant. The construction of temporary drains, ditches and dykes is also a phase of fire control which is especially valuable if a boil-over becomes imminent. Blanketing unignited pools of oil with foam will also guard against fire spread.

Fires in storage tanks can be extremely hazardous, and as a general rule firefighting personnel should NOT be allowed to go on to the roof of a tank which is on fire, unless it is essential for rescue purposes.

Refinery personnel with their technical knowledge will sometimes deal with small fires in tanks, particularly at the seal of floating roof tanks, at roof level; generally they will try to deal with the fire from the wind girder at the perimeter, using a single or multi-pour foam system, or failing that using handlines. Conditions on the top of a floating roof tank can be dangerous, especially when the pontoon is low, as vapour can collect above the pontoon if there has been a leak at the seal, standard operational procedures for rim seal fires should be actioned.

The following factors need to be considered before going onto the roof of an external floating roof tank:
- Have all measures to extinguish the fire without having to go onto the roof been taken? i.e. direct or indirect foam system operated.
What extent of seal fire?

Have tank operations ceased?

Position of fire, is it below the access to internal ladder?

Position of floating roof, high or low?

Weather conditions prevailing.

Availability of protective clothing/breathing apparatus.

Safe access to the roof to size up the extent of the seal fire. Are there alternate routes of escape from the roof?

A floating roof lower than eight feet (2.5m) from the top should be treated as a confined space.

Is a foam dam fitted?

What is the availability of safety-harness and lines?

Possibility of escalation, e.g. pontoon explosion (if flammable vapour/air mixture present within pontoons).

Is product on the roof?

Is a fixed system available for fire suppression?

Are landing valves available for handline operation?

Successful fire extinguishment results from the systematic application of planned procedures. Those born of panic often add to the seriousness of the emergency, and at every stage, expert advice should be sought from operatives or refinery fire personnel who have a much greater and more intimate knowledge of the processes and risks involved. Refinery personnel will attend to such control procedures as elimination of fuel supplies by closing pipeline blocks or by routing flow elsewhere, depressurising systems, blowing down a complete unit or pumping out tanks. A water displacement procedure may be suggested whereby water could be introduced into equipment from which flammable liquid is leaking, although this can only be done if the temperature of the hydrocarbon is below the boiling point of water, such action will be closely monitored by plant operations supervision.

6.3.1 Process Unit Fires

These are extinguished principally by fuel removal. This depends upon operatives being able to reduce pressure, introduce steam or nitrogen to the systems and to depressurise part or all of the unit involved. The area and intensity of the fire will indicate the proper method of extinguishment. Small fires can be contoured with dry powder or steam, and foam should be used where it can blanket the burning fuel. Water in the form of fine spray is most effective on large areas or intense fires that threaten damage to supporting structures and adjacent equipment. Care should be taken in the use of water, as contraction may cause flanges and joints to leak, thereby adding more fuel to the fire. The water stream should be adjusted where necessary to very fine spray to lessen this danger.

Tower structures, such as fractionating towers, which form part of process units are often difficult to deal with on account of their height. The first step is always to get the feedstock shut off and the system taken out of service and depressurised. Water from spray branches may not have sufficient trajectory to reach fire at the top, and it may be necessary to use large solid jets which can be trained either to impinge on each other so that the spray is carried on to the structure, or so that they break up near the top of the structure and the wind or convection currents carry the spray to the tower. The jets must not be played directly on to the structure. If quantities of oil are flashed to lower levels and continue to burn in pools, foam or dry powder should be applied. Large fire areas should be covered with water spray so as to protect supporting structures, especially while operatives attempt to control the supply of fuel. Fixed deluge systems will be an added advantage.

It should be remembered, however, that water streams used on surrounding risks will soon flood the area and may float the contents of oily water drainage systems to the surface in a short time. To prevent flash over and immediate danger to personnel, a foam blanket should be laid down quickly and maintained even after extinguishment until all possible sources of reignition have been checked.

It should be remembered that where large quantities of water are being used, much of it will run to waste. It may be possible to recycle the water, i.e., to use pumps at suitable places where their suction can be directed back on to the fire.

6.3.2 Fixed Roof Tank Fires

On tanks from which the roof has blown or on which a seam has opened, foam should be used. Where fixed foam facilities exist, these should be used in the first instance if possible, providing sufficient foam concentrate is available, but if foam cannot be applied immediately, the tank shell should be protected, particularly near the fixed foam chambers.
and riser with cooling water, until foam is ready to be used through this equipment. If there are no fixed chambers or risers but portable foam towers are available, foam should be applied through these and discharged over the rim of the tank in sufficient quantity to maintain the recommended minimum delivery rate i.e., at least 1 gallon of foam per square foot (50 l/m) of surface area per minute. Advantage can also be taken of fixed multi-pour foam systems on floating roof tanks, directly exposed to flame contact or radiated heat, to assist with suppression of hydrocarbon vapours within the seal area.

Foam towers should not be erected and placed over burning tanks until such time as the equipment necessary to produce foam is ready. Without the cooling effect of the foam passing through the towers, they will be liable to rapid overheating and collapse. With some types of tower, foam should not be pumped through them until they are resting against the tank shell, as they are not designed to handle the hydraulic load without the support from the shell. Normally, however, portable towers are only supplied at a refinery to replace fixed chambers that may be damaged in an initial explosion, so there may not be sufficient available to give the required rate of foam application. If portable towers are not available in sufficient number, foam monitors should be used.

Initially, fires burning outside the tank should be extinguished to avoid heat being applied to the tank shell. Fires in bunded areas, however, associated with tank fires are infrequent.

Cooling water should be applied to the tank shell above the liquid level and to any intact portion of the roof of the burning tank, provided that the water running off does not enter the tank.

**Water streams should on no account be directed into the tank as this will destroy the foam blanket and possibly cause a slop-over or a boil-over.**

Any tanks within 150 ft (45 m) downwind of the tank on fire should be cooled with water streams. Cooling a tank, the contents of which have not ignited but which is exposed to the heat of an adjacent fire, by means of water applied to the roof and/or shell, will prevent excessive evaporation and will lessen the danger of fire spread. Alternatively, screens of water can perhaps be projected downwind between tanks at risk. The spray must be angled as wide as possible and should be at a height sufficient to prevent flames passing over the top of the spray curtains.

If the tank contains asphalt or other heavy stock and the roof has blown clear, one method of extinguishment is that water streams should be directed high into the air upwind so that the spray will fall through the flames into the burning oil. This will cause foaming and may extinguish the flames. Such an application of water, however, must be done very carefully in intermittent waves to avoid an extensive slop-over. If foam is used in attempting extinguishment, it should be introduced at one point only and must be shut off immediately if a slop-over occurs.

(a) **Slop-overs.** The probability of slop-overs should be reckoned with under the conditions conducive to producing them. Sometimes when the tank is almost full and has little outage at the beginning of a fire, the thermal expansion of the oil may cause sufficient increase in the volume of the oil so that the contents overflow. These preliminary overflows are referred to as ‘slop-overs’ and although they may look serious they are usually small in extent.

Slop-overs may occur at almost any time during the fire. They may occur spontaneously with ‘wet’ oil (i.e., oil containing a percentage of water); they may occur from the sudden application of foam; from rain or sprays from branches, or they may result from the thermal expansion of the oil as it heats or from boiling of the surface.

**Warning of a slop-over is given by the lighter colour of the smoke at the top of the tank on the windward side owing to the formation of steam, while a sizzling sound indicates wetness in the oil. If conditions are such that a slop-over is likely, preparations should be made to extinguish any burning oil which may reach the bunded area by water from hose lines equipped with fine spray nozzles. All firefighting personnel should be withdrawn to outside the bund wall whilst such conditions prevail.**

(b) **Boil-overs.** Some crude oils and unrefined oils when burning develop a ‘heat wave’ that travels downward from the burning surface at a rate of from 15 to 20 in. (380 to 1,270 mm) per hour. The temperature of the oil in this heat wave may reach 250°C to 300°C, that is well above the boiling temperature of water. When this heat wave reaches
the bottom water or reaches the bottom oil in which sufficient water is suspended, a violent ‘boil-over’ will occur. A boil-over is a sudden eruption under the liquid whereby some of the liquid is carried out with the generated steam. Since water flashed into steam increases in volume 1,700 times, if the steam be entirely held by the oil, one gallon of water would produce 1,700 gallons of froth. Unless this frothy steam can break out on the surface in large bubbles, it becomes entrained in the oil and a wave of burning oil which may amount to several hundred tons is thrown out. The burning oil first violently erupts and then falls, possibly spreading beyond the bund walls of the tank. Pre-fire planning should take into account that up to four tank diameters could become involved.

Three conditions must exist simultaneously if a boil-over is to occur, namely:

(i) water must be present;
(ii) the oil must produce a heat wave;
(iii) the oil must be viscous enough to form a froth when the heat wave hits the water and turns it into steam.

An oil containing fractions of widely differing gravities and boiling points can be expected to cause a heat wave as it burns, and the production of this heat wave and its rate of travel is mainly caused by the impurities and free carbon in it. Distilled oils, such as petrol, kerosene, diesel and lubricating oils with their narrower boiling ranges and lack of impurities do not produce a heat wave. The daily oil inventory which is maintained at each refinery should be consulted to determine the product in the tank, and bottom water gauges will confirm if and when a boil-over is expected.

A boil-over is usually preceded by a marked heightening and brightening of the flames for a period of a few minutes, and the officer in charge should always be on the lookout for these warnings (or should delegate an officer for this purpose) so that positions of safety can be sought (Safety of personnel). The signs of warning of a boil-over are somewhat similar to those for a ‘slop-over’. A vertical stripe of temperature paint can be used on tanks to indicate the progress of the heat wave, use of thermal imaging camera could be an advantage.

Where no indicator paint is available, water thrown on the side of the tank will indicate the bottom of the hot layer. The location of the heat wave can also be determined from the wavy appearance of the air adjacent to the shell of the tank at the depth to which the hot oil has reached.

If extinguishment has not been achieved by the time the heat wave has reached a point 5ft (1.5m) above a known bottom water level, all personnel must be immediately withdrawn from the area.

It may be possible to use the draining pipes at the base of the tank to remove water, and so reduce the chances of a boil-over. There is a danger in using this procedure as it may not be possible to close the drain valves once they have been opened, with the

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<tr>
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<th>Rate of expansion of ‘heat wave’ per hour</th>
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After a boil-over has occurred, the oil at the base of the tank will have been cooled, but subsequently it will again be heated by conduction from above. A second heat wave may occur and if there is any water at the bottom, a second boil-over will occur. This sequence can continue so long as there is any water in the tank. Incident Commanders should therefore continually be on their guard against the possibility of successive boil-overs.

Because there is no vapour space beneath the roof of a floating roof tank, there should be no danger of product in the tank, and bottom water gauges will confirm if and when a boil-over is expected.

A boil-over is usually preceded by a marked heightening and brightening of the flames for a period of a few minutes, and the officer in charge should always be on the lookout for these warnings (or should delegate an officer for this purpose) so that positions of safety can be sought (Safety of personnel). The signs of warning of a boil-over are somewhat similar to those for a ‘slop-over’. A vertical stripe of temperature paint can be used on tanks to indicate the progress of the heat wave, use of thermal imaging camera could be an advantage.

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The same precautions should be taken for any
fire is of such a magnitude to affect other tanks. Floating roof tank seal fires are not, however, usually of great magnitude.

Should the floating roof have been displaced by explosion or fire, the fire should be tackled with foam as for a fire in an open tank.

6.3.4 Storage Tank Vent Fires

If a fire at a tank vent is burning with a yellow-orange flame emitting black smoke this indicates a vapour-rich condition within the tank that is above the flammable or explosive limits. This type of fire is usually dealt with by refinery personnel by smothering with steam, dry powder, carbon dioxide or wet blankets. Danger of an explosion is not indicated under these conditions.

If a fire at a tank vent burns with a snapping blue-red nearly smokeless flame this indicates a vapour-air mixture within the tank that is within the flammable range. There is danger of an explosion should the flame reach the inside of the tank and no one should go on to the roof while this condition exists. The vapour space of the tank might be converted into a vapour-rich condition by refinery operatives pumping liquid into the tank, thereby maintaining a positive pressure, or by the introduction of fuel gas or other light flammable products. When a vapour-rich condition is indicated by a change in the flame character to a smoky or yellow-orange flame, danger of an explosion has subsided. Extinguishment can then be attempted by smothering with steam, water spray, dry powder or wet blankets.

Any attempt to convert the vapour space within the tank into a vapour-rich condition should not be attempted by firefighters without prior consultation and agreement with responsible officials at the refinery, and every precaution must be taken to prevent exposure of personnel to the danger of explosion.

Any direct flame impingement on the shell, valves, piping, flanges resulting from a dike fire

Weather conditions (high wind, wind-direction, raining or not)

Status of dikes, drainage, any penetrations in dikes walls

Availability of water and foam supplies

Coned or floating roof (position of roof)

Direct exposures (cooling priorities)

Condition of fixed foam facilities.

Extinguish the fire using fixed foam systems (should they be intact) or a combination of remaining fixed systems supported by portable foam monitors for over the top foam application.

Cooling of exposures take top priority

The foam selected, proportioning percentages and foam application rates will depend on several factors:

Size of tank

Tank capacity

Flammable liquid involved.

Presence of fixed fire protection systems. The following general guidelines are provided.

N.F.P.A.11 recommended.

Minimum foam application rates. 0.10 gpm/ft (4.1 lpm/m) fixed systems application for hydrocarbon fuels (cone roof tanks with foam systems). Foam chambers – sub surface.

Any potential to extinguish a tank vent fire using only dry chemical must take into consideration that the pressure vacuum valve may have been damaged by heat from the fire and may not close after the flames have been extinguished. Under these conditions a P/V valve failed in the open position could enable FLASH-BACK into the tank if the fire is initially extinguished with dry chemical and re-ignition occurs. Flashback into a tank containing a flammable vapour/air mixture could produce an internal explosion resulting in the roof being blown off or severely damaged, with possible fragmentation.

6.3.5 Roof Partially or Completely Separated (cone roof tanks)

If the roof is still partially attached to the tank shell it may well restrict effective foam application, due to the surface of the burning liquid being obstructed by the wreckage, making extinguishment difficult. Foam chambers may also have been damaged.

Preplanning and the production of standard operating procedures will be of great value to the emergency responders.

6.3.6 Factors Influencing Level of Risk

Some factors that influence the level of risk at a tank fire will include the following:

- The flammable liquid on fire (hydro-carbon or polar solvent)
- Flash point of product (high or low)
- Temperature of product
- Level of product in the tank
- Status of tank e.g. was the tank being filled or emptied at the time of fire?

NOTE: Any attempt to extinguish a tank vent fire using only dry chemical must take into consideration that the pressure vacuum valve may have been damaged by heat from

Floating roof tank rim seal fire
Some factors which may influence the level of risk with a seal fire in an internal floating roof tank are as follows:

- Flammable liquid involved.
- Floating roof design (fibre-glass - aluminium pan).
- Status of tank. Had there been movement of product in or out at time of incident?
- Type of primary or secondary seals installed.
- Any direct flame impingement on the tank shell above roof level.
- Level and position of the floating roof, had the roof landed on its support legs.

6.3.9 Fire Management

Storage tank fires represent a major risk within the petrochemical industry, such incidents can pose a major threat to life and property not only to those persons on site but also to the surrounding community. When presented with a serious incident, firefighters can exert some control over the sequence of events, to keep loss of life and damage to property to a minimum. This will be achieved through confinement control, established operating procedures, tried and tested, realistic meaningful training with a common understanding of tank design, fixed fire protection systems, tank firefighting techniques and fully understanding the value of firefighting foam concentrates. Close liaison between industry and local authority fire and rescue service is of paramount importance, and every opportunity should be taken to train together.

Fire Management recognises that maintenance of fixed fire protection systems is critical to a successful operation. To achieve success in extinguishing a tank fire using mobile and portable equipment close attention must be paid to a number of important factors including:

- Adequate water supplies (is a supplementary water supply available?)
- Adequate foam supply (is a 24hr call out system to foam manufacturers established?)
- Pre-incident plans – individually prepared documents which focus on specific tanks in each facility providing all significant information concerning tactics, water and foam concentrate to comply with anticipated requirements (Foam Application Rates). Details of any fixed fire protection (foam systems – water deluge systems).
- Suitable foam making equipment that will meet the design foam application rate.
- Is operational access acceptable? Are there some areas with restricted access? (ie single approach – rail tracks – low overhead product pipework – road bridges with restricted weight.
- Adequate and effective communication systems.
- Large capacity foam monitors 14000 gpm (56,000 lpm) output demand large water flow rates. The use of large diameter hose six inch (150mm) complete with Hi-Vol distribution equipment is now being favoured by refinery fire departments.
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6.3.10 Overpressure Failures of Fixed Roof Tanks Exposed to External Fire.

Whilst in the industry many are aware of the floating tank seal fire scenario, the firefighter needs to be conversant with other fire mechanisms perhaps not so widely known. A multi-tank fire at an oil terminal in 1986 clearly highlighted the problem associated with severe ground (dike) fires providing an exposure hazard to a number of fixed roof tanks 40m diameter with products ranging from fuel oil, gasoline and crude oil. Generation of fire load vapours within these tanks resulted in the failure of the roof to shell seam occurring after 36–48 hours of severe external fire exposure. Firefighters were unable to provide cooling to these tanks during this period. The duration of induction period necessary to generate a vapour load that will overpressurise a tank depends on the product, product level, size of tank and extent of flame contact. In one 40m diameter fuel oil tank that overpressurised it is believed that an internal explosion was caused following a short induction period of ground fire (5 hours) as a direct result of “spiking” contamination (addition of volatile hydrocarbon) to the fuel oil. This theory was one attributed to the tragic loss of life in Venezuela in 1982 when a 180th (54.9m) diameter fuel oil tank boiled over during a full surface fire, taking the lives of 150 people and destroying 60 firefighting vehicles.

6.3.11 Heat Conduction

The firefighter should be aware that the prolonged heat input from external ground fires and internal surface fire when fuel oil is involved can result in the bulk of highboiling oil being so heated until any water at the bottom of the tank reaches boiling point. Under these conditions the heat transfer mechanism is thus primarily conduction rather than heat wave progression as when crude oil burns freely. It is not dependent on the presence of light fractions and would be favoured by the following: tank of small diameter; low product level; prolonged exposure to both external and internal fire. Under these conditions, the firefighter should consider the frottover scenario.

6.3.12 Fire Fighting Foam Attack

Much has been said and written regarding the use of major foam monitors when dealing with storage tank fires, for the “over the top” foam application, however, experts appear to agree that concentrated foam landing on small an area in the tank as possible is the best tactic, ensuring that sufficient foam reaches the fuel surface for a specified period of time. Remember that the thermal updrafts and the winds created by the fire are the natural enemy of foam. Common sense dictates that the foam attack should be concentrated on the windward side of the tank as the flames roll and escape from the tank rim, (sometimes referred to as the “window”). Circumstances will dictate just how successful the foam attack will be, based on a number of key issues, given that the foam application rate is achievable and that sufficient foam concentrate and water are guaranteed. Topography of the tank farm is important, whether it is a tank standing alone, is a tank in the centre of a tank farm, or is built into a hillside.

Consideration must be given to general accessibility for firefighting purposes, tank diameter and height, not least wind direction. Whilst it is accepted that larger foam production equipment is now available, many petrochemical companies still rely on the small capacity foam monitors. To use this smaller equipment effectively firefighters must recognise that under certain conditions it may be necessary to place such monitors within the dike of the tank on fire. It must be stressed that this is only acceptable when a refined product is involved, where there is no danger of a “boil over”. Once the required equipment is sited then personnel should be withdrawn to a safe area. Under no circumstances should fire fighters be committed to the DIKE AREA of a crude oil tank total surface area fire.

Basic precautions to consider:

6.3.13 Open Top Total Surface Area Tank Fires

(a) Tank operation (tank on fire)

- Pump out or gravitate tank contents at maximum rate, limited only by pumps and ability to contain product.

- Monitor product temperature by surface contact thermometer on pump out lines outside of dike wall. If crude oil is involved, remember that any product removal will enhance “boil over potential”.

- Consider use of tank mixers to disperse water droplets (this will be dependent on position of the roof).

- If safe to do so consider water run off. When tank cooling control depth of water in dike area using dike drain value, check dike walls for possible leakage.

(b) For crude oil tanks on fire

Do not operate within Dike area

- Create an area of 500m diameter as an exclusion zone - to all except firefighters. Do not assume that only one boil over may occur.

- For mounting a foam attack using smaller capacity monitors, site monitors as close together as is practical, keeping monitor streams together to land as one “foot print”.

- Make full use of the “Window Effect”.

- Prior to foam attack cool tank shell to assist foam sealing ability.

- Remember – on fixed roof tanks fitted with top pourer systems, whilst damage to the roof may have occurred it may still be possible to utilise all or part of the system.

6.3.14 Sunken Roofs with no ignition

- Floating roof tanks with partially/fully sunken roofs are vulnerable to full surface fires.

- Under such circumstances and faced with the problem of a sunken or tilted roof with an unignited surface area exposed, an immediate risk assessment should be made by operations personnel as to the inherent risk to safety and as to the inherent potential ignition sources, such as electrical storms (lightning) or the formation of a large vapour cloud that could reach other ignition sources, such as furnaces and vehicles.

- Stop product flow into the tank.

- Applying foam to exposed surface will assist in suppression of flammable vapours, but it must be done “carefully” - avoid plunging foam into hydrocarbon surface and ignition from static generation. Foam must be applied to run down the tank wall onto the fuel surface.

- The generation of foam and its subsequent discharge from the nozzle can produce an electrostatic charge which can cause ignition of the fuel. The breakdown of foam applied to a fuel surface into foam solution which then falls through the fuel as droplets of effectively water, is thought to have the potential to generate enough charge to cause ignition. Research has established that this problem relates only to non-conductive fuels (refined spirits) where there is an appreciable depth of fuel (more than 0.5m).

- Pump out of product should only be carried out after considering potential for frictional sparking from moving steel parts, the roof should be secured or if possible refloated.

- Landing the roof may result in the tank floor being punctured by the roof legs.

- Consider the use of a water curtain between process equipment (FURNACES) and tank involved.

- Resources should be deployed to deal with a total surface area fire.

Oxygenated Gasoline Blends (Methyl - Tertiary - Butyl rher)

- Oxygenated gasoline blends containing M.T.B.E and ethanol may be destructive to foam blankets at high concentrations. Currently M.T.B.E is typically 15% to 16% by volume and Ethanol is 10% to 11% by volume.
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- Oxygenated gasoline blends can be controlled and extinguished using fluoroprotein foam or an alcohol-resistant AFFF/ATC foam.
- There is currently no uniform consensus on a specific application rate for either neat M.T.B.E or M.T.B.E blends. Application rates between 0.16gprnlft (6.5 lprnlm) and 0.24 gprn/ft (9.8 lprnlm) are usually required.

6.3.15 Dike Area

Typical tank storage bunds in the U.K are 3m high sloping sided earth banks topped with a 3–4m wide roadway. The height of the dike (bund) wall as measured from outside ground level should be sufficient to afford protection for personnel when engaged in firefighting and the wall should be located so that a reasonably close approach can be made to a tank fire to allow the use of mobile firefighting equipment. In many cases, concrete stepped walkways are provided to give access to personnel. Concrete faced bund walls to prevent erosion by weather and vermin will also be found.

Special care is required in bund maintenance to ensure no points of weakness develop, product lines running through bund walls must be sealed to prevent any leakage of product spreading to other tankage.

As a general safe operating practice, dike areas should be treated as confined spaces during firefighting operations. Personnel required for operational necessity to enter a dike area, must follow standard procedures for safe entry and accountability.

A dike area fire can present the firefighter with many problems, not least radiated heat as experienced for many hours at a crude oil tank fire, 1983.

In the past many firefighting professionals have recommended fixed systems protecting storage tanks, but have had to rely on portable equipment for dealing with dike emergencies.

The U.K Standard B.5.5306. Sections 6.1 and 6.2 1988/89 is the first International Standard to recognise bunds/dikes as dangerous areas. It makes specific recommendations to protect bunds with foam at 4 litres/m per minute (polar solvents) and 6.5 litres/m per minute (hydrocarbons) with minimum application rates for 15 minutes duration using medium expansion, and 60 minutes duration using low expansion foam.

6.3.16 Spill Fires

This type of fire can be most difficult to deal with especially if it is flowing and being fed by a storage tank or pressurised pipeline. The source of the leak should be identified and isolated as soon as possible.

Should the leak be continuous (e.g. tank bottom failure) refinery personnel will endeavour to take the equipment out of service, however emergency personnel must be aware that this action may be prolonged over a course of many hours.

Small fires can be blanketed with steam or dry powder, but care must be exercised to avoid surface disturbance and spreading the burning product.

Larger fires areas should be attacked using diffused water spray in order to protect supporting structures, this attack should be maintained until refinery personnel can control the flow of fuel, the inherent danger of flash-back should be remembered.

Large pools covering greater areas should be blanketed with foam using low expansion and medium expansion foam branches, firefighters making every effort to apply foam gently where possible using spray techniques to avoid surface disturbance.

With a flowing spill fire it is generally best to commence at the furthest point of the fire and work towards the source of spillage, it is good practice to form a deep blanket of foam beyond the farthest this attack should be maintained until refinery personnel will endeavour to take the equipment out of service, however emergency personnel must be aware that this action may be prolonged over a course of many hours. A further complication can be created when spillage enters the refinery sewer system, situations will arise where flammable liquid causes explosions within the sewer network flowing into interceptor bays (oil/water separators); under these conditions large foaming operations may well be required.

6.3.17 Loading Rack Fires

Fires involving road tankers or rail cars at a petrochemical plant usually occur whilst filling operations are in progress. Loading operations should be stopped immediately, loading pumps shut down, emergency isolation valves in product lines supplying the loading rack should be closed (depending on design this may be an automatic operation linked into automatic leak fire detection). In the event of a fire situation, cooling water sprays from a deluge system, fixed monitors or portable trailer monitors should be used to provide protection, covering road tankers or rail cars.

In many gasoline road/rail facilities automatic foam deluge systems will be provided, supplemented by portable equipment.

Water from spray-branches should be maintained to cool the tankers and all metal parts and should be maintained after the flames have been extinguished until all danger of re-ignition has been eliminated, where foam has been used, ensure foam blanket is

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Figure 6.10 Tank and dike fires

Figure 6.11 Spill fire

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With a flowing spill fire it is generally best to commence at the furthest point of the fire and work towards the source of spillage, it is good practice to form a deep blanket of foam beyond the farthest point at the lowest level so that flowing burning product will flow beneath it and be extinguished. Under certain circumstances it may be necessary to dig a trench or provide earthen dikes to retain burning product, sandbags may also prove adequate.

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In many gasoline road/rail facilities automatic foam deluge systems will be provided, supplemented by portable equipment.

Water from spray-branches should be maintained to cool the tankers and all metal parts and should be maintained after the flames have been extinguished until all danger of re-ignition has been eliminated, where foam has been used, ensure foam blanket is
maintained (consider medium expansion foam for product coverage).

If possible close valves on a tank truck providing they are operable and accessible, to shut off supply of fuel to the fire.

Adjacent refinery equipment and other tankers should be protected by cooling. Where possible unaffected rail-cars should be removed from the vicinity.

6.3.18 Pump and Compressor Fires

- Shut down the machine involved and isolate.
- For small fires use steam or dry-powder fire extinguishers.
- If fire extinguishers are inadequate, cover the fire area with water spray from fixed or trailer monitors. Direct diffused water into the source of fuel until the operators have succeeded in isolating suction and discharge. Handlines may be necessary to protect operators should manual isolation be required.
- Apply foam to any trenches or drainage where burning product may accumulate.
- Maintain adequate drainage of the fire area.

6.3.19 Furnace Split Tube

- In case of a split-tube, the furnace may be shut down, if this action is implemented, fuel gas/oil supply to burners will be isolated and process feed stream through coil stopped. In event of fire, structural steel in the flame zone should be protected by applying diffused water from fixed or trailer monitors.
- Snuffing steam will be applied into the firebox, this will assist to control the temperatures inside the firebox and smother the fire.
- Should product escape outside of firebox (distillate fire) foaming operation maybe necessary.

6.3.20 Fire in Tower Structures

- Operators should immediately determine the source of release and isolate if possible. If it is a continuous release that cannot be stopped the equipment involved must be shut down, isolated and depressurised.
- Small fires may be tackled using steam or dry-powder fire extinguishers.
- Large area fires (pressurised until isolation is achieved, should be attacked using fixed monitors, trailer monitors and where installed degule systems, to protect supporting structures, elevated equipment and adjacent exposures.

Maintaining adequate drainage of the fire area is essential due to the high volume of water that will be required, light portable pumps may be required to remove excess water.

Pool fires should be considered for foaming over and area must be closely monitored.

6.3.21 Fires in Tanks Under Repair or Demolition

Although for the sake of convenience, this section is included in this chapter on oil refineries, it should be borne in mind that there are many wharves or industrial concerns where flammable liquids are stored in tanks, and it is generally in these smaller establishments where the greatest risk arises as they do not always maintain the high standards of safety and efficiency which are to be found at the major refineries. The firefighting techniques which are suggested for dealing with fires in tanks under repair or demolition should be taken as applying to all establishments where such work is carried out.

Information which will be of value to the fire brigade officer will include:

- The name of the Safety Officer or other person with whom contact should be made on arrival;
- The type of flame that is burning, whether it is oil, gas, or electrically produced;
- The nature of the contents of the tank;
- The pressure, temperature, and volume of the tank;
- The diameter of the tank;
- The location of the tank;
- The number of people accessible to help.

For small vessels, such as motor car fuel tanks, and tanks up to about 6,000 gallons (27,276 litres), both vapours and residues can usually be readily removed by steaming out. (Whenever steaming out is attempted, the steam nozzle should be bonded to the tank to dissipate the generation of electrostatic charges.)

With larger tanks, the problem is somewhat different. Owing to the high heat capacity of the tank, steaming out cannot be relied upon to volatilise all residues unless very large quantities of steam are readily available. However, explosive concentrations of vapour in the tank can usually be eliminated either by forced ventilation using a blower or eductor system or, for vertical tanks, by natural ventilation by removing top and bottom manholes. Ventilation by itself, however, will ultimately only remove the volatile materials present in the tank and will never remove the heavy ends or solid residues and tars. These types of residue themselves can contain considerable quantities of volatiles and unless they are removed, can and do give rise to a very high fire risk.

The types of storage tank most likely to be encountered are vertical cylindrical tanks, usually with a roof of light construction, either fixed or floating, or horizontal tanks of uniform construction without lightweight sections. These latter tanks generally present the greater hazard.

(b) General Precautions. If the fire brigade is called to a fire which has broken out when a tank is being demolished or repaired it will be likely that the proper safety procedure has not been observed. (Although it is less likely, fire may occur in any empty storage tank not under demolition or repair; but the advice in the following paragraphs is equally relevant.)

The situation should be treated as potentially extremely hazardous. Normally for a fire to be sustained in a tank there must be openings in the tank to admit air. If these openings are limited the fire may have extinguished itself before the brigade arrives. But even if the fire has apparently gone out, the vapour mixture in the tank may still be highly dangerous because the fire may have caused decomposition or vapourisation of residues which
may produce a flammable or explosive mixture, probably with toxic hazards as well.

**It should always be assumed that there is a risk of a violent explosion except when the top or end of the tank has been previously removed.**

In no circumstances should personnel go on top of or inside a tank in which there is a fire or in which one has recently occurred unless it is essential for rescue purposes. If it is essential to enter a tank, the probability of toxic hazards should be borne in mind and breathing apparatus should be worn. If anyone is on top of a tank, they should be told to come down. Nor should anyone go on top of an adjacent tank unless it is essential for operational reasons. No attempt should be made to open or close manholes or other fittings, because this may adversely affect the atmosphere in a tank. If forced ventilation is being used, for example by means of a blower or eductor, it should be switched off if this can be done remotely.

(c) **Firefighting techniques.** Neither water jets nor high or low pressure sprays must be directed into a tank in which there is fire (or a fire is suspected) because entrainment of flammable materials – i.e. gases or vapours – by the water can cause rapid mixing to give a potentially explosive mixture. Similarly, the cooling of the outside of a tank in which vapour has been ignited should be avoided, because of the danger of an intake of air following condensation of the vapours inside the tank. The following paragraphs describe alternative situations in which either firefighting procedures are recommended (differing according to the system of venting or inerting in use during demolition or repair, the nature and location of the fire, or the size of the tank), or it is suggested that the fire should be allowed to burn out. The advice should be regarded as no more than a general guide, because the action to be taken must in the final analysis depend upon the circumstances of each case, and be subject to a risk assessment.

In addition to deciding whether the situation is one in which one of the recommended firefighting procedures is appropriate, fire brigade officers should bear in mind that any attempt to tackle a fire will possibly involve some degree of risk to their men, and they must judge whether the need to save lives and/or to prevent further damage to the tank itself or the spread of fire to surrounding property justifies taking that risk. In any event whether the fire is fought or allowed to burn out, action should be taken to protect persons in the area from the effects of a possible explosion and to minimise the effect of radiant heat on adjacent property and installations.

(i) **Fire in a tank being steamed.** If a fire occurs in a tank which is being steamed, the supply of steam should be maintained and, if possible, increased as a means of both inerting the tank and purging it of hazardous vapours. If this is unsuccessful, the fire should be allowed to burn out, notwithstanding the possibility of explosion. Water should under no circumstances be used in or on the tank, for the reasons given in part (c) above.

(ii) **Fire in a tank not being steamed.** If a fire occurs in a tank not being steamed, then, unless it is clear when the brigade arrives that the fire has gone out, one of the following procedures may be appropriate:

- **If there is a gas or vapour flame burning outside an opening on the top of the tank,** an attempt should be made to achieve quick extinction by means of a high pressure jet from a distance in order to remove the risk of a flash-back. The jet should be swept quickly across the aperture, care being taken to avoid as far as possible large quantities of water either entering the tank or cooling the outside surfaces, for the reasons given in part (c). If the attempt shows no sign of immediate success, or after initial success the flame reappears, the attempt should be discontinued since the implication is that the primary source of the fire is inside the tank. In these circumstances the fire should be allowed to burn out notwithstanding the possibility of an explosion.

- **If there are signs of fire but no external flames are visible,** the fire may have to be allowed to burn out notwithstanding the possibility of explosion.

If, however, a bottom manhole is open, and it is felt that, for example because of surrounding risks, the fire must be tackled, this may be practicable in the following circumstances. Assessment of the location of the fire within the tank will be difficult because only a very restricted view of the inside of the tank can be obtained from a distance, and even this is likely to be obscured by smoke. It is still possible that the source of the fire inside the tank may either be visible or can be confidently estimated from a safe distance. If so, and if the fire is at the base of the tank, low expansion foam may be introduced. If, however, the fire is higher up and high expansion foam is available, it can be used provided its application does not entail undue risk to personnel and is operationally feasible.

If available, the use of carbon dioxide may be considered as an alternative to foam, but only if the tank is known to be on fire, because of possible static hazards during discharge operation which may themselves give rise to fire or explosion. Even if the foam or carbon dioxide does not succeed in extinguishing the fire it should have the effect of restricting it. Whatever extinguishing agent is used, it must be introduced only at entry points that are already open at the base of the tank.

(iii) **Fire in a small tank.** If a fire occurs in a small tank (which as a general rule should be regarded as one having a maximum capacity of approximately 2,000 cubic feet (about 60 m3) or 12,500 gallons (about 56,800 litres) which has only one manhole open, the fire can only be attacked by playing a low expansion foam jet through the manhole from a distance. It should be appreciated that this is a difficult operation to carry out.

(iv) **Fire in a tank with the top or end off.** If the top or end of the tank has been completely removed, normal firefighting procedure with low expansion foam or water spray should be effective and there should be no risk of disruptive explosion. Water should not be used if light residues are present and likely to float.

(d) **Subsequent action.**

In all cases the situation should be treated as hazardous. The period of danger must be regarded as lasting until the whole of the tank and its contents are cold – 24 hours should be sufficient for this. It will not always be easy to tell whether the fire has in fact been extinguished. It must also be remembered that the atmosphere in a tank in which a fire has occurred may still be both explosive and toxic and strict precautions must be observed before such tanks are entered. If the owner of the tank is a small operator (i.e. the tank is not at a major refinery) the operator should be warned that it is essential that all materials involved in a fire should be removed from the tank or other positions before demolition or repair work is resumed. He should also be advised to get expert guidance on what to do next, and to consult the District Inspector of Factories as to sources of advice. He should be particularly warned against further use of any heating device until expert advice has been obtained.
Chapter 7 - Liquefied Natural Gas

7.1 Fire Control Systems for L.N.G.

Liquefied Natural Gas (L.N.G.) vapour forms a highly flammable mixture with air, and so an accidental spillage in the bunded (diked) region around a bulk storage tank poses a severe cryogenic fire hazard. The most widely accepted means of controlling such hazards is by using high expansion foam.

Such cryogenic liquids are in fact gases at normal ambient temperature and pressure, but are stored at very low temperatures of around -164°C to reduce them into their liquid, rather than gaseous state. Clearly this makes processing, storage and transportation for distribution easier and more cost effective.

7.1.1 The Hazard

L.N.G. is 83-99 per cent Methane which, if ignited, generates vast quantities of heat radiation very quickly (93,000 kcal/m^2/hr), typically twice the heat produced by an equivalent quantity of gasoline/petrol. However unlike petrol the volume increase of L.N.G. gas from its liquid phase is around 600 fold.

Consequently, any accidental leakage of L.N.G. boils instantly, gaining heat from its surrounding environment, the ground, concrete, pipework and even the air into which it is rapidly evaporating. Initially the gas is heavier than air (as it is closer to its liquid storage temperature), but as more heat is absorbed with time, it gets closer to ambient temperature making the gas lighter than air. In this ‘lighter than air’ state the evaporating gas is carried away by the air currents and wind, and will ignite very easily at very low concentrations in air (typically 5-15 per cent volume). It is, therefore, the edges of the gas cloud that are most likely to find an ignition source causing a risk of explosion and rapid burnback towards the evaporating liquid pool. The plant and its surroundings will be seriously damaged by the radiant heat flux, unless proper provision is made to protect against such spill hazards.

The longer the spillage continues the larger the gas cloud is likely to become, although with time the spillage pool also dramatically cools the surrounding environment down towards the cryogenic temperature (~164°C). The rate of evaporation or ‘boil-off’ is consequently reduced, reaching a steady state where there may be insufficient heat input at the liquid/gas interface to make the gas lighter than air. The LNG could then spread out at ground level until ignition occurs – the longer the delay the bigger the potential disaster.

7.1.2 Controlling an L.N.G. Spillage

(a) Passive Protection

Firstly, the design of storage tank and its associated bunded or diked area to contain the spill is an important means of passive protection. A high bund wall serves to contain the L.N.G. spill and disperse the vapour safely to high level. Sub-dividing the bund with low walls or sloping sides to a deeper trough will also help to minimise the surface area for evaporation of the L.N.G.

When the bund wall is low, additional water curtain systems may be required to reduce the radiant heat flux to surrounding tanks and associated plant.

Tanks may be partially buried, often called ‘inground tanks’, with low bund walls to permit the
Figure 7.1 High bund wall protection.

Figure 7.2 Low bund wall protection with water curtain.

Figure 7.3 Partially buried with low bund wall and water curtain.

(c) Vapour Dispersion

Vapour dispersion is chosen to reduce the danger of an unattended L.N.G. spillage by assisting effective dispersion of the vapours that are boiling off. This reduces vapour concentration levels at ground level where there is greatest risk of potential ignition. One must accept that if ignition does subsequently occur this dispersion system may be insufficient to provide fire control.

(d) Fire Control

For fire control, the objective is to control the fire if ignition of the L.N.G. spillage occurs, preventing catastrophic failure. This is achieved by means of a controlled burn off that will also reduce the radiated heat flux to surrounding plant.

Clearly making the right choice here is crucial. Overall system cost for each of these two applications may well be a significant factor in this decision, since each system will need to have very different application rates, operating times and quantities of protecting equipment.

The first requirement for either scenario is a suitable detection system, which must be capable of immediately identifying any spillage that has occurred. This should be linked to a suitably rapid method of warning all site personnel and emergency services of the spillage hazard. This detection system must also establish whether the spillage has ignited.

Time to initiate actuation of the fire protection system is a critical factor in both scenarios, whether for L.N.G. fire control or L.N.G. vapour dispersion.

7.1.3 Standards

International standards like the American National Fire Protection Association NFPA 11A: 1994 and British Standard Institute BS5306 section 6.2:1989 both recommend high expansion foam systems for the protection of L.N.G. hazard areas. Recognising the complexity of this cryogenic hazard, neither standard provides any specific application rates (a measure of how much foam is being applied to the hazard area, each minute) or discharge times.

Factors affecting the overall effectiveness of any high expansion foam system are complex and interrelated. They include the:

- size of L.N.G. spill
- application rate
- expansion ratio
- foam concentrate (formulations vary and can produce widely varying performances)
- foam induction rate (accurate proportioning is crucial to consistent foam production)
- foam generator (different technologies will produce widely varying foam qualities)
- foam bubble stability (size uniformity and ability to retain water)
- depth of foam blanket
- speed of system operation
- prevailing weather conditions

7.2 How Does the Foam Work?

7.2.1 Fire Control

The gas produced by vaporising L.N.G. under accidental release conditions is at a temperature close to that of the L.N.G. itself (-164°C). Vapours boiling-off are heavier than air and form a cold vapour cloud hanging above the spillage. As one would expect boil-off rates are very rapid immediately following a spill during the so-called 'transient' phase, but soon settle down into a 'steady state' condition. Unless immediate action is taken, air movements will begin spreading this cloud horizontally in all directions from the spill until it is sufficiently diluted with air to become flammable. Then, somewhere at the edge, where the L.N.G. vapour is well mixed with air, forming a 5-14 per cent gas concentration, it will find a source of ignition, ignite and burnback to the liquid pool. If the L.N.G. vapours in this initial 'transient' boil-off phase do ignite, a major problem exists in addition to the vapour cloud— that of severe radiated heat. The degree of severity depends on how far away the fire is from surrounding buildings, plant and personnel on site, as well as the prevailing environmental conditions at this time. However, buildings a considerable distance from the fire will be at risk even during still air conditions and any wind will dramatically increase the radiated heat in the downwind direction, so protective action must be taken.

The mechanism for fire control using high expansion foam is quite complex. Essentially a foam blanket is rapidly produced to reduce the rate of heat transfer from the fire to the liquid L.N.G. pool, slowing the initial boil-off rate down to a steady state situation. Foam bubbles with expansions above 650:1 can provide a degree of fire control but achieve poorer reductions in radiation heat flux and are generally slower to achieve control than expansions of 500:1. Such higher expansions also generally require higher application rates and more frequent topping up to maintain fire control. Considerable test data has shown that an expansion ratio of 500:1 (when produced from a high quality foam concentrate) appears to be optimum for minimising the time required to gain control of an L.N.G. spill fire. Despite the intense radiant heat from the burning L.N.G. pool, the 500:1 foam blanket quickly freezes at the foam-L.N.G. interface. At this 500:1 expansion the foam freezes to form an open cellular ice layer, light enough to float upon the L.N.G. surface and also strong enough to support several feet of foam build up, without breaking or sinking. Near this interface ice tubes also begin forming where the escaping cryogenic vapours are boiling through the foam blanket. This occurs despite the presence of flames at the foam surface. Rapid application of such foam dramatically reduces radiation flux levels, with over 90 per cent reductions achievable, until the surface flames burn back the foam bubbles when further foam is applied to reach a steady state condition. Ongoing fire control is achieved by periods of topping-up after each burnback. Repeated applications of foam are continued until the L.N.G. pool has completely boiled away, vapour levels return to normal and the incident can be declared over.
Increasingly operators are opting to maintain fire control with foam rather than completely extinguish the fire with dry chemical powder, to avoid the risk of flammable vapour levels drifting or accumulating downwind and reigniting, causing increased danger to personnel and plant alike.

When a high degree of exposure protection is also required for controlling large L.N.G. spills, these high expansion foam systems can offer major cost savings over conventional waterspray exposure protection systems. Such water curtain systems are far less efficient at reducing radiation heat flux than results obtained with high expansion foam systems even though considerably higher water flow rates and supply pressures need to be used. This is especially significant on a first installed cost basis, since greatly reduced water flow rates and pumping capacities are required by high expansion foam systems. Operating costs would be higher for foam systems, but their anticipated usage should be severely limited and their effectiveness would be superior if needed.

7.2.2 Vapour Dispersion

Not all accidental spillages of L.N.G. ignite in the early stages of release. Some operators recognise that the configuration of their particular plant would mean a catastrophic failure if ignition took place, with the complete destruction of the facility, however quickly action was taken. In these instance high expansion foam systems can also be highly effective in dispersing the L.N.G. vapours upwards and away from potential ignition sources.

It is to minimise this risk of vapour ignition that such systems are required to take immediate action by covering the bunded area around these L.N.G. storage tanks with foam bubbles of uniform 500:1 expansion ratio.

This 500:1 expansion ratio foam covers the surface of the cryogenic liquid in its 'steady state' providing sufficient water content to warm the L.N.G. vapours as they rise through the foam layer. This buoyancy effect will reduce the down wind travel of flammable concentrations near ground level and assist dispersion of the L.N.G. vapours to higher and safer levels in the atmosphere.

As water slowly drains out of the foam it freezes on contract with the L.N.G. pool and forms an open cellular ice layer light enough to float on top of the L.N.G. and not sink through it. Additionally this ice layer is strong enough to support the several feet of foam above, which are necessary to maintain the heat input for the vapours to continue rising. A secondary but unstable ice-like solid may also form at the water-L.N.G. interface.

For a high expansion foam system to be effective the generators must be located at the edge of the bund (dike) wall or edge of the pump pit, so that any L.N.G. spillage can be quickly covered with foam either to reduce the risk of ignition by warming the vapours to disperse them directly upwards and away from an ignition source, or to reduce the radiated heat flux by fire control, if the L.N.G. has ignited already. Extended foam discharge ducting may be required on the outlet of each generator to ensure the foam bubbles are delivered onto the floor of the bunded (diked) area, shielded from the worst effects of wind. Such generators cannot be located remotely from the bund because of the potential foam transit time delay.

Another factor is similarly important here, that of wind. Unusually for a high expansion foam system, L.N.G. applications are normally outdoors.

7.2.3 Which Foam?

The choice of foam concentrate is also an important factor in optimising foam stability and expansion ratio, to gain maximum effectiveness, whether for Fire Control or Vapour Dispersion Systems. Lower quality concentrates usually exhibit less stability as indicated by their relatively faster drainage times (the time taken for 25 per cent of the water contained in a known weight of foam bubbles to drain out). When the foam is more fluid with less uniform bubble production, its effectiveness at reducing vapour concentrations above the foam blanket are significantly impaired. An increased frequency of 'topping up' will also be required to maintain the foam layer over a given period of time. Additionally the faster drainage of water from the foam bubbles at the L.N.G. interface may produce a deeper and less predictable, ice layer.

7.2.4 Conclusion

High expansion foam systems are the most credible solution to reducing the fire and vapour risks associated with L.N.G. Knowledge and testwork in this area is limited, further work is hampered by the extremely hazardous nature of the L.N.G. itself, the obvious reluctance from a safety standpoint in carrying out testwork and the costs involved in monitoring any test spillage. In addition to (and partly because of) these factors the amount of L.N.G. expertise around the world is concentrated within a few organisations who have made a substantial commitment to understanding these problems and investigating ways to overcome them with effective solutions.
Chapter 8 - Liquefied Petroleum Gas

8.1 Characteristics and Significance of Physical Properties

The term liquefied petroleum gas (L.P.G.) refers to varieties of hydrocarbons derived from crude petroleum processes or from natural gas, being gases at normal temperatures and pressures, but which become liquid with either a moderate increase in pressure, or a moderate drop in temperature, or both.

These hydrocarbons include propane, propylene, butane, isobutane and butylenes. The more liquefiable gases of this group are commercial propane and commercial butane, each of which may contain in varying amounts, several of the other hydrocarbons mentioned. Butadiene is also a liquefied petroleum gas; it does not occur naturally, but is obtained by process. It is chiefly used in the rubber industry and not as a constituent of L.P.G. fuels.

8.1.2 Density

Liquid L.P.G. is only half the weight of water. L.P.G. as a gas is twice the weight of air.

Being so much heavier than air, it is difficult to disperse and will gather and settle in low lying areas if allowed to escape.

8.1.3 Vapour Pressure

Vapour pressure varies exceptionally with temperature.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Butane</th>
<th>Propane</th>
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<tr>
<td>°C</td>
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Normal pressure relief valve settings on road tanker and storage vessels are:
- Butane: 100 psig
- Propane: 250 psig

8.1.4 Boiling Point

This varies with vapour pressure.

At atmospheric pressure, propane boils at -40°C and butane at -2°C.

The low boiling points and associated rapid vaporisation can cause severe first degree burns if allowed to come into contact with the skin.

Therefore, protective clothing such as gloves and visor/goggles, should be worn whenever handling L.P.G., particularly when making and breaking connections.

L.P.G. is colourless both as a liquid and a vapour. However when liquid L.P.G. leaks, this can often be seen as the cooling effect on the surrounding air causing condensation and even freezing of water vapour in the air. This may show itself as frost at the point of escape.
8.1.5 Coefficient of Liquid Expansion
The coefficient of liquid expansion for L.P.G. is 12 times higher than that for water.

100°F increase in temperature results in volume increase of liquid L.P.G.:

- Butane: 10%
- Propane: 17%

Ullage space must therefore always be left for safe storage.

Similarly if a liquid line is sealed by valves without a thermal pressure relief, a 10°F rise in temperature can cause a pressure rise of approximately 1 tonne per square inch.

8.1.6 Latent Heat of Evaporation (Vapourisation)
The latent heat of evaporation for L.P.G. is approximately 1/6th that of water.

- Propane: 102 cal/gm
- Butane: 96 cal/gm

Therefore, L.P.G. liquid requires only a small amount of heat to become gaseous.

When L.P.G. liquid stored under pressure spills, the following occurs:
- Rapid initial boiling
- Temperature drop and boiling slows down/ stops
- Liquid warms up and evaporates

Propane boils more rapidly than butane due to its lower boiling point.

This lower temperature associated with propane can also cause problems with vessels as the steel may become brittle.

8.1.7 Limits of Flammability (explosive limits)
The flammability of propane and butane range from a lower flammable limit (LFL) or LEL of just under 2 per cent in air to an upper limit of approximately 10 per cent in air at atmospheric pressure. At higher pressures the flammability range is increased.

Outside this range, any mixture is either too weak or too rich in L.P.G. to burn. Within the range, a risk of explosion exists.

Gas detectors are normally calibrated to give a 100 per cent reading at the lower limit of flammability of 2 per cent. Therefore, a 10 per cent reading will be equivalent to a gas/air mixture containing 0.2 per cent L.P.G. in the air.

8.1.8 Liquid to Gas Expansion
1 volume of liquid will create approximately 250 volumes of vapour.

Given the above limits of flammability, 1 volume of liquid could create up to 12,500 volumes of flammable mixture, and it has been known for such a mixture to be ignited hundreds of feet from the point of escape.

8.1.9 Odour
L.P.G. is odourless, but is normally saturated before distribution by the addition of an odorant such as methyl mercaptan, to enable detection by smell of the gas at concentrations below 0.4 per cent of the gas in air.

Note: New unsaturated butane for use as an aerosol propellant may not be odourised.

8.1.10 L.P.G. as Automotive Fuel
L.P.G. has been used as an automotive fuel in many countries for some time, and this trend is growing in the UK.

It should be noted that if in the event of an L.P.G. leak, particularly propane, the vapours enter the air intake to a diesel engine, the engine will begin to run wild and in due time will seize up.

In such an event, the emergency stop button on the engine will have no effect and the only remedy is to stop L.P.G. entering the air intake.

8.2 Factors/Events Affecting Evaporation and Spread During an L.P.G. Spill
Although predictions can be made on the amount of liquid L.P.G. that can be discharged from a broken valve or a split in a vessel (these are normally based on computer simulations), it is very difficult to assess how fast or how far an L.P.G. liquid will spread and evaporate.

Usually a judgement and risk assessment will have to be based on the following factors:
- Rate of spill
- Whether the spill is butane or propane;
- Propane spills boil rapidly, and temperature drops well below zero.
- Butane, any rapid boil quickly ceases, and evaporation can be relatively slow.
- Rate of evaporation affected by:
  - ambient temperature
  - weather conditions
  - slope of the ground
  - conductivity of the ground
  - surface area of the spill (any obstructions such as boundary walls will slow rate of evaporation).

REMEMBER – if water is sprayed onto an L.P.G. liquid spill, it will act as a heat source and increase the evaporation rate.

8.3 How Explosions Develop from Initial Low Velocity Flames

- Pressure and shock waves develop as the flame travels through large volumes of combustible gas. These increase burning velocity and pressure across the flame front.
- The limit situation is where the shock wave and the flame front coincide; Flame moves at local velocity of sound – approximately 3,000 metres/second.
- Very high pressure developed (20–30 atmospheres).
- Can occur very rapidly
- when gas is confined/uncconfined.

8.3.1 Types of Incidents Arising from Combustion
(a) 'Normal' fires
- Often result from immediate ignition following a spill
- Usually burn with a diffused flame with no explosion
- Radiation can ignite other combustibles in the area

Solution
- Cut off air/fuel supply to flame.

(b) ‘Flash Fires’
- Ignition of over-rich cloud of fuel in air
- Flame burns back against cloud
- Generally no explosion
- Can ignite other sources of fuel

Solution
- Vapour cloud fires/explosions cannot be stopped once started
8.3 Storage

(a) Identification

The gases are marketed under a number of different names which vary from country to country e.g. Sigas, Supergas, Shellgas, Calor gas, Botogas. Bulk storage may also be marked "L.P.G."

(b) Bulk storage

Storage methods will usually depend on the amount and the proposed use of the particular gas.

Conventional refinery practice is to store L.P.G., such as butane and propane as liquids under pressure in tanks or spheres.

Where the capacity is in thousands of tonnes, very large refrigerated storage vessels are used and the cooling of the L.P.G. enables it to be stored at near atmospheric pressure. Several of these facilities are

- Double wall tanks
  - They contain any escape of liquid. The space between the inner and outer shell is filled with an insulation material such as 'Perlite', and in many cases is nitrogen purged.
  - The main features of this type of tank are a low-temperature steel shell surrounded by insulation to minimise heat gain, with the insulation held in place by a waterproof outer cladding.
  - This type of tank contains both an inner and outer skin. The purpose of the outer skin is to support and protect the insulation and to contain product vapour and its pressure. It is not designed to contain any escape of liquid. The space between inner and outer shell is filled with an insulation material such as "Perlite", and in many cases is nitrogen purged.

- Single wall tanks
  - The main features of this type of tank are a low-temperature steel shell surrounded by insulation to minimise heat gain, with the insulation held in place by a waterproof outer cladding.
  - The planning of catchment areas for any liquid which might escape, and the provision of low diversion walls will tend to ensure that the liquid will be directed to run away from tanks, pipelines and valves to a suitable area where it can be dealt with safely. Likewise main valves are positioned where they will be accessible in an emergency.

Currently, there are two main methods of storing L.P.G. Deciding which method should be used usually depends on the quantity of L.P.G. that is to be stored. These methods are:

(i) At ambient temperature under pressure in spheres or horizontal cylindrical tanks. This method is used for the storage of relatively small volumes of L.P.G.

(ii) Refrigerated storage at atmospheric pressure. This method is usually considered economical only for amounts of more than 5,000 tonne of L.P.G.

There are two main types of tanks used to store L.P.G. in the full-refrigerated state; these are:

(c) Single wall tanks

(d) Double wall tanks
All tankers and pipelines incorporate a number of special features which are designed to ensure safe operation.

Cylinders are transported by delivery vehicles which are operated by the major L.P.G. marketing companies and third party contractors and also by thousands of small dealers and stockists. Again there are Regulations, Guidance Notes and Codes of Practice covering the correct carriage of cylinders, but as with storage, on occasions, failure to conscientiously follow the rules leads to accidents.

Bulk movement by sea, both around the country and for import or export, is also subject to strict regulation and is mainly carried out using three different types of L.P.G. carriers. These types are:

- The construction, maintenance and operation of these tankers and pipelines are subject to Regulations, Codes of Practice and other applicable guidance, including the Road Tanker Regulations, the Pipelines Act, HAZCHEM, the Railways List of Dangerous Goods (LDG), the various Codes of Practice of the Liquefied Petroleum Gas Association (formerly the LPGITA).

- Large scale storage of cylinders, at filling plants or large dealers’ premises is covered both by legislation and guidance issued by the Health and Safety Executive and the Liquefied Petroleum Gas Association. This guidance provides details of the segregation of cylinder stacks, separation from buildings, boundaries and fixed ignition sources, and the requirements for fire protection. If there is failure to comply with the codes, or a lack of supervision, mistakes will occur, and in consequence, serious and spectacular fires have and will result.

- The separation of the gases is carried out. Bulk movement of L.P.G. by land about the country is carried out by road tankers (up to 17 tonne per vehicle), rail tank wagons (from 20 to 100 tonne per wagon), pipelines and various combinations of these methods.

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- another method of bulk storage, which is only used in a few instances in the UK, is using huge underground caverns. These caverns are either leached from salt deposits or mined from rock formations. The stored L.P.G. is usually discharged by submerged pumps or, in the case of salt caverns, brine displacement may be used instead.

(e) Cylinder storage

The use of L.P.G. for many domestic and commercial purposes has meant that the number of different sizes of cylinders has proliferated.

Commercial propane and butane is used for domestic heating and cooking, industrial heating and furnaces, by roofing contractors and plumbers, in boats and other leisure activities, in animal rearing and horticulture, and in the case of propane, for oxy-propane cutting equipment, and as a fuel for vehicles, especially fork-lift trucks.

Re-fillable cylinders range from 8 to 108 litres capacity but there is also a large market for the smaller re-fillable cylinders e.g. camping Gaz, ranging from 1 to 6 litres, as well as small disposable cartridges.

L.P.G. cylinders should preferably be stored outside in a suitable secure compound, but indoor storage is permitted provided that special precautions are taken, including appropriate ventilation and flameproof lighting. Firefighters should be aware, however, that very often cylinders may be found in lockers in boats and caravans and virtually anywhere in premises.

On building sites, cylinders are frequently kept in site huts, firefighters should, therefore, always exercise caution in approaching such structures if they are involved in a fire.

Large scale storage of cylinders, at filling plants or large dealers’ premises is covered both by legislation and guidance issued by the Health and Safety Executive and the Liquefied Petroleum Gas Association. This guidance provides details of the segregation of cylinder stacks, separation from buildings, boundaries and fixed ignition sources, and the requirements for fire protection. If there is failure to comply with the codes, or a lack of supervision, mistakes will occur, and in consequence, serious and spectacular fires have and will result.

8.4 Transport and Distribution

The L.P.G. industry obtains its products from the oil refineries or from the North Sea land terminals where...
Horizontal L.P.G. bullets with deluge in operation

Bulk vessels at cylinder filling plants are required to have automatic fixed water drenching systems. The increase in pressure within the vessel would then cause the shell to rupture, resulting in a Boiling Liquid Expanding Vapour Explosion (BLEVE). If the radiant heat falls on the lower part of the vessel, where the L.P.G. is in the liquid phase, the liquid can absorb more heat, and the general consequence is that the pressure relief valve on the vessel will open to allow vapour to escape. The escaping vapour will then probably become ignited, and it will be necessary to protect the top of the vessel from radiant heat issuing from the relief valve.

Smaller bulk storage

For small domestic tanks, water drenching systems are not required, but a water supply for use by the fire brigade should be available within 100 metres. For tanks at industrial premises, dry powder fire extinguishers should also be provided, together with either a hose reel or water extinguishers. At commercial premises, if trained personnel are not available only water extinguishers need be provided for dealing with small incipient fires that may endanger the L.P.G. installation.

The protection of tanks from fire is the subject of various regularly revised and updated Codes of Practice and Regulations produced by organisations such as the LP Gas Association and the Health and Safety Executive. These deal with all aspects of L.P.G. safety and will include the adequate separation of tanks from each other, buildings and boundaries.

8.5 Fire Protection

(a) Tanks

The protection of tanks from fire is the subject of various regularly revised and updated Codes of Practice and Regulations produced by organisations such as the LP Gas Association and the Health and Safety Executive. These deal with all aspects of L.P.G. safety and will include the adequate separation of tanks from each other, buildings and boundaries.

L.P.G. establishments having on site quantities exceeding the thresholds laid down in guidance to Schedule 1, are subject to the Control of Major Accident Hazards Regulations 1999 (COMAH) and amendments: if the storage capacity exceeds 50 tonnes, Regulations 4 and 5 will apply, and if over 200 tonnes storage capacity, all the Regulations will apply. No more than 6 tanks, or in some cases no more than 3 tanks, can be grouped together, and fire separation or a firewall must be provided between groups of tanks.

Mention has already been made regarding proper catchment areas and disposal of any run-off of the liquid gas.

(b) Drenchers

A means of applying cooling water should be proved for all tanks over 50 tonnes capacity, preferably an automatic drenching system, but this provision should also be considered for all tanks of over 7 tonnes capacity. The system should be designed so as to enable water to be applied over the entire surface of the vessel. It is vital that the top surface of the vessel is cooled and thus protected, from the effects of radiated heat. The top of the tank only contains vapour, and as this is capable of absorbing only a small amount of heat, the metal may rapidly become overheated, and thus weakened.

The increase in pressure within the vessel would then cause the shell to rupture, resulting in a Boiling Liquid Expanding Vapour Explosion (BLEVE). If the radiant heat falls on the lower part of the vessel, where the L.P.G. is in the liquid phase, the liquid can absorb more heat, and the general consequence is that the pressure relief valve on the vessel will open to allow vapour to escape. The escaping vapour will then probably become ignited, and it will be necessary to protect the top of the vessel from radiant heat issuing from the relief valve.

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8.6 Fire Fighting and Gas Cloud Control

Because L.P.G. vapour is heavier than air it will flow along the ground and into drains etc. sinking to low levels.

In still air conditions any accumulation of vapour will take some time to disperse. This means that a flammable mixture may become ignited some distance from the point of leakage and flame may travel back to that point.

L.P.G. is colourless, odourless, and has anaesthetic properties producing suffocation in high concentration. For this reason L.P.G. is usually odourised before distribution enabling detection by smell down to one fifth of the lower limit of flammability (i.e. approximately 0.4 per cent gas in air). However in some circumstances, where the odourant would be harmful to a process this may not be used.

Escape of L.P.G. may also be recognised by its smell down to one fifth of the lower limit of flammability (i.e. approximately 0.4 per cent gas in air). However in some circumstances, where the odourant would be harmful to a process this may not be used.

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8.6.1 L.P.G. Hazards

8.6.1.1 Pressurised Containers (Road/Rail Tanker Storage Vessels)

When L.P.G. containers are heated they should be fully understood that unless adequate cooling is implemented a BLEVE will be the probable result.

8.6.1.2 The Term

BLEVE is an acronym for Boiling Liquid Expanding Vapour Explosion, which refers to two almost simultaneous events involving compressed liquids stored within containers.

Event 1 – Failure of Containment

The walls of the pressurised container may fail for a variety of reasons:

(a) Rise in vapour pressure due to external heating.
(b) Rise in vapour pressure due to internal heating; e.g. exothermic reaction.
(c) Impact; e.g. crash, damage to tanker vehicle.
(d) Overfilling (expansion of liquid contents generating hydraulic pressure on walls).

(e) Crack growth from a defect.
(f) Corrosion of container.

Event 2 – The Flash Evaporation of the Liquid Gas

The sudden release from a container of any liquid at a temperature where its vapour pressure exceeds atmospheric pressure causes rapid boiling of the liquid, which gives rise to an expanding vapour cloud. In addition, in the case of L.P.G.s, expansion of the gases above the liquid. The energy stored within the liquid plus the energy released by the conversion of liquid to gas causes severe pressure effects.

8.6.1.3 BLEVE Examples

(1) Explosion following failure of water boiler due to water/steam expansion.
(2) Explosion involving 'over pressured' L.P.G. tanker – no fire.

However, the term BLEVE is usually synonymous with the sequence of events following the release of a flammable liquid from a container and ignition of the release, giving rise to a fireball. The following paragraphs concern the hazards posed at incidents involving the storage and transportation of L.P.G.

BLEVE is a term that has become increasingly well known due to tragic consequences, entailing loss of life and property.

BLEVEs (Boiling Liquid Expanding Vapour Explosions) have made the headlines and become the object of special studies as the quantity of liquid gases in transport has increased.

The sudden release from a container of any liquid at a temperature where its vapour pressure exceeds atmospheric pressure causes rapid boiling of the liquid, which gives rise to an expanding vapour cloud. In addition, in the case of L.P.G.s, expansion of the gases above the liquid. The energy stored within the liquid plus the energy released by the conversion of liquid to gas causes severe pressure effects.

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BLEVEs (Boiling Liquid Expanding Vapour Explosions) have made the headlines and become the object of special studies as the quantity of liquid gases in transport has increased.

BLEVEs have occurred in storage and distribution plants, often with catastrophic results, fatalities have occurred and extensive property damage has entailed heavy economic consequences.

The following illustrates a typical sequence of events at a road or rail tanker incident:

- In a typical situation a tanker truck derails. The truck, which contains condensed gas, is exposed to heat at some points. If the heating occurs in the area of the tank where the gas is liquefied the situation is still under control. But when the liquid reaches its boiling point it becomes gas.
  - The safety valve is opened and the vaporised liquid escapes.
  - The level of liquid in the tank falls and the heating becomes dangerous since it now takes place in that part of the tank that contains gas (dry wall).
  - The heat accelerates the vaporisation. The container is torn open by the pressure and vaporised liquid escapes. A BLEVE is on the way.
  - The container breaks open and half of the liquid streams out. It vaporises immediately and creates a large gas cloud that also contains droplets of liquid gas. The gas cloud is extremely flammable.
  - If there is a fire nearby the cloud is ignited immediately. The vaporisation and ignition create an enormous force, so powerful that pieces of the container can shoot off some 1,000 m or more.
  - The burning front line spreads along the ground in the initial phase. When condensed gas is involved there is a risk for severe burn damage in a 300–400 m radius.
  - A shock from the BLEVE can break windows several kilometres away. The flames rise. A higher temperature (1200°C), spreading of gas and turbulence giving the gas cloud a mushroom shape.
  - The gas and the vapoured liquid that escapes burn out in less than a minute. But the rest of the liquid continues to burn. In addition, the enormous heat has probably ignited other buildings, and objects near the derailed tanker car.

To summarise there are up to 5 results of a BLEVE:

- The fireball has a radius of 300–400 m.
- The liquid lost is mainly evaporated but part of it may escape for some distance.
- The released gas forms a cloud that can expand for some distance.
- The released products form a fire and flame at the point of release.
- The released products form a large cloud that can be flammable.
8.7 L.P.G. Hazards: Pressurised Containers

8.7.1 Operational Considerations

8.7.1.1 Introduction

There is no safe period when a pressurised L.P.G. container is subjected to heat especially when heating is due to direct flame contact. Expect a BLEVE at any time if adequate cooling is not available.

Heating of a dry wall is far more dangerous than heat applied below the liquid level. In such cases the container is cooled by the liquid gas. However, it should be remembered that the liquid level will rapidly decrease due to conversion to vapour and pressure venting. It is therefore prudent to assume that the container is in its most dangerous condition.

NB. This section does not discuss fixed fire protection at L.P.G. installations. The provision of such equipment has an obvious bearing on operational considerations.

8.7.1.2 Points to note

(a) A hydrocarbon flame burns at temperatures up to 2000°C.

(b) Steel begins to seriously weaken at temperatures in excess of 350/400°C.

(c) When the dry wall attains a temperature of 300°C failure of the vessel is likely to occur - unless immediate massive cooling is achieved.

8.8 L.P.G. Hazards - Pressured Containers

8.8.1 Firefighting Procedures - BLEVE Situations

(a) Where there is no risk to life or property, serious consideration must be given to employing a "non-attack strategy".

(b) Where property only is at risk it may still be necessary to consider not committing crews for cooling. Remember there is no safety period, a BLEVE can occur at any time.

(c) If a decision is made to attack the fire then immediate, massive water cooling must be undertaken, concentrating on exposed vapour space.

(d) Personnel should be fully briefed and made aware of the danger confronting them.

(e) The Incident Commander must exercise strict control and supervision over personnel involved.

(f) Change from hand held branches to ground monitors as soon as possible.

(g) Consider "flame bending" to force any pressurised ignited releases from impinging on other pressurised containers (use monitors).

(h) Reducing the inventory/removal of product can bring on a BLEVE quicker, because by removing L.P.G. a larger "dry wall" is created above the liquid.

(i) Remember that in the event of a BLEVE the fireball could engulf both firefighting crews and their equipment. The use of heavy, coarse sprays on exposed crews may provide a measure of protection against fire effects.

(j) With a BLEVE the ground flash may well exceed the size of the rising fireball. The risk to fire crews is obvious.

(k) Evacuation of the surrounding area - assess the prevailing situation - although general guidance has suggested 1000 m, projectiles have been known to have flown up to 1,200 m.

(l) Where life is at risk a decision has to be made between committing all resources to evacuation and balancing the manpower resource between not only evacuation but also a massive cooling operation in order to secure adequate time to effectively evacuate.

(m) The probability is that a horizontal container vessel, in the event of a BLEVE, tend to project in an "end on" direction. It should be noted that this direction of the major fragment is affected by such things as pipe connections, tank supports and deflection. Although the relatively high risk area is an "end on" direction, fragments and major tank sections can fly in any direction.

8.9 Water Injection Into L.P.G. Vessel (Water Bottoming)

If the escape of burning L.P.G. is from an outlet near the base of the vessel and the installation includes a fire brigade inlet, water may be pumped into the vessel to lift the liquid L.P.G. above the outlet which will extinguish the fire at this point, and allow personnel to approach the vessel and carry out the necessary actions to stem the flow of liquid. If a fire brigade inlet is not provided, and the incident is likely to be prolonged, consideration should be given to making up an adaptor on site so that the above technique can be employed.

However, extreme caution should be exercised when using this method of dealing with an incident, particularly to ensure that only sufficient water pressure is used to lift the vessel's contents above the outlet. If such precautions are not observed liquid L.P.G. could be forced out of the safety relief valves in the top of the vessel, which could lead to a far worse situation that the original incident.

This technique must not be used under any circumstances for refrigerated containers because the water will freeze.

Specialist advice is imperative prior to pumping water into an L.P.G. vessel, to ensure that other dangers are not introduced - such as over pressure in the vessel due to admission water in excessive quantities or at excessive rates, and freezing of leaking valves, etc., where evaporation of L.P.G. will cause cooling below the freezing point of water. Such ice formation could later melt, possibly resulting in undetected leakage of L.P.G.
If the incident is in a built-up area, one hazard to guard against is the possibility of the liquid entering the drains. It may be possible to divert the liquid away from drains or culverts by the use of sand or other suitable material, but if this is unsuccessful the appropriate water authority must be informed and precautions taken to warn people of the danger downstream. There may also be more chance of ignition sources being present and evacuation will need to be considered.

8.10.3 Incidents Involving Road or Rail Tankers

A road or rail incident involving L.P.G. is only marginally different from the above in that, if the tanker is overturned, the pressure relief valve, normally at the top of the tank in the gas phase, could be brought into the liquid phase and any release would be of liquid, rather than the gas which the pressure relief valve is designed for.
8.10.4 Cylinders

Storage of L.P.G. cylinders or containers, as stated in 8.3.2 (e), is regulated, but fires do occur. Any cylinders involved in fire can burst and expel a gas cloud which immediately ignites. Consequently, at any fire involving stacked or stored cylinders, evacuation of nearby premises is a first priority. The affected cylinders often act like missiles and can be found some hundreds of metres away from the fire, penetrating windows and walls.

Firefighting is best carried out from behind some cover and must obviously aim at cooling with the maximum amount of water that can be brought to bear, preferably in the form of spray or fog. The area should be patrolled partly to assist police in the evacuation and also to extinguish any fires which could be started by itinerant cylinders; although, once the gas is expelled, a cylinder usually lacks the means to start fires.

Firefighters should always bear in mind that L.P.G. cylinders are found almost anywhere, but especially in industrial premises. Boats, caravans, sheds, lock-up garages, camping sites and camping shops are other examples.

If involved in fire they should be regarded as dangerous and appropriate measures taken.

8.10.5 Vehicles Using L.P.G. as a Fuel

Industrial vehicles such as fork-lift trucks, off-highway tractors, etc. have used this fuel for many years. The use of L.P.G. in road vehicles is rapidly increasing in response to the requirement for 'greener' fuels and such vehicles may use L.P.G. as their sole fuel source or in combination with other fuels.

These vehicles can be:

(i) Single fuel
   - operated solely on L.P.G.

(ii) Dual fuel
   - petrol or L.P.G.
   - another fuel or L.P.G.

Road vehicles are only allowed to use permanent refillable fuel tanks, never portable cylinders. Each L.P.G. fuel tank must be fitted with a safety valve which will discharge escaping gas to the air by a vent pipe to the outside of the vehicle preferably away from the exhaust or fuel tanks.

Small warning notices should be fitted to vehicles using L.P.G. as a fuel either near the safety valve or the filler valve of the L.P.G. tank. Even if fitted it may be difficult (because of their small size), in a fire situation, to determine whether, or not, the vehicle is using L.P.G.

NB: It does not matter if the vehicle is actually using the L.P.G. as, in a fire, the hazard is still present, and a firefighter may be faced equally by an exploding petrol tank and/or an exploding L.P.G. tank.

Fire Service Manual Petrochemical Incidents

Figure 8.22 Small bulk vessel at domestic premises.

Figure 8.23 Installation supplying gas to houses on a metered supply.
Figure 8.24 Small bulk vessel adjacent to a building.

Figure 8.25 Two 60 tonne vessels with vaporisers.

Figure 8.26 Storage vessel at an LPG cylinder filling installation.

Figure 8.27 Mounded vessel.
Petrochemical Incidents

Chapter 9 – Safety

9.1 Managing Incidents Safety

Serious petrochemical incidents are a rare occurrence. Even those brigades, who provide cover for fires and emergencies within the petrochemical industry, have a limited opportunity to build up experience of such incidents.

As a direct result, operational personnel are themselves unlikely to gain very much experience in dealing with petrochemical firefighting.

It is, therefore, imperative that brigades have systems in place to ensure the personal safety of personnel who are likely to be committed to this infrequent but hazardous activity.

Key Risk Control measures that brigades need to include to ensure ‘Fire Fighting’ safety must be preplanned and will include:

- **Risk Assessment**

An assessment will need to be made that takes account of both the likelihood and the severity of any petrochemical incidents. For fixed special risks, for example: L.P.G. installations, marine terminals, chemical plants and storage tanks, site specific risk assessment is essential.

- **Liaison**

Brigades will need to liaise with a number of external agencies when preplanning their response.

- **Pre-determined attendance of resources**

Having established the likely nature of any incident, the brigade will need to consider the level of response that would be appropriate. This will include the provision of specialist personnel, appliances and equipment.

- **Local procedures and collaboration**

Significant petrochemical incidents will require that all personnel and external organisations are familiar with all local arrangements for access, for example, a site plan issued to each responding fire appliance, and information pertaining to the site. Collaboration with other brigades is essential to ensure the availability of adequate resources (Mutual Aid).

- **Specialist operational information**

Brigades need to ensure, as far as is reasonably practical, that suitable and sufficient information relating to the hazards, risks and control measures is available to crews at the time of the incident. This can be achieved in a number of ways. The information must be clear, concise, current and relevant. The information may be of a generic or specific nature.

- **Training**

Personnel who are likely to attend petrochemical incidents will require specialist training. Training will be based on the outcome of the site risk assessment and to a great extent on the information contained within this manual. Training will be both technical and practical, designed to satisfy the identified needs of the individuals involved. Wherever possible, practical training should be conducted on the risk itself thus enabling firefighters to gain ‘hands on’ training moving around in relevant structures and to become conversant with the onsite firefighting equipment.
The information contained within this manual provides firefighters with guidance relating to petrochemical incidents. The information is designed to assist brigades to pre-plan their organisational arrangements which will ensure so far as is reasonably practical, the safety of operational crews who have to deal with such unusual and arduous conditions.

### 9.2 Safe Systems of Work

Safety awareness and safe working procedures will continue to apply at all times, additional factors will need to be considered when training and dealing with petrochemical incidents. Fires and emergencies are handled safely and effectively when emergency response teams are working to a pre-determined approved system for managing such events. General Standard Operating Procedures (S.O.P) should be adopted in conjunction with refinery and chemical company emergency teams.

Tactical decision making objectives must include the ability to:

- Manage and control the site
- Identify the problem
- Evaluate hazards and risks
- Select the appropriate protective clothing
- Develop plan of action and co-ordinate resources
- Implement response objectives
- Perform decontamination and clean up operations
- Terminate the emergency

Firefighters should be afforded the opportunity to visit tankers and chemical ships at petrochemical plant marine terminals to familiarize themselves with the vessel layout, and all fixed fire protection – suppression systems, both on the vessel and marine terminal.

Approaching a vessel at a marine terminal can be hazardous especially at night, it is not always possible to drive fire appliances alongside the vessel, indeed, it may not be desirable, given the hazards that may exist (e.g. L.P.G. vessels). It may be necessary for firefighters to walk carrying equipment with them along narrow walkways further congested with product pipelines, control valves switchboxes etc.

Some refineries are equipped with firefighting tugs that during a marine emergency may be manned by both onsite and local authority firefighters.

It should be common practice that training is conducted on fire tugs for equipment familiarisation, testing of all firefighting equipment and firefighters exercising in passing from one vessel to another, ensuring that their hands and feet are clear of the sides to avoid crushing accidents. Lifejackets should be worn at all times.

Firefighters should be aware that on structural fires within process plants metal ladders, landings will become oily and, coupled with a water cooling application, present an extreme slipping hazard, so all necessary precautions should be taken. It must also be recognised that metal ladders may become extremely hot from a fire, firefighters should take care how they proceed.

The principal hazard in the refining, blending and storage of petroleum is the flammability of crude oil and its derivatives. Potential health and hygiene hazards that may be encountered present few problems, however these must be understood and appropriately taken care of. The characteristics of refinery plant or installation is that it is designed essentially as a series of enclosed systems so that exposure to hydrocarbons or other process streams is normally very low. However, it is essential that all persons likely to encounter these varied processes, especially under emergency fire conditions where potential large spillages may occur, should ensure that they are fully aware of the hazards involved.

- **Typically some crude oils and various process gas or liquid streams in refinery plant may contain hydrogen sulphide at levels which will give rise to dangerous or lethal concentrations if released to atmosphere.**

Measures and techniques, which should be covered in training, must include:

- **Communications:** valuable experience can be gained in running communication exercises on board tankers, and refinery plants, in areas where high pressure operations are identified
- **Storage tank construction and protection**
- **Supplementary water supplies and relay operation**
- **Specialist firefighting techniques**
- **Heat and humidity training**
- **Hot fire valving down operation**
- **Safety procedures to be adopted in relation to "BLEVE" L.P.G. incidents and "BOIL OVER" phenomena in Crude Oil storage tank fires.**

The list is not comprehensive, fire brigades should continue to carry out risk assessments to further determine their training needs.
Glossary

The following list contains terms and abbreviations which are widely used in the petroleum industry. They will be encountered in this and other publications.

Additive: A chemical which is added in small quantities to modify the properties of a petroleum product.

Alkanes: Straight and branched chain saturated hydrocarbons.

Anti-knock valve: See octane number.

Aromatics: Unsaturated hydrocarbons which contain one or more benzene rings.

Barrel: The standard barrel contains 159.1 litres (35 imperial gallons or 42 US gallons).

Bubble cap: One of a series of devices in a fractionating tower which ensures effective mixing of liquid and gas.

Catalyst: A substance which alters the rate of a reaction. Most catalysts are used to increase reaction rates.

Claus process: A two-stage process used to recover elemental sulphur from hydrogen sulphide.

Cracking-catalytic: A process in which large hydrocarbon molecules are broken into smaller ones using a catalyst.

Cracking-thermal: A process in which large hydrocarbon molecules are broken into smaller ones using heat.

Crude oil: A naturally occurring mixture consisting mainly of hydrocarbons, together with small proportions of sulphur, nitrogen and oxygen derivatives of hydrocarbons.

Cut: A mixture of hydrocarbons of similar boiling point obtained by distillation.

Cyclone: A conical vessel used to extract dust by centrifugal action.
DEA
Desalter
Distillate
Downcomer
Downstream
Feedstock (feed) material
Flare
Flashing off
Fraction
Fuel oil
Gasoline
Heat exchanger
Hydrocarbons
Hydrofining
Hydrogenation (de-)
Iso-octane
Jet tray
Kerosene
Kieselguhr
Knocking
LPG
Lubricant
MEA
Megapascal
MEK
Merox
Naphtha
Naphtha-light
Naphtha-heavy
Naphthenes
Octane number
Onstream
Petroleum
Pipestill
Plasticiser
Powerforming
Pressure

Diethylamine.

One of a series of devices in the primary distillation unit which removes salt residues from crude oil.

A product of distillation (usually liquid).

A passage down which liquid passes from one tray to the next tray below in a fractionating tower.

A collective term used to describe the refining, transportation and marketing of petroleum products (see Upstream).

Crude oil, or a crude oil derivative, which provides the starting in a process.

A device which burns unwanted gases.

An operation in which hot liquid under pressure is suddenly vaporised by reducing the pressure.

A portion of crude oil containing compounds whose boiling points are within a specified range.

A fraction of crude oil which may be burnt to provide heat on the refinery or may provide a feedstock for the Residfiner plant. Some fuel oil is sold for industrial applications but it is not normally used for domestic heating.

Petrol.

A device in which heat is transferred from one substance to another without the substances coming into contact.

Compounds which are composed of atoms of hydrogen and carbon only.

A term used by Esso to describe hydrotreating.

The addition (removal) of hydrogen.

2,2,4-trimethylpentane.

One of a series of devices in a fractionating tower which ensures effective mixing of liquid and gas.

A fraction obtained from the primary distillation of crude oil and used as a feedstock in the production of jet fuel.

A hydrated form of silica (also known as diatomite).

A sound which occurs in an engine when ignition occurs too soon in the combustion cycle.

Liquefied Petroleum Gas – essentially either propane or butane.

A substance which reduces friction between two surfaces as they move across each other.

Monoethanolamine i.e. 2-aminoethanol.

Methyl ethyl ketone i.e. butane-2-one.

Mercaptan oxidation using a liquid-liquid reaction.

The name applied to refined, partly refined or unrefined petroleum products. This is an important fraction from atmospheric distillation, which is used for blending into petrol or as chemical feedstock.

Low boiling point naphtha.

High boiling point naphtha.

Cyclic saturated hydrocarbons.

A value which indicates how smoothly a petrol burns in an engine. It is based on a scale of 2,2,4-trimethylpentane (100 octane) and heptane (0 octane).

The status of a unit when it is performing its process function.

A term used to describe products formed by the processing of crude oil.

A primary distillation unit used to separate crude oil, or crude oil derivatives, into various components of different boiling points.

A chemical added to plastics during manufacture to make them more flexible.

A term used by Esso to describe the process of reforming.

1 atmosphere or bar is approximately 100,000 pascals (100 kPa); 1,000,000 pascals (Mpa) = 10 bar.
Quench oil
This is oil which is injected into the reaction mixture leaving a cracking or reforming heater in order to reduce the temperature and prevent any further reaction.

Raffinate
A substance which is purified by a solvent extraction process.

Recycling
The recirculation of a substance which is unchanged at the end of the process and can be re-used in the process.

Refinery gas
A mixture containing hydrogen and low molecular mass hydrocarbons which is burnt to provide heat on the refinery.

Refining
The separation and modification, by physical and chemical processes, of crude oil into a range of petroleum products.

Refining capacity
The maximum volume of crude oil which can be refined per year.

Rerunning
The process of separating small quantities of very different chemicals from the main process stream.

Residue
The material which remains as unevaporated liquid or solid after distillation or cracking.

Scrubbing
A process in which an impurity is removed from a petroleum product.

Slurry
A free-flowing mixture of liquid and solid.

Sour gas
Hydrocarbon gas containing sulphur compounds such as hydrogen sulphide and thiols (similarly sour water).

Splitter
A fractionating tower which separates a mixture into two product streams only.

Stabliser
A unit of fractional distillation equipment for removing low mass hydrocarbons from an oil in order to reduce the vapour pressure.

Steam stripping
The removal of volatile components from a mixture using steam.

Sweet
A term used to describe a product stream or gas which is relievly free of unpleasant-smelling sulphur compounds (opposite of sour).

Treat gas
A mixture of gases produced by the reforming plant on the refinery. It contains a high proportion of hydrogen and is used in hydrogenation reactions on other plants.

Upstream
A collective term used to describe the exploration for, and production of, crude oil and natural gas (see Downstream).

Vacuum distillation
Distillation carried out under reduced pressure. This lowers the boiling points of substances and prevents decomposition or cracking of the material being distilled.

Vacuum gas oil
A general term used to describe any product of vacuum distillation.

Viscosity
A measure of the resistance to flow of a liquid.

Viscosity index (V.I.)
A scale which indicates the effect of temperature change on the viscosity of a substance.

Yield
The amount of product(s) obtained from a process as a percentage of the feedstock.
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Further Reading

- Guide for firefighting in and around Petroleum Storage Tanks – American Petroleum Institute
- Last Fire – Joint Oil Industry Project
- Storage Tank Emergencies – Hildebrand, Knoll
- Guidelines and Procedures – Hildebrand, Knoll
- Fire Service Manuals
  - Volume 1: Firefighting Foam – Technical
  - Volume 2: Firefighting Foam – Operational
  - Volume 2: Incident Command
  - Volume 2: Marine Incidents
- Fire Service Guides to Health and Safety
  - Volume 1: A Guide for Senior Officers
  - Volume 2: A Guide for Fire Service Managers
  - Volume 3: A Guide to Operational Risk Assessment
  - Volume 4: Dynamic Management of Risk at Operational Incidents
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- Knowsley SK
- Strebor Fire Protection
- Williams Fire Control - Texas
- Refinery Terminal Fire Company - Texas
- Essex County Fire and Rescue Service
- Calor Gas