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BP Process Safety Series

Hazards of Air and Oxygen

A collection of booklets describing hazards and how to manage them

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This booklet is intended as a safety supplement to operator training courses, operating manuals, and operating procedures. It is provided to help the reader better understand the 'why' of safe operating practices and procedures in our plants. Important engineering design features are included. However, technical advances and other changes made after its publication, while generally not affecting principles, could affect some suggestions made herein. The reader is encouraged to examine such advances and changes when selecting and implementing practices and procedures at his/her facility.

While the information in this booklet is intended to increase the store-house of knowledge in safe operations, it is important for the reader to recognize that this material is generic in nature, that it is not unit specific, and, accordingly, that its contents may not be subject to literal application. Instead, as noted above, it is supplemental information for use in already established training programmes; and it should not be treated as a substitute for otherwise applicable operator training courses, operating manuals or operating procedures. The advice in this booklet is a matter of opinion only and should not be construed as a representation or statement of any kind as to the effect of following such advice and no responsibility for the use of it can be assumed by BP.

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Contents

1

Some fundamentals

Petroleum products are present in refinery and petrochemical equipment and processed in several forms (solids, liquids, gases, vapours and mists). Each form has a personality all of its own, yet each has characteristics that cause it to behave like the others. By the application of basic principles of chemistry and physics, we exercise controls under which petroleum products are handled safely in the refinery units. We may (through the application of heat, pressure, vacuum, chilling, the addition of chemicals, contact with catalyst, etc.) change the form of the petroleum product. To do it safely requires much 'know-how'—your 'know-how.'

Most of the refined petroleum products are used as sources of heat energy by being burned with air in engines or burners. The same type of combustion can occur on a larger scale in petrochemical and refining units with potentially hazardous results if air (or oxygen) mixes with petroleum fractions in the wrong places or in the wrong proportions. Units which use air for regeneration provide many opportunities for flammable combinations of air and hydrocarbon. All units when being brought on-stream or being shut down need special attention to avoid hazards.

You can contribute to the safety of your plant by knowing and applying the basic fundamentals covered in this booklet.

2

The chemistry of fire

Let us take a look at some of our most common products (gasoline, kerosene, lubricating oil, grease, wax and coke). In liquid or solid form, these products will not burn readily. However, this is not true for the vapours or mists (see Figure 1). Under the right conditions, each of these products will release vapours which can burn. Under some conditions, these vapours can explode. An explosion differs from a fire only because of external factors such as confinement which cause a pressure increase as a result of the combustion.

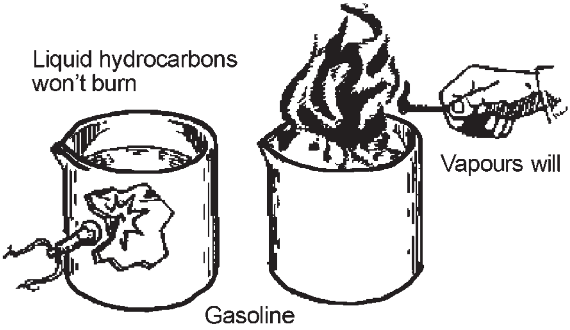
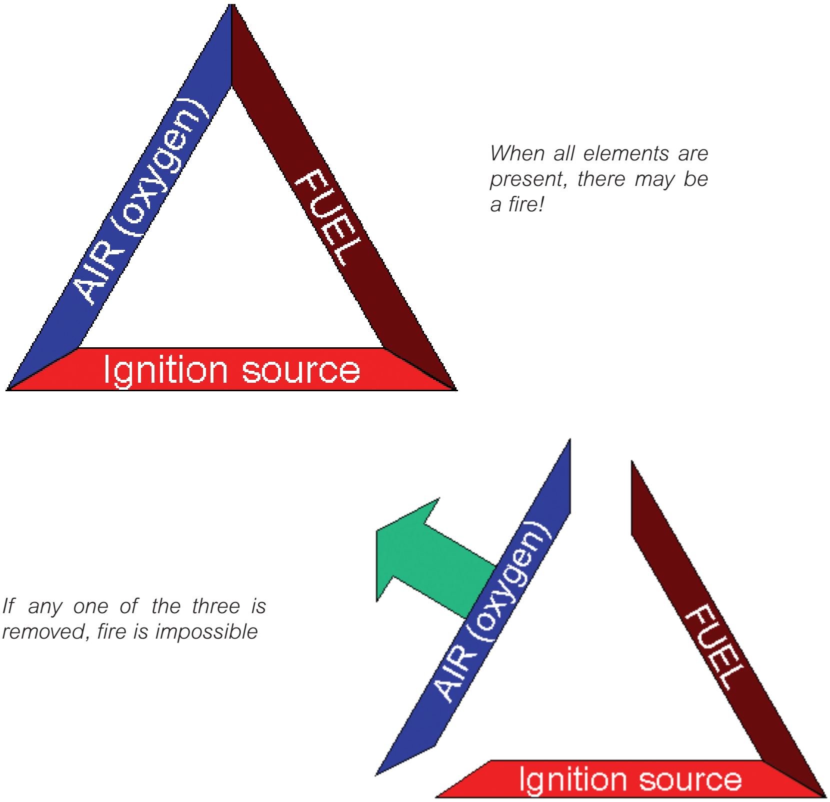


Figure 1 *Under the right conditions common products will burn readily*

This combustion process is frequently described by the use of the fire triangle (see Figure 2). The three sides represent fuel vapour, air (oxygen) and a source of ignition. A fire or explosion can occur only when all three are present. However, to be absolutely safe, fuel and air (oxygen) should only be mixed under rigorously controlled conditions, since there are many sources of ignition.



When all elements are present, there may be a fire!

If any one of the three is removed, fire is impossible

Figure 2 *The fire triangle. A fire or explosion can occur only when all three sides of the triangle are present.*

Actually, combustion is more complex than the fire triangle indicates because the fuel must be in the form of vapour or finely divided particles and must be mixed with air in the right proportion to make a flammable mixture of air (oxygen) and fuel. Further, some portion of the flammable mixture must be ignited by a source of adequate temperature and energy.

It is difficult in refinery or petrochemical operations to eliminate all sources of ignition, and it must be taken for granted that large quantities of fuel will be present. *Our effort, then, must be directed to eliminating air and oxygen. When the process requires the mixing of air or oxygen with fuel, it must be done only under rigorously controlled conditions*.

To do this, we require a better understanding of each branch of the fire triangle.

3

Oxygen

AIR (oxygen)

The earth and its creatures are submerged in a vast ocean of air. Normally, the air is colourless and odourless. It contains about 1/5 oxygen and 4/5 nitrogen by volume, with small amounts of other gases. Except in a few cases, the nitrogen in the air does not enter the chemical reaction of combustion but dilutes the oxygen, thus reducing the intensity of combustion. Oxygen in the atmosphere is consumed by most living things on earth in the process of slow combustion necessary for life. Usually in this chemical process, the carbon and hydrogen of fuel unite with the oxygen and form carbon dioxide, water vapour, and sometimes, carbon monoxide. This reaction releases energy in the form of heat. This process in creatures is, in many respects, identical with that of combustion in the controlled burning of fuels. Without the oxygen in the air, you cannot live. Likewise, oxygen is necessary for the combustion of fuels. Oxygen or air is an important part of our fire triangle and one that can be controlled. Since air is pressing down all around us at approximately 14.7 pounds per square inch (1 bar) at sea level and oxygen is used in some processes, we can expect oxygen or air from many sources to be present in refinery or petrochemical processes.

Some of these sources are the following:

- atmospheric air entering open lines and vessels;
- atmospheric air introduced with process or wash water;
- atmospheric air leakage into vacuum systems;
- atmospheric air leakage through open or defective valves;
- atmospheric air entering open equipment when liquid levels are lowered;
- compressed air used in line blowing;
- compressed air used for agitation;
- compressed air leakage from blower and compressor equipment;
- oxygen or air in solution in feedstocks or products;
- oxygen or air used in oxidation processes;
- oxygen contamination of nitrogen or other compressed gases used for purging or processing.

The alkylation unit shown in Figure 3 was extensively damaged (see Figure 4) through unrecognized introduction of oxygen—in this case, oxygen was carried in solution in the propane stream. Laboratory research has verified the fact that oxygen may be absorbed by oils and later released somewhat like

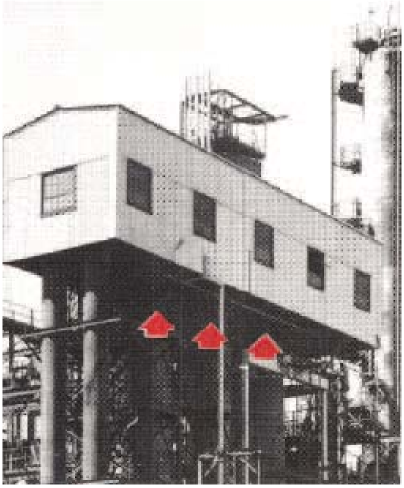


Figure 3 *Arrows indicate location of three propane storage drums near an alkylation unit.*

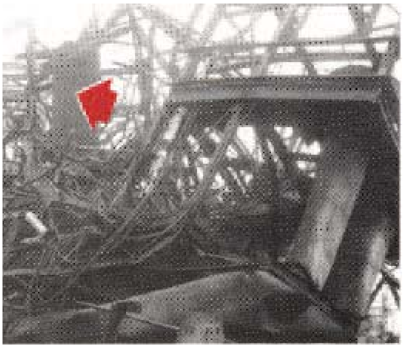


Figure 4 *Propane enriched with oxygen detonated. Ignition was probably caused by iron sulphide. The three propane storage drums shown in Figure 3 fragmented. Arrow (Figure 4) indicates remains of one of the propane storage drums. Other equipment was damaged by fire from the released hydrocarbons.*

bubbles from soda water. This may cause a nonflammable atmosphere to become flammable by the process of concentration or enrichment. Let us see how this is possible.

Assume that a propane stream contains a small amount of oxygen dissolved in the liquid. When the propane is pumped into storage, some propane vaporizes into the space above the liquid. Also, along with the propane vapour, oxygen leaves the liquid, and an equilibrium vapour phase is built up containing a much higher concentration of oxygen than does the liquid (see Figure 5). Suppose then the liquid level is raised in the vessel and the vapour space is not vented. Much of the propane vapour under pressure condenses back to a liquid, but the gaseous oxygen becomes more concentrated in the vapour because of compression. It redissolves very slowly back into the liquid (see Figure 6). The percentage of oxygen in the vapour thus has increased many times over what it was in the liquid entering the storage vessel.

Figure 5 *Vapour equilibrium is achieved*

Figure 6 *Oxygen is more concentrated in the vapour as propane vapour redissolves under increased pressure*

The flammable-limits graph (see Figure 7) indicates flammable limits at atmospheric pressure for propane vapour in all possible concentrations of oxygen and nitrogen. The lower slanting line represents propane in air, which is about 21-percent oxygen and 75-percent nitrogen. The upper slanting line represents propane vapour in commercial oxygen. Comparison of the intercepts of the flammable-limits curve with the two slanting lines indicates that propane vapour in commercial oxygen has wider flammable limits than propane vapour in air. Further consideration shows that as any propane-air mixture becomes enriched with more and more commercial oxygen, the flammable range increases.

Lighter hydrocarbons, such as propane and butane, are particularly hazardous. They pick up more oxygen than heavier hydrocarbons and may be stored under conditions leading to the oxygen concentrating effect described. Butane, for instance, is stored above ground in large vessels called *spheres*. When the atmospheric temperature falls below 31°F (−0.5°C), the butane will condense, and a vapour space under vacuum will be formed. The vapour in this space may not be flammable initially—however, subsequent filling may increase the pressure and create a hazard by concentrating the air (oxygen) fraction in the vapour space. Water used for process washing or for flushing can carry air into a hydrocarbon system. In the case of the alkylation unit, air transferred from washwater to the reactor effluent was the source of part of the oxygen in the propane stream discussed in the preceding paragraphs.

Water used to flush out hydrocarbons from a vessel normally filled completely with liquid may bring air into the vessel and create a vapour space. This space may contain a flammable hydrocarbon vapour-air mixture.

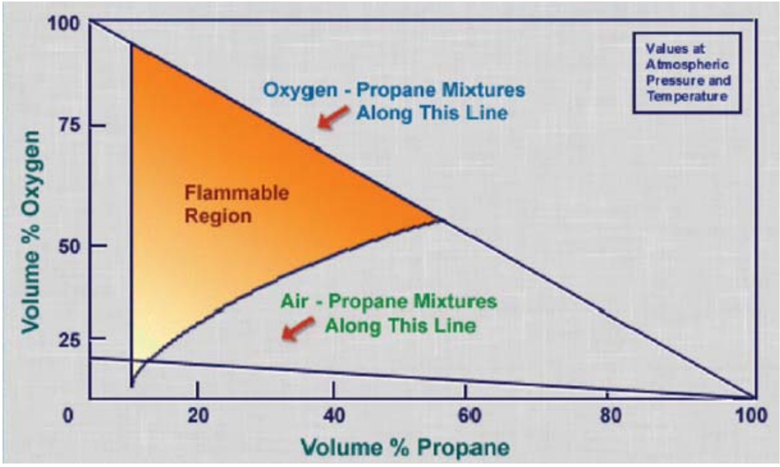


Figure 7 *Fuels are much more flammable in commercial oxygen than in air (see Chapter 10).*

Vapour spaces in tanks or vessels will be hazardous depending on the vapour pressure of the stock and the oxygen content of the vapour and air mixture (see Figure 8). If oxygen content is less than a minimum value (determined by the type of combustible and by pressure and temperature), a flammable mixture cannot be formed with any proportions of the combustible gas or vapour. The oxygen content can be measured with approved instruments or by laboratory sample analysis. Combustible gas mixtures may be purged from vessels or the vessels may be rendered safe by the use of approved inert gas (a nonflammable gas containing too little oxygen to support combustion).

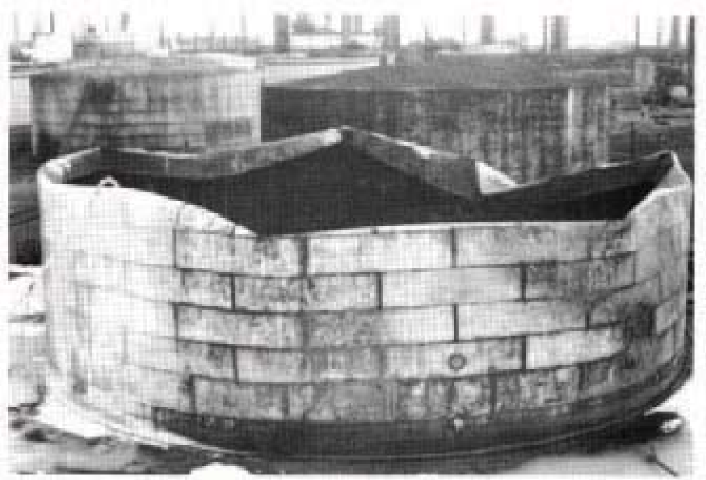


Figure 8a *Iron sulphide ignited an explosive atmosphere in this reduced-crude storage tank. Air entered when stock was pumped down. A partially submerged steam suction heater is believed to have vaporized some of the lighter fractions and also to have dried the iron-sulphide deposits.*

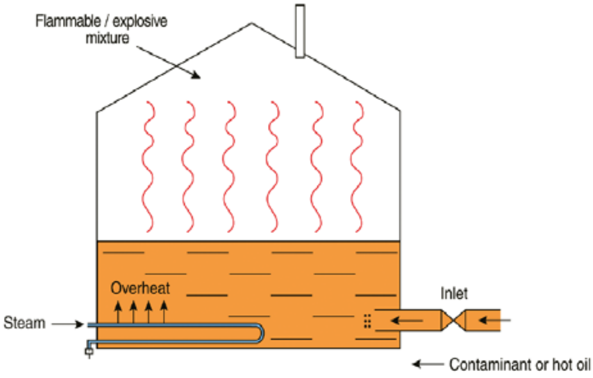


Figure 8b *Unexpected flammable/explosive mixture in the vapour space of a cone roof tank by overheating.*

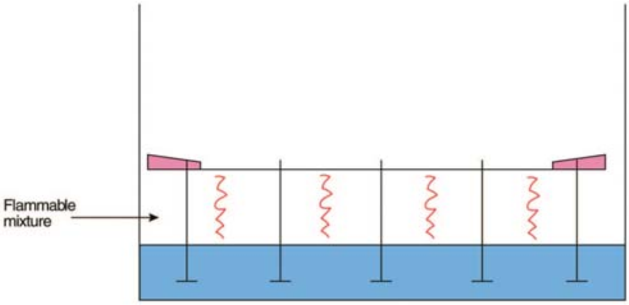
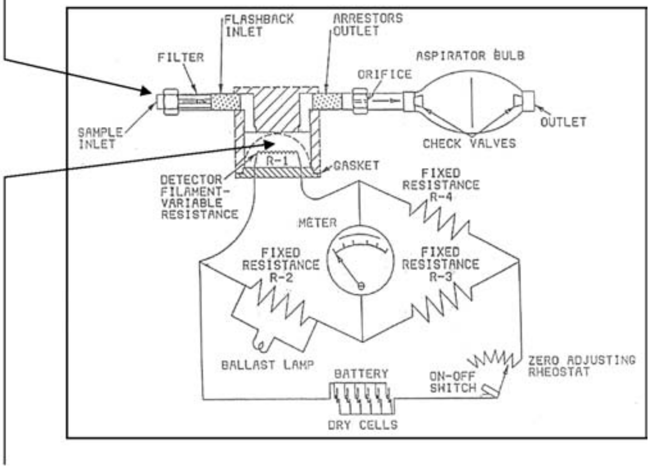


Figure 8c *Avoid landing floating roof on its legs during normal operations.*

Remember that the presence of impurities may make the gas something other than inert, so it is important that an inert-gas stream be monitored or checked frequently. It is also important to know that after flooding a vessel or tank with inert gas to remove the oxygen, the atmosphere will neither support combustion nor breathing, and that a person entering such a vessel must wear breathing apparatus that will provide an air supply. It should be remembered also that combustible gas indicators or vapour testers which are used for measuring combustible mixtures will not record properly in an inert atmosphere (see Figure 9).

Must have air/oxygen in sample.



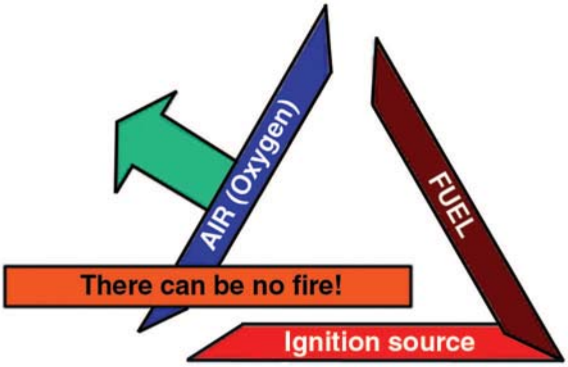
Controlled combustion takes place here: Oxygen + Flammable gases ⇒ $CO_2 + H_2O$ + Heat

Figure 9 *Working principle of an catalytic explosimeter.*

A number of processes require the use of air to circulate and regenerate catalyst, for oxidation, or for sweetening. The secret of safe operation is the strict control of air under the conditions for which the equipment was designed. Control usually depends on the proper use of instruments for measurement of conditions such as oxygen content, temperature, pressure or liquid level.

All vessels which have vapour spaces in which oxygen or air can accumulate must have the vapour spaces analysed for oxygen on a routine basis to avoid the formation of an explosive mixture.

Remember—if oxygen is not present . . .



4

Fuel

FUEL

Up to this point, we have only mentioned petroleum product fuel; but in refinery operations, other flammables may be involved. Refinery units may use or produce hydrogen, hydrogen sulphide, carbon monoxide, ammonia, alcohol and others. Each will burn and may explode under certain conditions when combined with oxygen.

So that we may treat all fuels with due respect, we should know about some of their characteristics. We said previously that these flammables are alike in many respects and different in others.

Some petroleum products will vaporize enough at room temperature to form combustible mixtures with air. Others will do this at very low temperatures, while still others must be heated to cause sufficient vaporization (see Figure 10). All hydrocarbons are equally hazardous when their vapours are mixed with air in flammable proportions. The 'lowest temperature at which enough vapours are given off to form a flammable mixture of vapour and air immediately above the liquid surface' is the *flash point* of the liquid fuel.

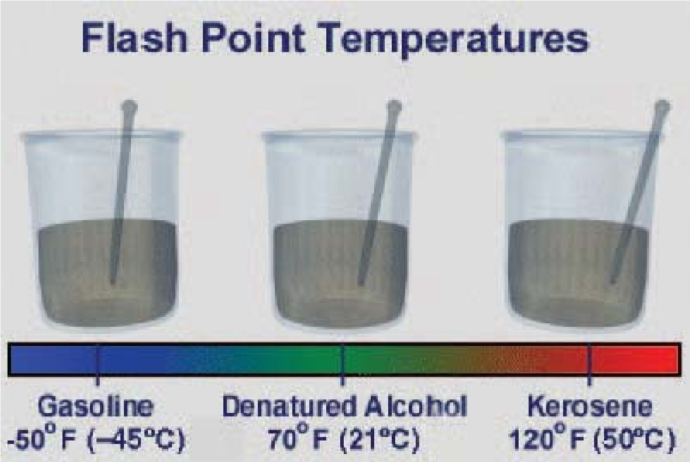


Figure 10 *Petroleum products vaporize at different temperatures*

Even a small amount of a liquid petroleum stock above its flash point can produce enough vapour to make a large volume of a dangerous vapour-air mixture. Never assume that an 'empty' vessel is safe (see Figure 11). Get a satisfactory gas test before starting any work.

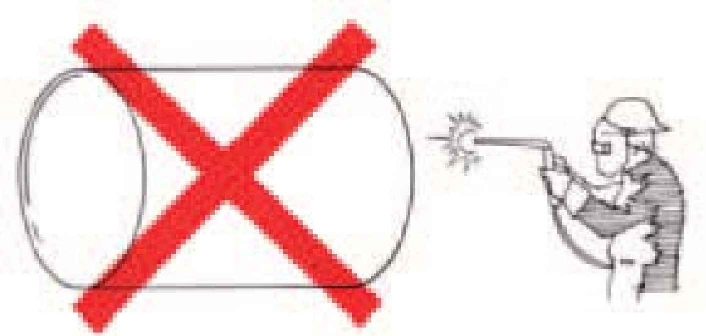


Figure 11 *One gallon (3.8 litres) of vaporized gasoline in a 15,000 gallon (57 m^3) 'empty' vessel can explode if ignited.*

Gaseous fuels can mix with air or oxygen in all proportions. However, the proportions must be within certain limits before these mixtures will burn (see Figure 12). The limiting proportions are referred to as *flammable limits* or *explosive limits* and are expressed as the percentage by volume of the fuel in the air-fuel mixture. The flammable range spreads between the lower flammable limit and the upper flammable limit. Fuel-air mixtures outside of the flammable range will not explode.

If the vapour concentration is less than the lower flammable limit, the mixture is called 'lean.' Mixtures containing more fuel than the upper flammable limit are called 'rich.'

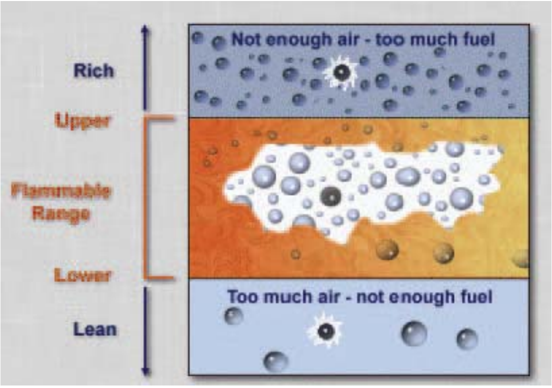


Figure 12 *Gaseous fuels must be within their flammable limits before they will burn*

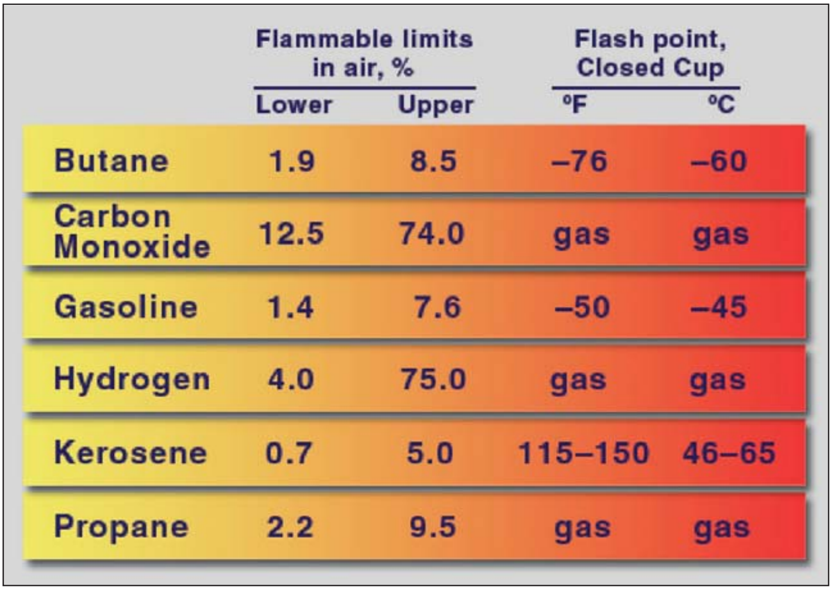
It should be remembered that mixtures of fine solid or liquid fuel particles (dusts, mists or sprays) with air or oxygen may burn as readily as vapour-air mixtures if the fuel concentration is within the flammable range. This means that atomized fuels can burn even at temperatures below their flash point if they are mixed with air in proper proportions.

A comparison of the properties of several fuels is shown in Table 1. In using the data in this table, it must be remembered that the flammable limits were determined under laboratory conditions, and the exact gas composition was accurately known. Great care must be taken in practice in using these data since a substantial safety factor is needed to take care of inevitable errors of sampling and analysis. In addition, the flammable limits will change appreciably with changes in temperature and pressure of the fuel-air mixture. These flammable limits show the amount of fuel which must be mixed with air to form a mixture that can burn or explode. If the oxygen content of the air is reduced enough by dilution with inert gas, flammable mixtures cannot be formed with any proportions of fuel.

Reducing oxygen content is the safest way to stay out of the flammable zone.

Remember that the ideal goal is zero (0.0) percent oxygen.

Table 1 *Comparison of properties of fuel*



	Flammable limits in air, %		Flash point, Closed Cup	
	Lower	Upper	°F	°C
Butane	1.9	8.5	–76	–60
Carbon Monoxide	12.5	74.0	gas	gas
Gasoline	1.4	7.6	–50	–45
Hydrogen	4.0	75.0	gas	gas
Kerosene	0.7	5.0	115–150	46–65
Propane	2.2	9.5	gas	gas

These values may vary slightly according to test procedures used and data source. Flammable limits listed are correct only at atmospheric pressure and room temperature. The flammable range is wider at higher pressure and temperature or if oxygen is substituted for air. A mixture of gasoline and kerosene will take on the fire hazard property of gasoline.

Do not confuse flash point with ignition temperature, which is discussed in the next section. A fuel may be safely handled in open vessels or containers if kept below its flash point.

ACCIDENT A tank cleaning contractor removed an empty drum from the refinery's scrap yard. He wanted to make oil containment pans/trays from it. The drum had been used previously for storing kerosene slops from the laboratory. After returning to the contractor's workshop with the drum, he washed it out with water before commencing the cutting using a grinding wheel. An explosion occurred (see Figure 13). Fortunately, no one was injured.

Figure 13 *Damage caused to an 'empty' drum following cutting with a grinding wheel*

5

Ignition sources

Ignition source

There are many sources of ignition. All of which ignite a flammable mixture by heating at least part of the mixture. The lowest temperature which will cause the mixture to burn or explode is called its *ignition temperature*. These ignition temperatures range from about 400 to 1,200°F (204 to 648°C). Thus, moderate temperature sources may cause ignition. Even a high ignition temperature does not make a flammable mixture safe because the temperature of common ignition sources is much higher. For example, the temperature of a match flame can be about 1,600°F (870°C) and an electric arc about 10,000°F (5,500°C).

When fuel vapour mixes with air or oxygen in the right proportions, be sure that a source of ignition will be found without going too far. Some sources of ignition are given below—they may or may not be readily recognized:

- welding;
- cutting;
- hot lines;
- furnaces;
- pyrophoric iron sulphide;
- friction heat;
- sparks from electric equipment;
- static;
- lightning;
- autoignition;
- catalytic effect of fresh metallic surfaces;
- engine driven vehicles.

The reaction product or iron and hydrogen sulphide will burst into flames at ambient temperature in the presence of air if dry. The material is black or brown and will appear grainy, scaly, lumpy or powdered. It can be in a mixture with coke, oil, sand, etc.

Hot hydrocarbons will ignite when exposed to air. Ignition temperatures of hydrocarbons in air at atmospheric pressure vary from 356°F (180°C) for benzaldehyde to 1292°F (700°C) for acetone. Most oils are expected to ignite at temperatures between 500 and 800°F (260 and 427°C).

Research conducted at the University of Utah led to the conclusion that a mixture of hydrogen and oxygen could be ignited by a catalytic effect occurring when the mixture contacts fresh metallic surfaces exposed while a valve is being opened. This could explain observations of several explosions of hydrocarbon-air and hydrocarbon-oxygen mixtures occurring exactly when valves were being opened (see Figure 14).

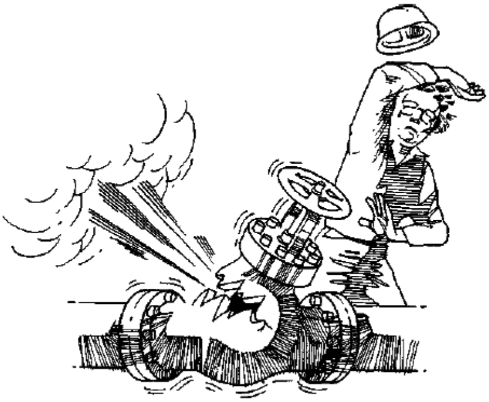


Figure 14 *Ignitions may arise from unexpected sources*

Process operators must see that ignition sources are not brought into hazardous areas. However, ignition sources are so numerous that safety cannot depend solely upon elimination of the generally recognized sources.

To read more on ignition sources and on fuel characteristics, refer to ‘Sources of Ignition’ by John Bond, ISBN 0 75061 180 4.

6

Detonations

Detonations are a special kind of explosion. They can occur in solids or liquids, but here we will consider only those occurring in flammable mixtures composed of hydrocarbon vapours with air or oxygen.

Detonations are particularly destructive because:

- they travel at very high speed (through pipes, vessels, etc.); and
- they produce very high localized pressures.

The total elapsed time from ignition to detonation is generally no more than a fraction of a second and at most not more than 2 or 3 seconds.

6.1 How detonations develop

A vessel or pipe filled with a flammable mixture (i.e., air and fuel gas) at atmospheric pressure is shown in Figure 15. Ignition occurs near the closed end at the left. As the gas burns, it gets hot, expands and sends ahead pressure waves which push into the unburned gas. These waves cannot be seen by the human eye, but they can be seen with special photographic equipment and their pressure measured with special high-speed instruments. The pressure waves compress the unburned gas ahead of the flame and heat up this gas. As the flame follows through the now heated but unburned gas, a normal explosion occurs at the flame which builds a shock (pressure) front just ahead of the flame and also sends ahead additional pressure waves.

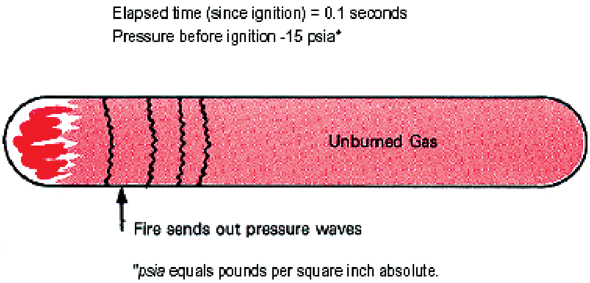


Figure 15 *Ignition starting at atmospheric pressure (15 psia).*

These pressure waves are now moving faster than the earlier waves because of the hotter gas. Eventually, these waves overtake earlier waves, causing a piling up or a moving pressure step within the pipe (see Figure 16).

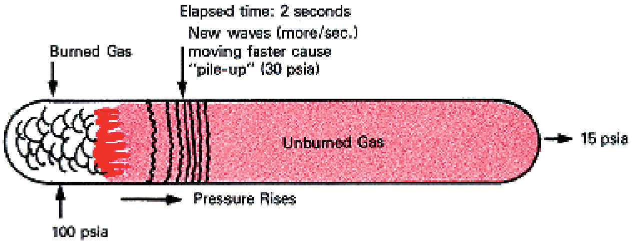


Figure 16 *Shock waves building up far ahead of the flame and just in front of the flame.*

When this happens, the pressure step is called a *shock wave*. Weak or low pressure shock waves travel at the speed of sound (about 1,100 feet (335 m) per second in air at room temperature, and faster in hot gas); however, strong shock waves can travel at speeds many times that of sound.

The flame follows the shock and travels through gas which is heated more and more by these growing pressure pulses.

At this stage, there are two principal shock fronts, the forward one and the one immediately ahead of the flame.

The gas which the flame overtakes has been heated twice by the compression effect of each shock front. It becomes quite hot even before it begins to burn. This speeds up the rate of burning, and the flame travels faster and faster. Because the flame is confined by the vessel or pipe, the heat energy of the flame is not readily dissipated, and this also helps increase the reaction of the flame (see Figure 17).

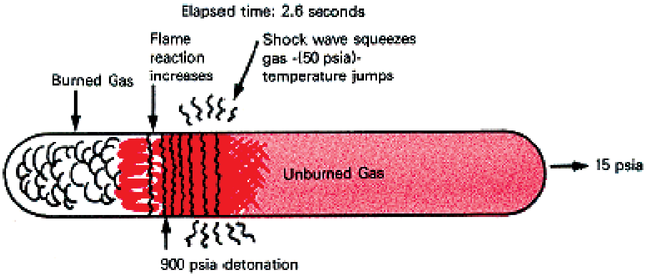


Figure 17 *Initial stage of detonation.*

This process continues and the flame keeps speeding up. When the flame reaction becomes most vigorous and the flame reaches the maximum speed at which it can travel, a detonation starts to form. The detonation in this initial stage travels at a speed many times that of sound. It races through the well-heated but unburned gas until it catches up with the slower-travelling shock wave or pressure pulse which earlier went out from the flame. The detonation races through this pressure pulse, absorbing it so that a single pressure pulse continues down the vessel or pipe through unburned and unpressurized gas and reaches the final stage (see Figure 18).

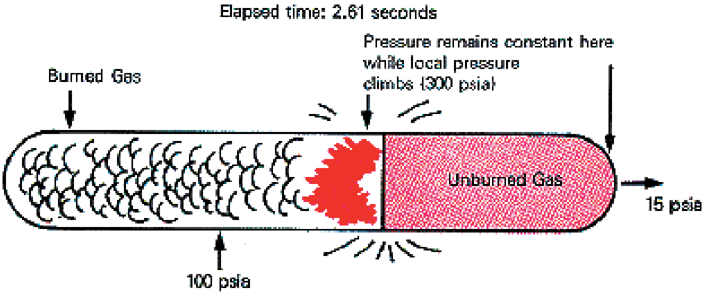


Figure 18 *Final stage of detonation.*

When the detonation is first established and it is moving through pressurized and heated—but unburned—gas, the pressure multiplication at the detonation front can be as high as 60 to 100 times the initial pressure in the vessel or pipe. This pressure is the product of the pressure rise due to the forward shock wave multiplied by the pressure rise due to the detonation.

Fortunately, this very high pressure lasts such a short time that it has little damaging effect. After the detonation has overtaken and joined the shock wave and is now moving through unheated and unpressurized gas, the pressure multiplication at the detonation is about 20 to 40 times the initial pressure.

The detonation wave very quickly slams into the other end of the pipe with tremendous force. The detonation acts like a piston and bounces off the end of the vessel or pipe, at least doubling the detonation pressure and at times even raising this pressure by a factor of 8 (Figure 19).

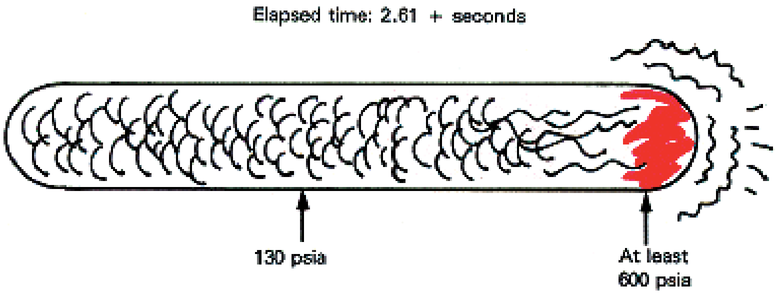


Figure 19 *Pressure multiplication due to detonation bouncing off the end of the pipe.*

The preceding explanation of a detonation applies to saturated hydrocarbons mixed with air starting at atmospheric pressure with no turbulence.

The development of a detonation will be more rapid and require less distance if all or even just one of these occur:

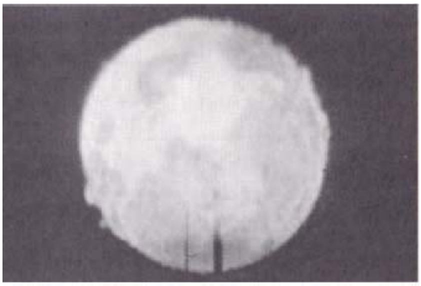
- the mixture is turbulent;
- hydrogen or unsaturated hydrocarbons are present;
- the air is enriched with oxygen.

All of these increase burning velocity.

With many of the flammable mixtures found in industry, detonations also develop more rapidly at initial pressures above atmospheric. If the initial pressure is high, detonation pressures will be much more severe since the detonation effects are multiplied by the initial pressure.

The development of the detonation just described required a long pipe to permit the initial explosion to increase in intensity enough to form the high-speed detonation. If an ignition source of very high energy is used, a detonation can form immediately and grow in all directions. Hence, it is called a *spherical* detonation. An ordinary detonation in a pipe entering a vessel can be a sufficiently intense ignition source to trigger a spherical detonation in the vessel under proper conditions (see Figure 20).

Figure 20 *Spherical detonation in a balloon filled with propane-oxygen mixture initiated by detonation in pipe connected to balloon. Detonation developed in 1/4000 second.*
Print taken from high-speed motion picture film made for Amoco Oil movie 'Detonations.'



6.2 Properties of detonations

Extreme pressure

Detonations produce much higher pressures than ordinary explosions. In many cases, vessels will not be strong enough to contain an ordinary explosion where the pressure will rise to 6 to 10 times the initial pressure. An initial detonation may produce extreme pressures of 60 to 100 times the initial pressure. It is impossible to design most vessels to contain detonations (see Figures 21 and 22), and is usually impractical to design large piping to contain detonations. The only safe procedure is to avoid detonations by preventing the formation of flammable vapour and air mixtures in vessels and piping.

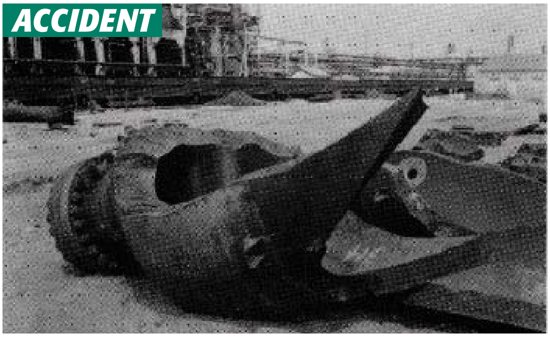


Figure 21 *Three vertical drums—4'4" ID344' long with 5-1/2" wall thickness fragmented.*
Damage was caused by a detonation, probably spherical, of oxygen-enriched propane.

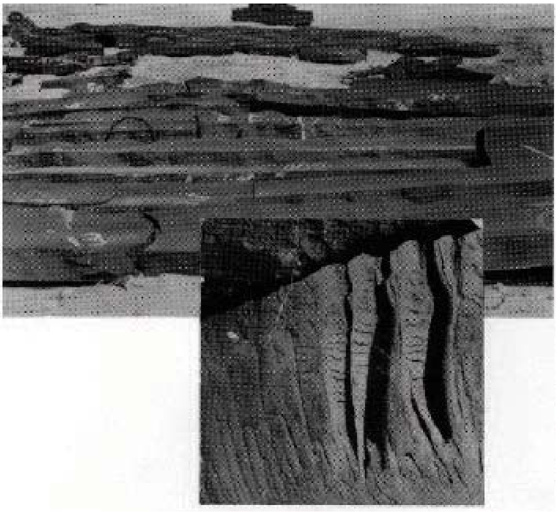
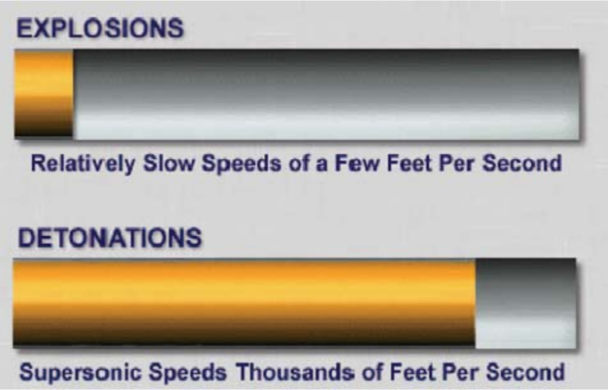


Figure 22 *Drum fragments resulting from detonation reassembled on the ground. Note longitudinal fractures and 'dragon teeth' embrittlement pattern.*

High speed of travel

While explosions travel at relatively slow speeds (a few feet per second), detonation waves travel at supersonic speeds (thousands of feet per second).



This is one reason why detonations are unusually destructive (see Figures 23 and 24). First of all, it means that they *can travel against normal gas flow almost as rapidly as with the gas flow* (just as a supersonic plane is little bothered with wind direction). This does not happen in the case of normal explosions. Also, because of their high speed, detonations can travel very quickly from one part of a complicated unit to another regardless of any gas flow. In cases of detonations in refining units, the detonation travelled against the rapid gas flow in lines leading from pressurized vessels to the open atmosphere.

ACCIDENT

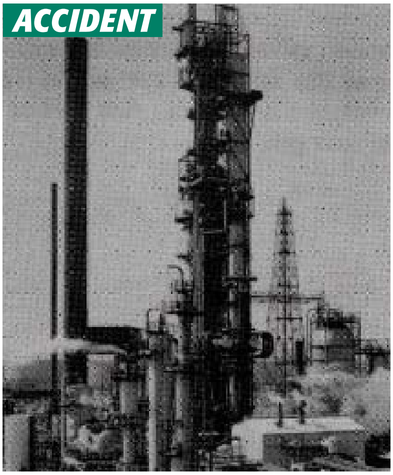


Figure 23 *Fluid hydroformer unit.*

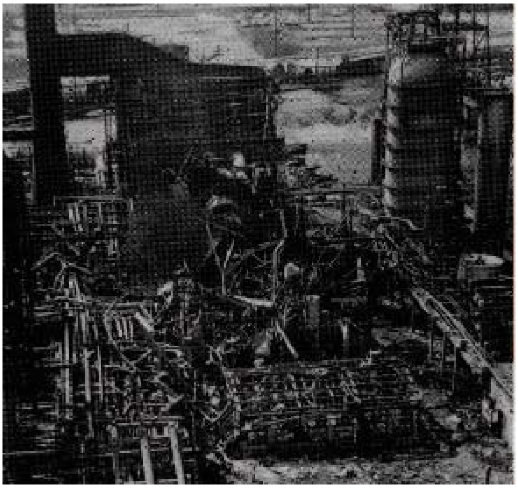


Figure 24 *A fluid hydroformer being brought onstream was destroyed by a series of internal detonations. Air accidentally entered the unit and contaminated the circulating inert gas and naphtha vapours. This air backed in through one or both valves in the catalyst circulating lines which had failed to close even though exterior inspection indicated them to be closed. The most probable source of ignition was the heated walls of the recycle gas furnace tubes. The explosion was violent enough to throw a 65-ton piece of steel 1,200 feet (365 m).*

Impact and reflections in closed vessels and pipes

Sharp impact

As previously stated, a detonation develops at least 2 to 4 times the pressure of a normal explosion. This, however, is only part of the story of their destructiveness. To this must be added the effect of impact blows, which are dangerous for two reasons.

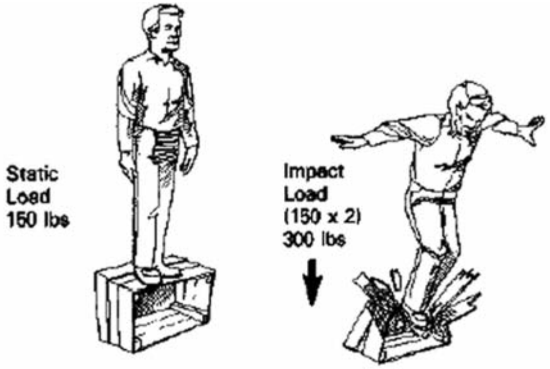


Figure 25 *An impact load can cause twice the stress as a load applied statically*

The *rapid pressure build-up* of a detonation results in the delivery of an impact blow to the container (vessel or pipe) which causes the container wall to move out so fast that it is overstretched by the time it stops moving out. This can cause twice the stress as the same pressure gradually applied (see Figure 25).

There is yet another way in which the impact of a detonation makes it more likely to break the container. The rapid impact tends to make the steel brittle (to make it break without stretching first).

If the vessel or pipe contains a defect (notch, sharp corner, etc.), the stress will be highest there unless the metal around the defect can stretch and relieve itself of the high stress. Under rapid impact, the metal around the defect does not have enough time to stretch fully and the stress there becomes very high and starts a crack. This may happen when the rest of the container has stretched partly and has developed only about one half of its full strength.

Putting those two effects together, we find that an impact blow can be $2 \times 2 = 4$ times as destructive as an equal blow delivered gradually.

Shock-wave reflection

Detonation waves are intensified greatly upon reflection from solids walls. The intensification here depends upon the angle at which it strikes the solid surface, the velocities of travel and upon a number of other factors; but in the simple case of a head-on collision, the peak pressure is at least doubled and can even be multiplied by a factor of eight if the shape of the vessel permits multiple reflections. Considering all these factors together, we arrive at the rather amazing conclusion that under the worst conditions an established detonation may produce a damage effect in a closed vessel equivalent to a pressure more than 1,200 times the initial pressure. More commonly, the pressure-multiplication effect is 300 to 400 times, which still makes a detonation at least 20 to 30 times more severe than an ordinary explosion.

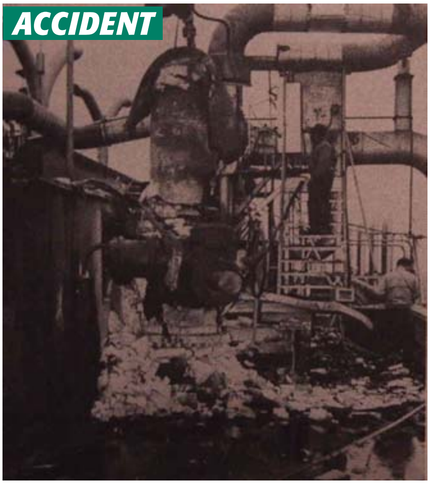


Figure 26 *This damage resulted from a detonation which occurred when a hydrocarbon compound used for heat transfer purposes was inadvertently mixed with air at high pressure and high temperature. The mixture detonated when it was unexpectedly ignited by autoignition.*

Figure 27 *A detonation in a vapour space of this salt drum in a copper-chloride oxygen treating plant blew the head off the vessel and split the remaining shell. Commercial oxygen was used in the process. The plant was onstream at the time, sweetening a 13 to 15-pound (90–103 kPa) RVP natural gasoline. A plant upset, during which the flow of oxygen continued, resulted in an accumulation of oxygen in the top of the salt drum. The source of ignition is unknown.*

6.3 Conditions necessary for a detonation to occur

Mixtures

In general, it is felt that almost any gaseous mixture that will burn can be made to detonate under the right conditions. However, mixtures of gases which burn easily and rapidly also detonate much more readily than slow-burning gases. Thus, different flammable vapour and air mixtures may be grouped roughly according to burning velocity to indicate the ease with which they detonate.

- Flammable mixtures easy to detonate: all fuel gases and hydrocarbon vapours with oxygen; and certain fuel gases (such as hydrogen, acetylene and ethylene-mixed with air).
- Flammable mixtures difficult to detonate: broadly include most refinery fuel gases and hydrocarbon vapours mixed with air. Outstanding exceptions are Ultraformer or hydroformer recycle gases, which are rich in hydrogen.

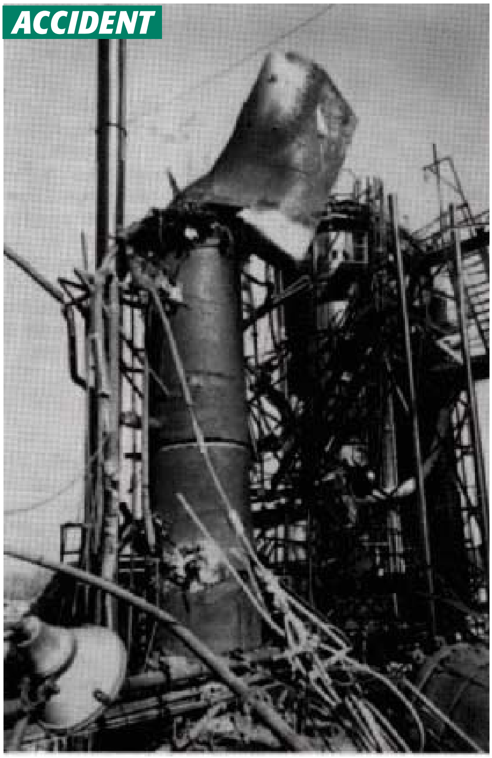
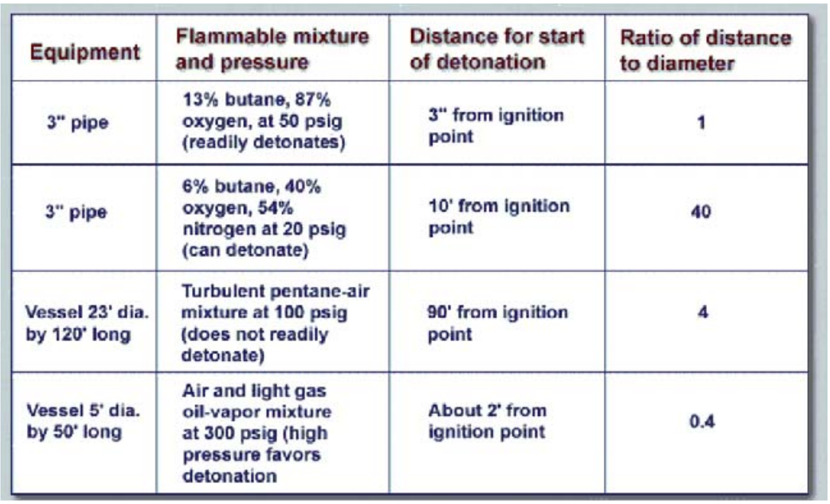


Figure 28 *A detonation in the top of a bubble tower in a delayed coking unit destroyed the upper 20 feet (6 m) of the tower and toppled a similar tower on an adjacent unit. Extensive damage both inside and outside the plant was caused by the blast and fragments from the tower. Tower fragments weighing up to 2,500 pounds (1,135 kg) were thrown 300–600 feet (90–180 m). The unit was being started up, and the tower was being filled with oil to displace air. The oil was being heated because of cold weather. Air and oil vapour formed the flammable mixture. Through an oversight, the air vent valve on the tower had not been opened, resulting in a pressure rise in the tower as it filled with oil. The high pressure enabled the detonation to form in a short distance. Spontaneous ignition occurred as a result of excessive oil temperature.*

Geometry of vessels and pipes

Flammable mixtures which readily detonate will usually do so regardless of the size of the vessel or pipe which contains them. However, other flammable mixtures will not detonate unless they are contained in long pipes or vessels, where it is possible for the slower-burning gases gradually to build up a shock wave as discussed before or where an extremely intense ignition source is present.

High initial pressure of a flammable mixture usually makes it easier to start a detonation in a short distance from the point of ignition. Turbulence and high oxygen concentration also promote detonation. Table 2 shows distances for detonation formation which have been observed in various pipes and vessels.



Equipment	Flammable mixture and pressure	Distance for start of detonation	Ratio of distance to diameter
3" pipe	13% butane, 87% oxygen, at 50 psig (readily detonates)	3" from ignition point	1
3" pipe	6% butane, 40% oxygen, 54% nitrogen at 20 psig (can detonate)	10' from ignition point	40
Vessel 23' dia. by 120' long	Turbulent pentane-air mixture at 100 psig (does not readily detonate)	90' from ignition point	4
Vessel 5' dia. by 50' long	Air and light gas oil-vapor mixture at 300 psig (high pressure favors detonation	About 2' from ignition point	0.4

Any baffle or similar obstruction which would impede the straight-line flow of gases through the pipe or vessel may also serve to impede the development of a detonation (see Figure 29), but this effect should not be counted on to prevent a detonation. In some instances, obstructions may even promote a detonation.

A rapidly circulating mixture of air or oxygen and hydrocarbon vapour (as in a recycle system) burns much more readily than does a stagnant gas. As a consequence of this, it will also develop into a detonation much more readily. Thus, ordinary hydrocarbon-air mixtures are more dangerous when they are circulating than when they are stagnant.

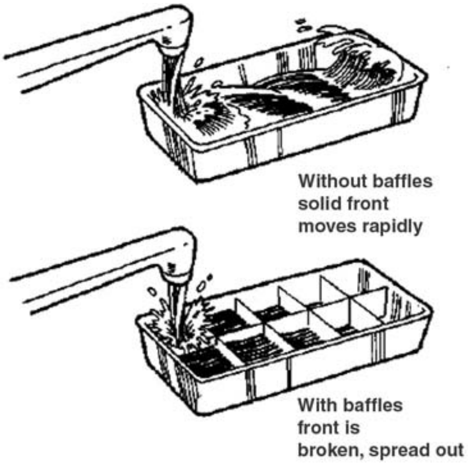
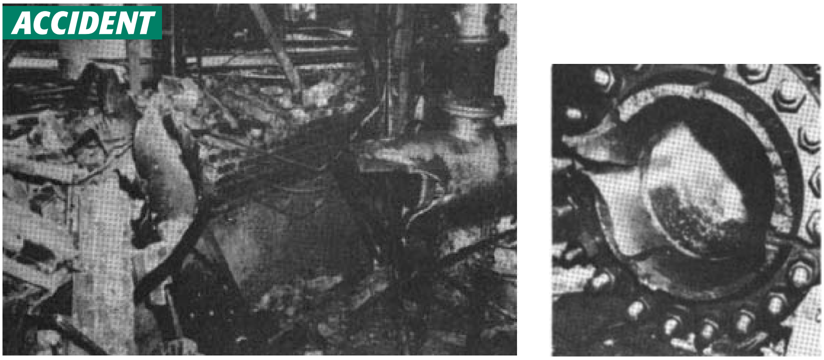


Figure 29 *Baffles which impede straight-line flow may impede the development of a denotation.*

6.4 Detonation summary

- Most gaseous mixtures that will burn will detonate under the right conditions.
- The detonation wave travels at a very high speed (4,000–8,000 feet (1,220–2,440 m) per second for air-hydrocarbon mixtures).
- Pressure in the detonating zone is very high, and multiplying effects of impact and reflection can make a detonation more destructive than a normal explosion.
- Knowledge of detonations was not associated with the operation of refinery equipment until 1955 when the fluid hydroformer shown in Figures 23 and 24 exploded (see pages 21 and 22). Detonations are not rare occurrences—as many as five in a single-year period have been recognized.
- The only way of operating a unit with complete safety is to avoid mixtures of oxygen and fuel gases. Processes which require mixtures of air and oil vapour to be present must be supplied with adequate controls and instrumentation to keep the mixtures outside the flammable range.



Figures 30 and 31 *A mixture of lube-oil mist and air in the suction piping of a centrifugal compressor operating in a test loop detonated. The detonation progressed upstream to the normal flow. Suction piping was ruptured in two locations, and internal damage occurred in the compressor and in a cooler. The building was wrecked (Figure 32), and other parts of the test facility were badly damaged (Figures 30 and 31). Ignition probably was induced by friction in the compressor.*

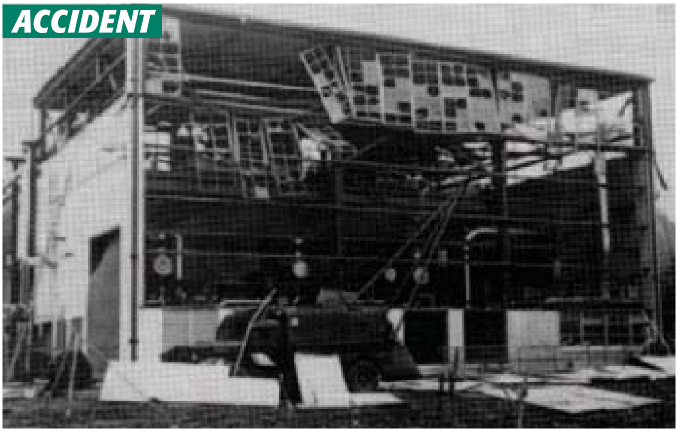


Figure 32 *Detonations in the discharge piping of a high-pressure centrifugal air compressor caused extensive equipment damage. Oil entered the compressor circuit from the compressor shaft oil seal and accumulated in the piping. Ignition started in the high temperature region in or near the compressor outlet and developed into a detonation in the discharge piping. The accident occurred very shortly after a start-up of the compressor. Many fragments of heavy wall piping were thrown throughout the compressor building, damaging motors, switchgear and other equipment. The blast from the detonation blew out the building wall.*

Figure 33 *An aerial view illustrating the effects of a detonating-type explosion in a 10-inch pipeline which had been transporting sour crude oil. Compressed air and a godevil were being used to remove oil from the line so that it could be repaired. An explosion occurred. The underground pipeline in this picture ran parallel to the pole line. The many dark areas, visible from the foreground almost to the horizon, indicate where the pipeline ruptured, blowing out the earth. The section of line which was destroyed was almost 30 miles long.*

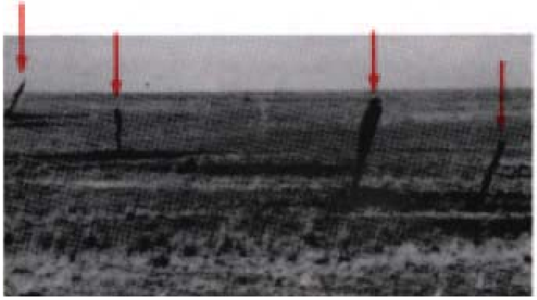


Figure 34 *Another view of the 1939 pipeline explosion shown in Figure 33. The arrows indicate broken pieces of pipe projecting vertically out of the soil at some of the points of rupture. The average speed of the detonating wave through the line was about 300 feet/second, which exceeds normal flame velocities.*

Figure 35 *Demonstration of a detonation experiment in a 2-inch buried pipeline. The detonation travelled from right to left in the photograph. Print taken from a section of high speed 16-mm film which was run at 5,000 frames per second. (This film was made in conjunction with the Ethyl Corporation training movie 'Danger! Air!')*

7

Other failures

Although detonations, as discussed in the previous section, are particularly destructive, there are other failures that can result in serious damages in refinery operations.

Containers* for sampling light hydrocarbon liquids can be dangerous, as demonstrated by failures in refinery laboratories. Failures have been attributed to overpressure because of liquid expansion. They could have been avoided if the potential danger had been recognized and certain precautionary measures taken.

*In containers for sampling light hydrocarbons, it is not feasible to use pressure-relief valves or rupture disks, in contrast to commercial LPG containers used for storage and transportation. Release of gas through pressure relieving devices could be nearly the same hazard as rupture of the container.

ACCIDENT One of the above-mentioned failures was a 1,900-ml sampling container that had been filled with field butane at a line pressure of 220 psi (15 bars) at a temperature of 26°F (−3°C) (Figure 36).

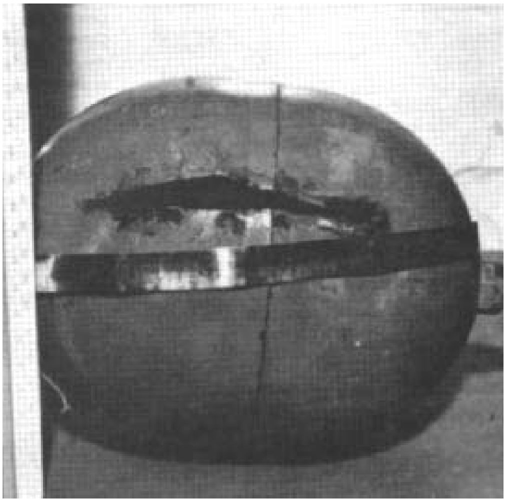


Figure 36 *A 1,900-ml sample container ruptured, and the vapour flashed. Thermal expansion of the liquid resulting from a 49°F (27°C) temperature rise could have subjected the bomb to 1,000-psi (69 bars) pressure—possibly higher.*

continued…

This was an Air Force surplus oxygen container with a design pressure rating of 500 psi (34.5 bars) and a working pressure rating of 400 psi (27.5 bars). The regular sampling procedure of venting the container, to assure vapour space, was apparently overlooked. The container was brought into the laboratory liquid full, without any contained air dissolved in the butane. In the laboratory, the container warmed up to the room temperature of 75°F (24°C). It appears, therefore, that the thermal expansion of the liquid, resulting from the 49°F (27°C) temperature rise, could have subjected the container to a pressure of at least 1,000 psi (69 bars), if bursting had not occurred. The vaporized contents flashed at a furnace in which carbon was being burned from a sample of cracking catalyst.

The sample bomb (in Figure 36) that ruptured is of two-piece welded steel construction. The committee appointed to make a complete study of the subject of sample bombs for high-pressure liquid hydrocarbons recommended (among other items) standardizing on 75 and 150-ml bombs manufactured of monel. The recommended pressure rating is 5,000 psi (345 bars). Figure 37 compares the Air Force type container with a 5,000-psi (345 bars) unit.

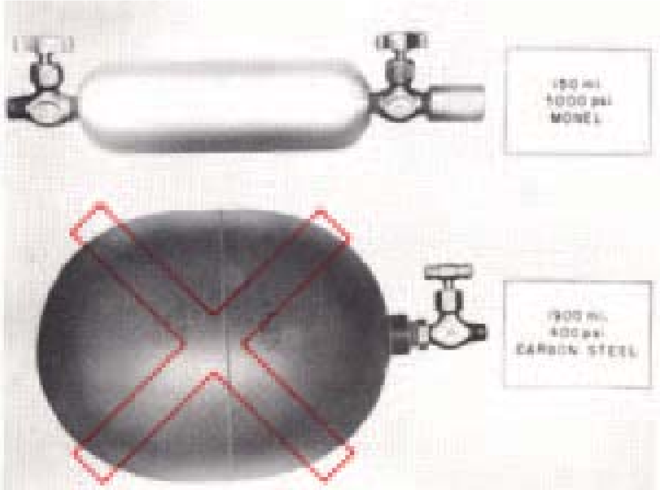


Figure 37 *Comparative data for an Air Force surplus oxygen container (similar to Figure 36) and a sampling bomb or container rated at 5,000 psi (345 bars) for liquid hydrocarbon service.*
A satisfactory 150-ml capacity light-hydrocarbon sample container with a 5,000-psi (345 bars) working pressure rating (top). The surplus 1,900-ml-capacity container with 400-psi (27.5 bars) working pressure rating (bottom) is unsatisfactory for use in sampling light hydrocarbons.

ACCIDENT A larger sampling container failed in another laboratory under similar conditions (see Figure 38).

Figure 38 *Damage to this laboratory building resulted from a flash fire and explosion following the rupturing of a sampling container.*

ACCIDENT

Figure 39 *Another example of thermal expansion effect on a LPG sampling bottle. Refer to BP Process Safety Booklet* Safe Handling of Light Ends *for more details on LPG sampling.*

ACCIDENT A 45,000-barrel spheroid ruptured and collapsed after it had been emptied of product, filled with water and the water partially drained (Figure 40). The consensus of three separate investigators was that a low-grade explosion in the upper part of the vessel must have caused the initial rupture.

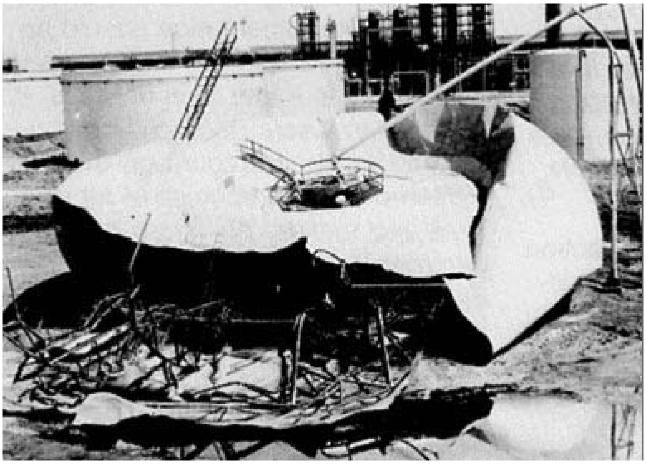


***Figure 40** Spheroid ruptured by low-grade explosion. Although this tank appears to have been damaged by vacuum, it was established by examination that the vacuum damage occurred due to the outrush of water after the explosion had ruptured the tank. Note the unbuckled condition of the supporting truss in the centre of the area which was pushed out.*

Investigation also disclosed that the nozzle through which the spheroid was vented during the filling with water was located below the high point of the vessel. This allowed a pocket of hydrocarbons, estimated to be as much as 4 ½ barrels, to remain in the top of the vessel even though it had overflowed with water. As the spheroid was drained, air entered through an open manway and mixed with hydrocarbon vapour.

The source of ignition is believed to have been a reaction between pyrophoric iron sulphide and the air entering the open manway.

This explosion failure points to the need for checking both new and existing equipment to make certain that vents are actually located at all high points so that a water purge can be fully effective in flushing out hydrocarbons.

8

Avoid flammable mixtures

The ultimate goal should be the elimination of mixtures of fuel with air or oxygen in processes and vessels where these mixtures are not part of the reaction. In regenerative-type catalytic cracking and reforming, and other processes requiring air, the addition of air must be *rigorously controlled*. Adequate safeguards must be provided to ensure that all mixtures of air and hydrocarbons which form will stay outside the flammable range.

In considering the hazard of flammable mixtures, careful distinction should be made between cone-roof tanks and vessels designed for pressure. The intentionally weak joint between the roof and the shell in a tank permits rapid relief of pressure in case of an internal explosion. As a result, a tank explosion will do little more than lift the roof.

In contrast, as was shown in Section 6, if a flammable mixture in a pressure vessel is ignited, a detonation may occur and send the characteristic missiles hurtling in all directions to cause widespread injury and damage.

While it is desirable to limit the number of tanks which may contain flammable vapour, particularly near public property or processing areas, strict avoidance of flammable conditions in tanks is not necessary.

In treating plants in which light hydrocarbons and gasoline are finished catalytically in the presence of air, it is usually possible to operate with only that

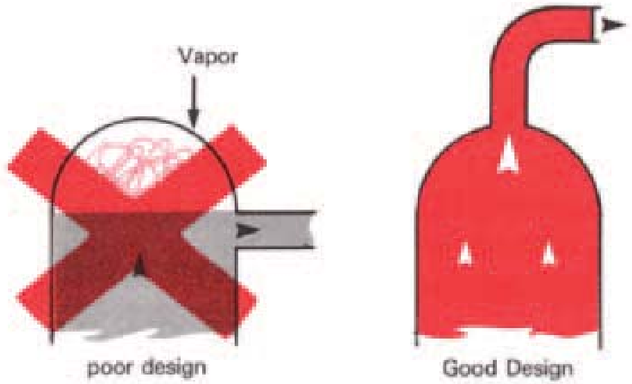


Figure 41 *Piping arrangements should be designed to avoid the formation of vapour spaces.*

amount of air which will remain dissolved in the liquid. Piping arrangements should be studied to prevent the formation of vapour spaces (see Figure 41). In addition, adequate instrumentation should be provided to stop the air flow if the oil flow drops to a low level or stops. It is true that a source of ignition is required, but do not count on the elimination of known sources of ignition. *If air and fuel are allowed to mix in flammable proportions, assume that a source of ignition will somehow be provided*.

In many refining processes, air is not required. On those units, the start-up or shutdown often represents the most hazardous period. At those times, particular care must be exercised to prevent the mixing of air and hydrocarbons. Techniques commonly used to expel air from vessels prior to starting up include the following:

- purging air from the vessel with steam (Figure 42), followed by the introduction of fuel gas;*
- filling the vessel with water** to overflow, followed by the introduction of fuel gas;
- purging air from the vessel with inert gas from a conventional inert-gas generator or with nitrogen.

Absence of oxygen must be confirmed using one of several types of portable oxygen analysers suitable for this purpose.

With either steam or inert-gas purging, the vent gases should be analysed at the end of the purge to make sure that the air has been expelled to a safe level.

In the shutdown, recognized procedures of a similar nature must be followed with equal care to remove hydrocarbons from vessels before air is admitted.

Before vessels are opened for internal inspection or repair, a gas test should be made to confirm the absence of hydrocarbons.

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* See BP Process Safety Booklet *Hazards of Steam* also.

**See BP Process Safety Booklet *Hazards of Water* also.

Figure 42
This is a device for determining the amount of air, or other noncondensibles, present in steam. A representative portion of the steam flows through the sample chamber, heating the sample chamber to steam temperature. Placing the sample chamber in the insulated container speeds up this step. A sample of the steam is then trapped in the chamber by closing in quick succession the inlet valve and outlet valve. The chamber is then lifted from the insulated container and cooled to 100°F (38°C). Condensation of the steam produces a vacuum in the chamber. The amount of pressure

reduction is a function of the relative proportions of steam and non-condensibles (air) in the original mixture, and the air content can be calculated. This instrument cannot be used to determine concentration of air in inert gas. After purging with inert gas, absence of oxygen must be confirmed using one of several types of portable oxygen analyzers suitable for this purpose.

ACCIDENT Due to a combination of unusual circumstances prior to and during an unscheduled shutdown of the Fluid Catalytic Cracker unit, a flammable mixture of air and residual tail gas reached the flare system where an explosion occurred in the knockout drum. The force of explosion deformed the knockout drum and blew a 2-inch nozzle and valve off the end of the vessel. The source of ignition was probably pyrophoric scale.

ACCIDENT A fire occurred inside a FCCU reactor which resulted in severe bulging of a 7 ft. × 6 ft. (2.1 × 1.8 m) section of the hemispherical head with extensive cracking of weld and parent metal. A large quantity of soft coke, up to 5 ft. (1.5 m) thick had accumulated within the top head, over a period of three months' operation following a change in the reactor cyclone configurations. The air used to purge the instrument connections accumulated locally in the head resulting in the formation of coke by partial combustion of hydrocarbons, and a subsequent increase in air accumulation permitted ignition of this coke.

9

Eliminate oxygen

Certain processes and facilities that contain hazardous materials may be protected against fire and explosion by the use of inert gas. This procedure requires the exclusion of the oxygen from the equipment or the reduction of oxygen content to the point where combustion cannot occur.

The maximum amount of oxygen allowed in the various operating units differs, as do procedures for eliminating or reducing the oxygen in the unit. It is important that you know and follow the specific operating instructions for the unit to which you are assigned and that you watch instruments closely and make tests when they are required.

Elimination or dilution of oxygen may involve one or more of the following:

- operate vessel flooded;
- test and bleed off oxygen-bearing mixture;
- fill with high-flash stock or water to drive out air;
- steam until oxygen is dissipated;
- reduce oxygen content by inerting with nitrogen or carbon dioxide;
- blanket with nitrogen or with oxygen-free fuel gas;
- continuous injection of a purge gas through ‘flare type’ blowdown systems while the unit is in operation.

The following incident highlights some of the potential consequences of unloading liquefied petroleum gas* (LPG) trucks and tank cars by pressuring with compressed air.

ACCIDENT While a truck was being loaded with LPG in a refinery, gas displaced from the truck was vented to a low-pressure gas system. The gas line became red hot at the point where the vent entered the line. Subsequent investigation disclosed that the truck had last been emptied with compressed air, and that the gas line contained pyrophoric iron sulphide. During the loading, the iron sulphide ignited the air/ LPG vapour mixture which was being vented into the line. Recognizing that the practice of unloading with compressed air may occur, the hazard can be reduced if a sample of vapour (see Figure 43 on page 38) from every truck or tank car to be loaded with LPG is first checked for oxygen content with a portable oxygen analyser and no LPG is loaded until oxygen has been eliminated. No truck or tank car containing air should ever be loaded with LPG.

*Liquefied petroleum gas, or LPG, as it is usually abbreviated, is propane or butane or a mixture of the two. It is generally used as a fuel.

Figure 43 *Vapour sample being taken from an empty LPG truck.*

ACCIDENT An explosion occurred in the lubricating oil reservoir of a centrifugal gas compressor at an exploration crude oil gathering centre. It was discovered that there were several possibilities for entry of gas or oxygen into the reservoir.

Prime sources of air could be through leaks in the return oil piping, through normal tank breathing during shutdown or from an open manhole or filling connection during maintenance.

Some gas would be expected to pass through from the degasser if the loop seal between degasser and reservoir was dry or if the degasser was not operating efficiently. Operation of the buffer gas system or pressure in the compressor casing in combination with an oil system shutdown and leaking compressor seal could cause gas to enter the reservoir via the oil return piping. According to operators, the oil system was started before buffer gas was turned on, and the seal oil system was in operation just prior to the failure. Gas could have entered the reservoir before the start of the seal oil system from the other machines through the common vent header.

The investigation showed that the conditions were right for static electricity build-up and that a discharge may have taken place.

ACCIDENT An explosion and resulting fire killed 17 men and caused significant equipment damage. The accident originated in a 90,000 gallon (340 m^3) waste storage tank in the utilities area. The waste storage tank was designed to process waste water from the propylene oxide-styrene monomer (POSM) unit before disposal into a deep disposal well on site. The tank was designed as an atmospheric pressure tank with dual conservation vents to relieve pressure build-up and to break any vacuum resulting from normal operation (see Figure 44 on page 39).

Because gaseous-free oxygen was liberated in the tank from light peroxide decomposition, the tank was equipped with an inert nitrogen sweep system to purge the oxygen and maintain an oxygen concentration within safe limits. Due to the presence of light hydrocarbon liquids, the nitrogen sweep leaving the tank also contained hydrocarbon vapours. The tank vapour space was sampled and analysed for oxygen content with a continuous readout in the control room.

A compressor was used to transfer these hydrocarbon vapours from the tank to a pressurized recovery tower. The compressor had failed and was removed for repair and several modifications were made. This action required the shutdown of the nitrogen sweep, and this occurred some 34 hours before the explosion.

The underlying reason for the explosion was an accumulation of oxygen in the vapour space of the tank, which was not detected because of an apparent failure in the oxygen analyser. Since the oxygen analyser continued to show an extremely low and safe level, the nitrogen sweep was allowed to remain off, until just a few minutes before the explosion.

The compressor start-up created enough energy that would have been needed to have ignited the tank vapour space.

The resulting fire rapidly moved through the piping system to the tank vapour space, where the explosion occurred.

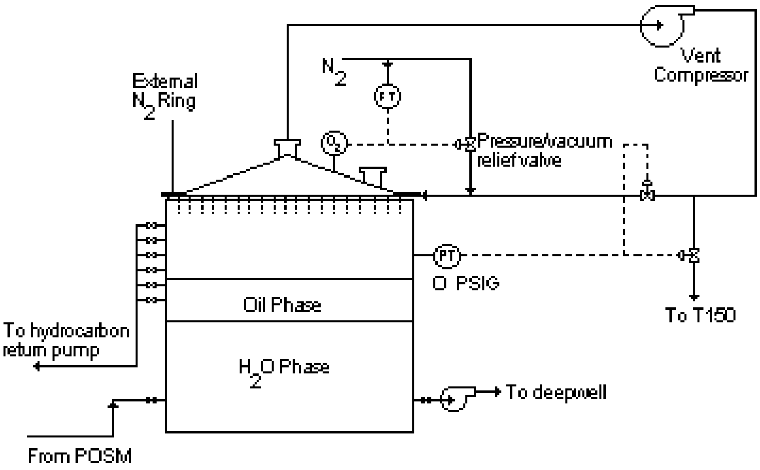


Figure 44 *Explosion in a waste storage tank.*

10

Specific hazards of pure oxygen

The amount of oxygen in normal atmosphere is less than 21% of the total mixture. This quantity is sufficient to cause metal to rust, fires to burn out of control, and certain foods to turn sour. Consider a source of pure oxygen! Pure oxygen is used in small quantities in compressed oxygen gas bottles (for on-line analysers, laboratories, first aid, etc) up to large quantities in liquefied oxygen pipelines (for example, to improve FCC units catalyst regeneration, etc).

Remember that oxygen is a very efficient oxidizer. Using oxygen enriched atmospheres will increase two hazards:

- corrosion rate;
- fire/explosion risk.

Therefore, introducing pure oxygen in a well-known process must be studied carefully—equipment that never corroded in the past may be subject to fulgurant corrosion process. Similarly, ‘incombustible’ materials (at 21% oxygen), may ignite easily or even burn explosively.

Not only will oxygen support a fire, but if the oxygen content in the atmosphere increases, it will dramatically affect:

- the flammable range;
- the energy required to ignite;
- the autoignition temperature.

Flammable range

The flammable range for a hydrocarbon is found to be considerably wider in oxygen than in air. Figure 45 shows the flammable ranges of propane gas for both air and a pure oxygen atmosphere.

The values shown are for atmospheric pressures. Figure 7 shows a graph representing the flammable limits at atmospheric pressure for propane in an atmosphere of oxygen and nitrogen, the two major components of air.

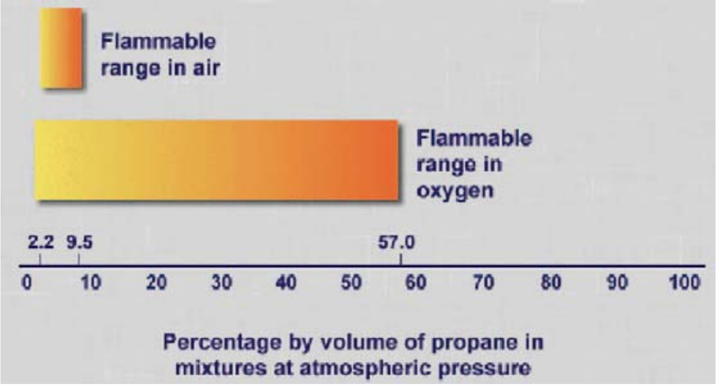


Figure 45 *Flammable range of propane gas in air and oxygen.*

Energy required to ignite

The lower flammability limit is usually determined using a very strong spark or arc produced by a high-voltage transformer. The flammability limit is determined by finding the lowest concentration of fuel vapour that will result in flame propagation for a given spark. As the spark is made weaker, the concentration of fuel vapour has to be increased for the mixture to remain flammable. The strength of a spark igniter is measured in terms of the stored electrical energy (Joules) used to create the electrical discharge.

The lower flammability limit is typically measured using a spark of energy 10 to 100 Joules. This is comparable to the arc created by a short circuit in household wiring. The lowest possible energy that will cause ignition of a flame is known as the minimum ignition energy. For most hydrocarbon fuels this has a value of about 0.25 mJ or about 100,000 times less energy than is used to determine the lower flammability limit. The minimum ignition energy is extremely small, comparable to the energy in an electrostatic spark created on bedding or carpets on a dry day. The minimum ignition energy occurs for a mixture with a large amount of fuel vapour in comparison to the lower flammability limit.

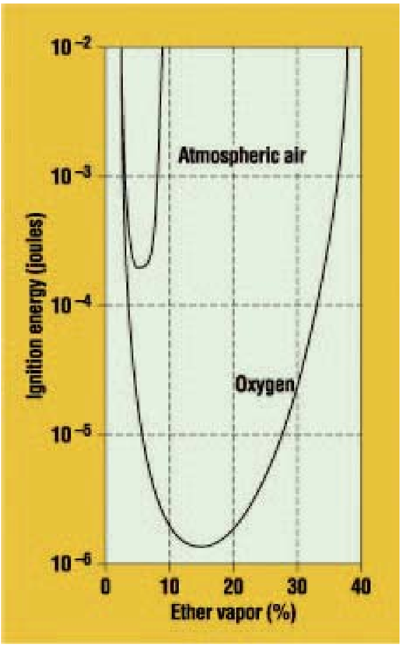


Figure 46 *Ignition energies for diethyl vapour in air and oxygen.*

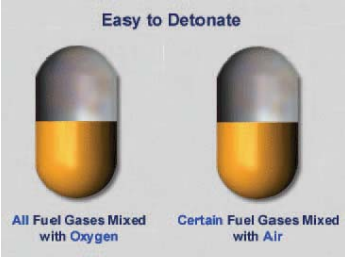


Figure 46 shows the ignition energies for diethyl ether vapour mixed with either pure oxygen or atmospheric air. For a concentration of approximately 16% ether vapour in pure oxygen, it takes only about 1μJ to start an explosion. For ether vapour in atmospheric air, the minimum ignition energy is about 0.2μJ (=200μJ) for a concentration of about 6% ether vapour (although the curves below are developed specifically for diethyl ether, they are fairly typical for a wide range of vapours of organic compounds: note similar lower energy limit for vapour air mixtures to hydrocarbons).

Autoignition temperature

Also, autoignition temperatures are affected by an oxygen increase. For example, as the oxygen content of the air goes from 21% to 100%, the autoignition temperature of kerosene drops from 700°F (370°C) to ambient.

ACCIDENT Everybody is aware of the tragic accident which occurred on 27th January 1967 at Cape Kennedy when the Apollo 1 Command Module burst into flames during a training session, killing all three astronauts on board. While strapped into their seats inside the Command Module atop the giant Saturn V Moon rocket, a faulty electrical switch created a spark which ignited the pure oxygen environment. The speed and intensity of the fire quickly exhausted the oxygen supply inside the crew cabin.

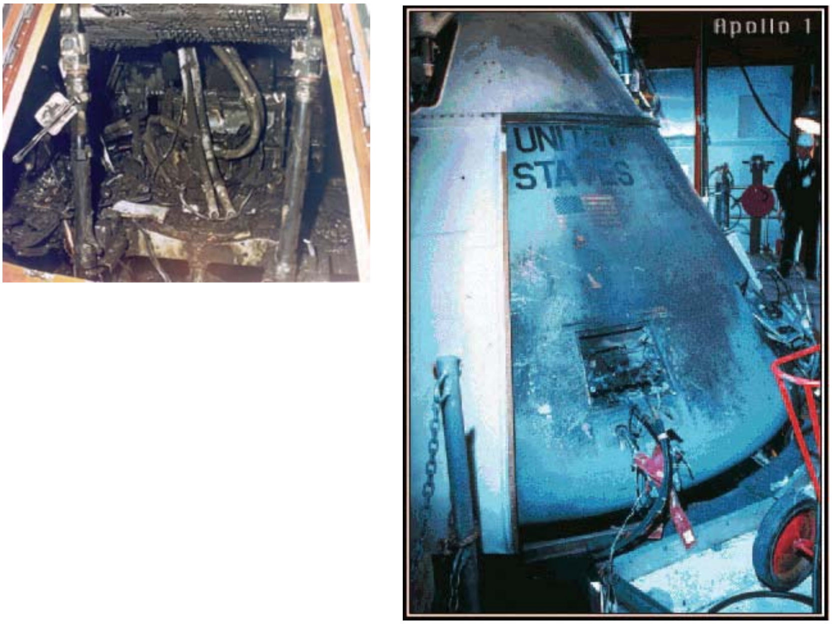


Figure 47a & b *The Apollo 1 tragedy.*

ACCIDENT A maintenance technician in an oxygen producing plant left his work for the smoking shed. When he lit his cigarette, his cotton overalls burst into flames. He was unaware that his clothes had trapped the oxygen-rich atmosphere in which he had been working.

ACCIDENT A welder entered a steel pipe (24 inch (60 cm) diameter) to grind a bad weld at a valve about 30 feet (9 m) from the entry point (see Figure 48). Before he entered, other crew members decided to add oxygen to the pipe near the bad weld. He had been grinding intermittently for about five minutes when a fire broke out enveloping his clothing. Another crew member pulled him 30 feet (9 m) to the pipe entrance and extinguished the fire. However, the welder died the next day from his burns.

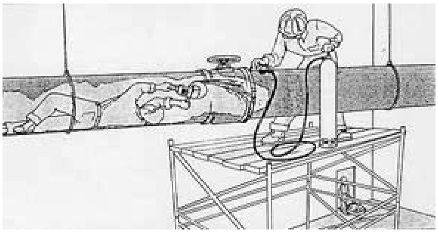


Figure 48 *Fire inside a steel pipe leads to fatality.*

ACCIDENT An explosion occurred in the cryogenic distillation column which generated gaseous oxygen in an air separation unit (ASU). The explosive rupture of the column was caused by the massive runaway combustion of sections of the aluminum plate fin type main vaporizer, which is located in the bottom of the low pressure column above a large inventory of liquid oxygen. The aluminum is presumed to have been ignited by combustible material, probably formed from hydrocarbons originating from the inlet air, which are assumed to have accumulated undetected on the aluminum surface from the liquid oxygen circulation through the closed sections of the main vaporizer.

Major pieces of equipment, some weighing several tons, were found up to 1.3 kilometers (0.8 miles) from the epicentre of the explosion. Blast damage extended to 5 kilometers (3.1 miles) (See Figure 49). A total of 12 people were injured, though none seriously. The closest personnel were located some 200 m (220 yards from the epicentre at the time of the blast but were protected by buildings.

Figure 49 *Explosion on a cryogenic distillation column.*

ACCIDENT Eight workers were killed in a fire that occurred during the fitting out of HMS Glasgow at a UK shipyard. Six other workers were injured. The fire took hold and spread rapidly to three decks. Seventy firemen attended the fire, which took over two hours to get under control due to difficulties getting to the seat of the fire in a compartment at the bottom of the ship's structure.

The investigation found that the fire had resulted from oxygen enrichment of the atmosphere within the compartment. Oxygen is used in conjunction with propane or acetylene for burning and welding. A bulk oxygen supply was provided for the ship from a storage tank located on the shore, and fed multiples individual manifolds.

Accidents involving flexible hoses and oxygen

Flexible hoses are routinely used to transfer oxygen in refineries or chemical plants. The two incidents below describe what can happen when using flexible hose, from small ones for laboratories to big ones for industrial use.

ACCIDENT Another accident occurred when a laboratory technician went to the gas cylinders shed to change an oxygen bottle before it was empty. Unfortunately, he used a greasy spanner—grease was the fuel, the flexible hose provided the oxygen. The explosion ruptured the flexible hose (rupture pressure = 980 bars (14,200 psi)), broke all laboratory windows and injured the operator (see Figure 50 a & b).

***Figure 50a** Damage caused by flexible hose rupture.*

***Figure 50b** The damaged hose.*

ACCIDENT A moored submarine started receiving gaseous oxygen into four banks of oxygen bottles located in the forward torpedo room. The oxygen was supplied from a mobile unit on the dock through a hose made up of three fifty-foot sections. The mobile unit carried liquid oxygen in a 500-gallon tank and had provisions for pumping liquid to a vaporizer on the unit, where it was converted to a gaseous state before delivery to the ship through the hose. A fire was started in the hose at a point about 40 feet (12 m) along its length measured from the mobile unit. The fire was caused by the escape of high velocity oxygen through a small hole in the hose which ignited the high carbon steel mesh in the hose. The fire caused an explosion within the hose which was severed. A great volume of high velocity oxygen escaped, impinging on inflammable material in the after room causing a fire which soon resulted in an explosion as other combustible materials in the compartment immediately became fuel for the pure oxygen. A sailor lost his life in this tragic accident. The oxygen-fueled fire was so intense that the after portion of the ship had to be submerged, with the hatches open, to extinguish it (see Figure 52).

Experience provided by two companies, using the same type of high pressure hose, revealed that they had also experienced catastrophic failures of the hose at high pressure. One company reported that there was a definite indication that there had been a fire in the hose. The company considered the probable cause of failure to be the ignition of the carbon steel mesh in the tube by the passage of oxygen at high velocity through pin point holes in the casing. A second company also reported failures of the hose in testing at high pressure and that there was definite evidence that there had been burning within the hose. They further attributed the failure (in the hose they tested) to the fact that in curing the hose, internal defects were sometimes developed which would cause turbulent flow at specific points while charging and eventually wear through to the carbon steel mesh with resultant combustion and explosion.

Figure 52 *After portion of submarine being submerged with hatches open to kill the fire.*

Note on oxygen depletion by fire-fighting systems: If oxygen sustains combustion, low levels of oxygen prevent ignition. This principle is used by some fire suppression systems that use inert gases (nitrogen, carbon dioxide, argon . . . or a mix of these) to kill fire. These systems must be installed and used with caution as they are designed to achieve oxygen levels which do not sustain life.*

ACCIDENT Workers were engaged in de-energizing electrical circuit breakers in preparation for preventive maintenance activity on the electrical system in a laboratory building. Thirteen people were in the building, including foremen, operators, electricians, and fire protection personnel. As the last electrical circuit breaker was opened, the CO_2 fire suppression system unexpectedly discharged without an evacuation warning alarm. Within seconds, the workers found themselves struggling to escape the potentially lethal atmosphere under near zero visibility and the disorienting effects of CO_2 (see Figure 53). The accident resulted in one fatality, several life-threatening injuries, and significant risk to the safety of initial rescuers.

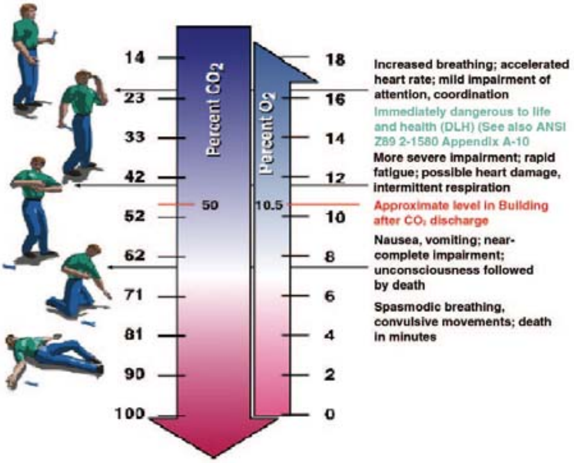


***Figure 53** The effects of increasing the percentage of CO_2 in the atmosphere.*

Some other systems are designed to deplete oxygen levels to around 16%, enough to sustain life, but sufficiently low to prevent or slow down fires. Generally, these systems are not acceptable as they introduce multiple hazards to the operators:

- by routinely operating below the internationally recognized safe levels of oxygen*, operators are induced to a false sense of confidence and standard detectors are not adequate (alarm level 19 or 19.5%).
- decreasing the oxygen level may have a long term effect to health, and even a short term one to some sensitive persons.

- Near inert gas inlets, oxygen levels may be unsafe. Air distribution in the protected space must be carefully studied and any change (e.g. equipment move in room, door opening, fan failure . . .) might create different, and therefore hazardous, conditions.
- It is nearly impossible to achieve a fail-safe system (reliance on oxygen detectors, fans . . .).

* See BP Process Safety Booklet *Hazards of Nitrogen and Catalyst Handling*

11

Trapped pressure hazard

Although it is not the main scope of this booklet, it must be remembered that compressed air is dangerous and must be employed with caution. Numerous accidents have occurred and the examples below are given only as illustrations. For more details, please refer to BP Process Safety Booklet *Hazards of Trapped Pressure and Vacuum*.

Remember that gases accumulate energy when compressed (see how an air rifle works…). Therefore, a system under gas pressure is exactly like a loaded rifle waiting to be discharged.

ACCIDENT A contractor was preparing to install fibreglass tanks. Prior to installation, the tanks were required to be air tested. The employee was under the erroneous impression that the air test required applying 80 psig of air pressure to the tank interior. The pressure gauge had already reached 40 psig when the employee left for lunch with the air compressor still running. Twenty minutes later, the tank blew apart. The explosion sent two neighbours to the hospital and damaged about a dozen cars. The 12,000 gallon tank broke into two pieces. The end cap dome of the tank travelled 110 yards (100 m) and landed on a parked truck. The remainder of the tank, 8 feet (2.5 m) in diameter and 30 feet (9 m) long, was blown half a block to the south.

ACCIDENT A leak test on a heat exchanger was being conducted using low pressure gas (4.5 bars) when the tube bundle was ejected with great force striking two of the employees (see Figre 54). One of them died from massive internal injuries as a result of the bundle striking him directly in the chest. The other was seriously injured.

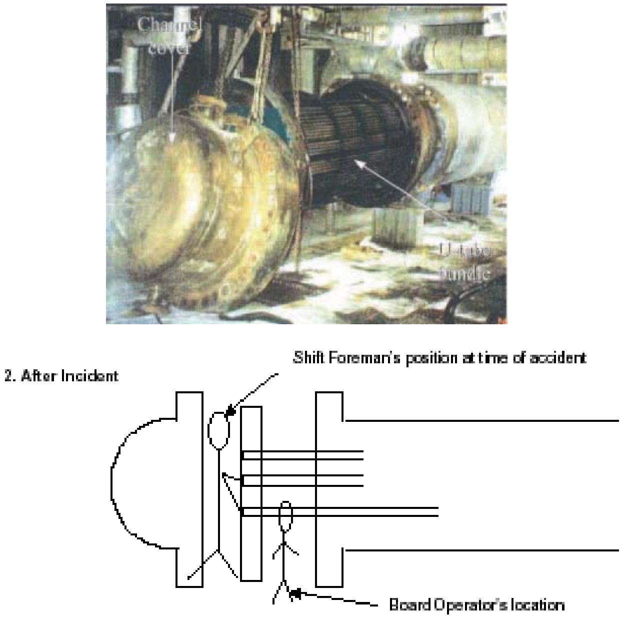


Figure 54 a & b *Fatality caused by ejection of a tube bundle.*

ACCIDENT A drum was being pneumatically tested for leaks and to meet a certain design pressure. The drum failed during the test, blowing the end off the drum, a 4-feet (1.2 m) by 4-feet (1.2 m) piece of steel, with enough force to throw the plate across the road narrowly missing an employee, who if hit would have certainly been seriously injured or killed.

ACCIDENT Figure 55 shows another example of how leak tests at low pressures can kill. This plug was ejected during a heat exchanger tube test.

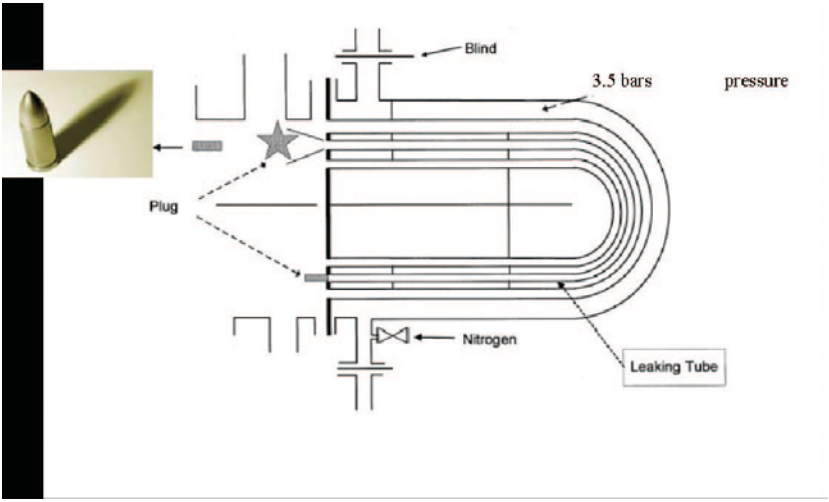


Figure 55 *An ejected plug.*

ACCIDENT While being filled with compressed air an old portable air tank ruptured and injured the owner (see Figure 56). Because of corrosion, the rupture occurred at 80psi (5.5 bars) when the tank was rated for 125psi (9 bars).

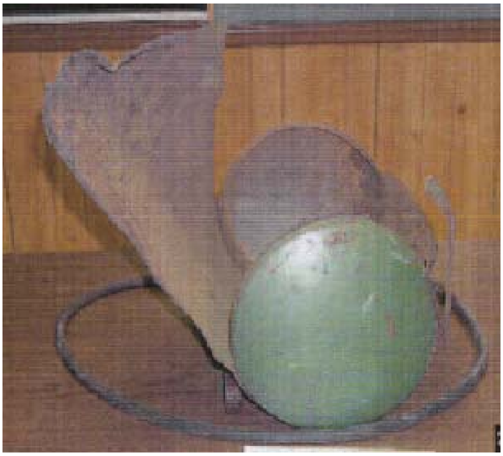


Figure 56 *Air tank ruptured while being filled with compressed air.*

- Never use air or gas for a pressure test. The energy stored in a pneumatic test is far greater than for a hydraulic test and therefore hydraulic testing is always safer.
- Always be aware of places where air or gas can accumulate in piping (high points, hydraulic legs . . .).
- When working on a piece of equipment that may contain air or gas, never stay in front of it (heater pipe plug, heat exchanger tube, pig receiver door . . .).

Also, remember that air can be compressed in a vessel when filling it with product, if the vents are not able to cope. This is what happened in the following two accidents, luckily without anybody being hurt:

ACCIDENT An atmospheric storage tank used to contain boiler treatment chemicals failed due to overpressure. The tank was being filled with water at the time of the failure. The tank was an insulated horizontal cylinder, with flat heads. The head on the north end of the tank separated from the cylinder, and struck piping about 10 feet (3 m) away, damaging a potable water line, safety shower, and a chemical injection day tank that was out of service. The concrete supports around the mounting studs were fractured.

The tank overpressured as a result of inadequate venting during the water washing operation. The vent on the tank was removed and a flanged water supply installed in its place (see Figure 57a). Air in the vapour space was compressed as the tank was filled because it had no way to escape.

Figure 57a *Vent and water hose installed.*

***Figure 57b** Ruptured vessel.*

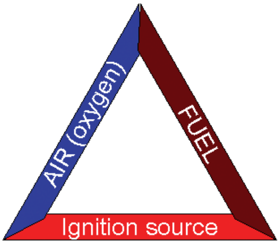
ACCIDENT Workers were filling one of two tanks with water from a fire hydrant. One worker had just checked to see if air was being forced from the pressure relief valve on top and had one foot on the bottom rung of the ladder and one foot on concrete after descending when a loud explosion was heard. The top of the tank blew off because the relief valve could not displace trapped air fast enough for the volume of water that was being forced in (see Figure 58).

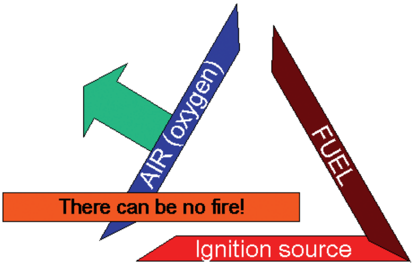
***Figure 58** Top of a tank blown off due to build up of trapped air.*

12

Some points to remember

1. Three elements are required for a fire:
    - Air (oxygen)
    - Fuel vapour
    - Ignition source
2. Remove one of the three elements and a fire cannot exist. This should be the fuel or the air (oxygen), since ignition sources are so plentiful.

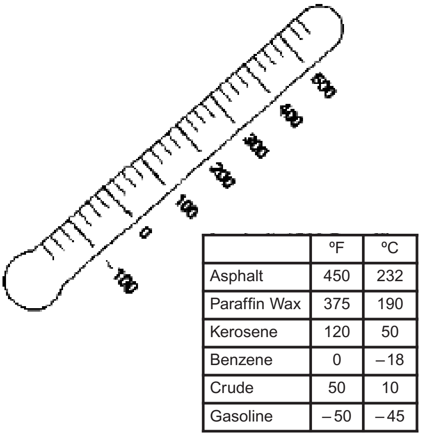




3. One-fifth of air is oxygen. Oxygen is always present if air is present.
4. A flammable mixture of commercial oxygen and petroleum vapours:
    - provides a wider explosive range;
    - makes the mixture easier to detonate;
    - creates a more violent explosion than air-petroleum vapour.

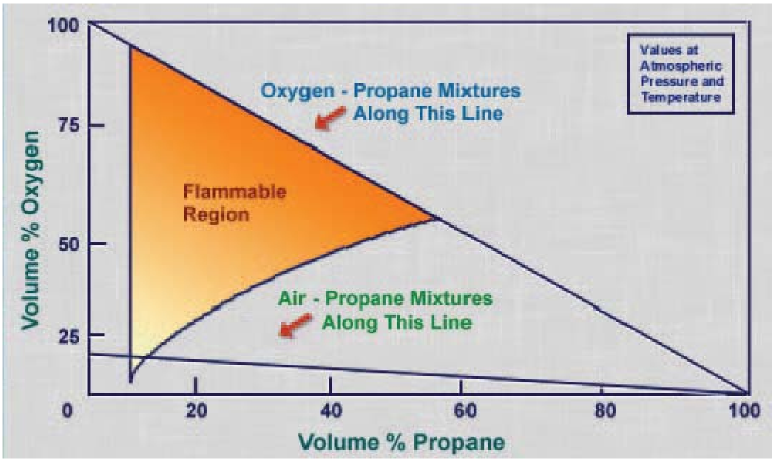
    Eliminate use of commercial oxygen and minimize likelihood of a detonation.
5. Detonations are violent. Vessels fragment and fragments scatter.
6. Old processes are not immune to uncontrolled hydrocarbon-air (oxygen) mixtures. A periodic re-evaluation of the process is recommended.

7. Petroleum products will vaporize enough to form flammable mixtures with air:
   - some at room temperature;
   - some even below zero;
   - some only by the addition of heat.



	°F	°C
Asphalt	450	232
Paraffin Wax	375	190
Kerosene	120	50
Benzene	0	– 18
Crude	50	10
Gasoline	– 50	– 45

8. Oxygen in process equipment can be either eliminated or diluted with inert gas, water or steam.
9. Don't guess—analyse mixtures for oxygen content.
10. The flammable range of any hydrocarbon is considerably wider in oxygen than in air.



11. Remove oxygen to prevent unnecessary flammable mixtures.
12. Follow directions. Know your unit and its limitations.
13. Remember:
    - assume that ignition sources will be provided;
    - assume that an explosion will be a violent, detonating type;
    - operate as far from flammable limits as possible—the ideal goal is 0.0 percent oxygen.
    - follow established procedures.

Acronyms and abbreviations

O_2	Oxygen
CO_2	Carbon Dioxyde
FCCU	Fluid Catalytic Cracker Unit
LPG	Liquefied Petroleum Gas (Propane–Butane)

Test yourself!

1. A fire can occur only when all three sides of the fire triangle are present.

   True ☐ False ☐

2. Catalytic gas indicators can perform well in inert atmospheres.

   True ☐ False ☐

3. The flash point is the ‘lowest temperature at which enough vapours are given off to form a flammable mixture of vapour and air immediately above the liquid surface’.

   True ☐ False ☐

4. Fuel-air mixtures outside the flammable range will explode.

   True ☐ False ☐

5. Mixtures of fine solid or liquid fuel particles (dusts, mists or sprays) with air or oxygen may burn as readily as vapour-air mixtures.

   True ☐ False ☐

6. Most oils mixed with air are expected to auto-ignite at temperatures between 500 and 800°F (260 and 427°C).

   True ☐ False ☐

7. Explosions travel at relatively slow speeds, detonations at high speeds.

   True ☐ False ☐

8. Oxygen is not a very efficient oxidizer.

   True ☐ False ☐

9. Autoignition temperatures are not affected by an oxygen increase.

   True ☐ False ☐

10. The flammable range for a hydrocarbon is found to be considerably wider in oxygen than in air.

    True ☐ False ☐

1T/2F/3T/4F/5T/6T/7T/8F/9F/10T