

J M Alexander*

Incidents are described of fires occurring within a process employing air oxidation of a hydrocarbon. A hypothesis based on a two film model is proposed to explain how these fires can occur below the auto-ignition temperature. Practical suggestions are made for dealing with this hazard.

INTRODUCTION

Considerable experience has been built up on the air oxidation of cyclohexane to cyclohexanol and cyclohexanone. Under certain circumstances the reaction medium has been known to burn in the air fed to the oxidisers, rupture lines and cause serious fires. No apparent sources of ignition were present, the process temperature being far below the auto-ignition temperature. The author proposes a mechanism (but no experimental proof) to explain this phenomenon and suggests that it is of general significance, other air oxidation processes could be subject to this hazard.

Liquid Phase Air Oxidation Processes

Many liquid phase air oxidation processes are carried out in essentially similar ways. Air is fed to the bottom of a vessel, usually the vessel is mechanically agitated, and the reaction is carried out under the necessary conditions. Various processes are described by Sheldon and Kochi (1973) and the safety aspects of a specific process by Claydon (1968).

The product of the oxidation process is recovered by crystallisation or distillation; any solvents used as the reaction medium are recycled. Sometimes a portion of the oxygen depleted off gases are recycled to reduce the oxygen concentration of the incoming air. Similarly oxygen is used to increase the oxygen content of the oxidising medium in certain processes.

* Imperial Chemical Industries Limited, Petrochemicals Division.

Incidents Involving Cyclohexane

For many years, it has been known that in the manufacture of KA (a mixture of the ketone cyclohexane and the alcohol cyclohexanol) by air oxidation of cyclohexane, occasionally a blackened product was produced. This "black KA" was always associated with restarting the plant after a shut down and caused by some of the contents of the oxidiser flowing back up the air inlet line, remaining there until the plant was restarted, and catching fire in contact with the air being fed to the oxidiser.

The temperature reached in this sort of fire is high enough to melt through the air inlet line. When this happens there is nothing to stop the contents of the oxidiser from being discharged and in view of the large inventories of many modern plants the resulting incident would be a major fire. Fortunately, none of the incidents known in ICI resulted in burning through the air inlet line. It is believed that major fires have occurred which caused extensive damage, due to this abnormality.

An examination of one incident of "black KA" revealed that a build up of solids had engulfed the air dispersion pipe to such an extent that the local agitation was suppressed, an almost immobile bubble of air formed on the under-surface of the air inlet pipe and initiated a fire. The formation of a large semi mobile air bubble is inferred from the extent of the heat affected parts of the air distribution pipe. Very hot gas was in contact with the underside of the pipe as a large bubble rather than small bubbles of cold air passing into the reaction mixture. This is shown in Figure 1, the heat affected area being clearly visible and in one place the pipe has been burned through.

When the incident occurs in this fashion, the danger is not so acute, since burning through the air pipe inside the oxidiser is not so serious as burning through the air pipe outside the oxidiser. All that happens is that the air can come out through a different hole within the confines of the vessel. However, if the semi mobile air bubble can contact the wall of the oxidiser then the oxidiser may become overheated locally and rupture under the normal process pressure.

Hazard Mechanism

From the liquid phase oxidation reaction conditions, the relevant auto-ignition temperatures and the conditions under which gas phase oxidations proceed, it would be thought most unlikely that incidents such as have been described could take place.

For example Hoot and Kobe (1955) refer to temperatures above 300°C being necessary for the uncatalysed vapour phase oxidation of cyclohexane. Short residence times of a few seconds were used.

The auto-ignition temperature in Table I for cyclohexane is taken from Hilado and Clark (1972) who note the lowest auto-ignition temperatures recorded in the literature where time delays of a few minutes were used. These are all values at atmospheric pressure except for one value of the auto-ignition temperature of cyclohexane at 10 bar (private communication). Both auto-ignition temperatures are

significantly higher than the reaction temperature, see Table I.

It is unlikely that gas phase residence times of as much as a few minutes are possible in the incidents described. Air passes over liquid trapped in the air inlet line and on through the line in a matter of seconds. The contents of semi-mobile bubbles in the oxidiser are again very unlikely to persist for as long as a few minutes, they will probably be exchanged every ten seconds or so. The liquid phase residence time, in the air inlet pipe certainly will be many minutes; but it is residence time in the vapour phase which is necessary for an auto-ignition reaction to develop. It is therefore very unlikely that actual auto-ignition temperatures are as low as the lowest quoted in Table I.

TABLE I

Process	Initiation Temperature (°C)	Typical Reaction Temperature Range (°C)	Auto-ignition Temperature (°C)
Cyclohexane oxidation by air (9 - 10.5 bar)	125 - 150	150 - 175	245 (1 bar) 220 (10 bar)

There seems little doubt that the incidents described in this paper are instances of ignition occurring at temperatures below the normal auto-ignition temperatures. The influence of the efficiency of air dispersion and of the liquid phase oxidation reaction of this apparent anomaly is now developed.

Incidents where cyclohexane has been ignited in the air line have only occurred when the temperature of the air fed to the oxidisers has been high enough to initiate a liquid phase reaction, the initiation temperature for cyclohexane oxidation is shown in Table I. When the air inlet temperature was above 120 - 150°C burning in the air inlet line was observed from time to time. When the air temperature was reduced to 100°C or less no more incidents were observed. It is concluded that an essential condition for an ignition of cyclohexane vapour to occur in the air inlet line is that cyclohexane is present in which a liquid phase oxidation reaction is taking place. However, why does the oxidation not take place merely as a liquid phase reaction in the air line? A common feature between the incidents in the air line and the incident in the cyclohexane oxidation within the oxidiser is the lack of normal air dispersion. It is believed that the lack of proper air dispersion results in the air bubbles having a much lower specific surface area and that this is the principal factor which will allow a liquid phase oxidation to initiate combustion in the gas phase.

A simple two film model may assist in explaining why poor gas dispersion leads to ignition of the flammable vapours when a liquid phase reaction is taking place. This is illustrated diagrammatically in Figure 2.

When air is bubbled through a cyclohexane oxidiser the reaction proceeds quite normally and even if the agitator stops the only effect is a reduction in total oxygen absorption. It is believed that by the time the bubble has been detached from the air inlet, perhaps half of the oxygen has been absorbed. The oxygen concentration at the interface between the air and the oxidiser contents, will then be well below the minimum for combustion to occur, (about 9% under oxidiser conditions). The oxygen concentration will fall away further through the liquid phase boundary layer. The liquid phase oxidation reaction will occur in the liquid phase boundary layer as well as in the bulk of the liquid. The temperature in the liquid phase boundary layer will be a little higher than the temperature of the bulk of the liquid, or of the gas, as long as a significant oxygen transfer rate is established which keeps concentration and hence the reaction rate higher in the liquid phase boundary layer.

The liquid phase oxidation proceeds by way of free radicals via hydroperoxides to the product, alcohol and ketone as in cyclohexane oxidation for example. It follows that there will be a continuous injection of free radicals into the gas phase side of the interface by evaporation.

Since free radicals are not ionic and are similar in structure to the molecule from which they are formed, it is assumed that they will not be involatile; they will be able to evaporate into the vapour phase, though for a very short life.

When the agitation is considerably reduced, either by a build up of solids or by isolating liquid in the air inlet line, the first thing to happen is that the bubble size is greatly increased. The transfer co-efficients of heat and mass on the liquid side of the interface are significantly reduced. The transfer co-efficient of oxygen on the gas side interface is probably not affected as much and for the present purpose it is considered constant. In other words the liquid side boundary layer thickens and the gas phase boundary layer stays the same.

Because the surface area to volume ratio of the bubble is very much reduced from normal, establishment of a concentration gradient and maintaining a transfer of oxygen to the liquid still leaves the centre of the bubble with a high oxygen concentration. The bubble appears to remain stationary and bubbles break away whilst fresh air is introduced; this must also be the case for air passing over liquid held up in the air line. The oxygen concentration is therefore maintained at a high level, probably close to 21% in the bulk of the gas.

The effect of maintaining the oxygen concentration at a higher level on an unchanged boundary layer is to significantly increase the oxygen transfer rate and to sustain it at a steady level instead of the normal rapid fall with time that happens in a normal air bubble. The oxygen concentration at or near the interface could therefore easily be as high as 10% at which point there will be sufficient oxygen present to sustain combustion in the volatile and flammable vapours evaporating from the bulk of the liquid into the air bubble. A higher oxygen concentration at the interface will give a faster reaction rate in the liquid side boundary layer, a greater heat output

and hence a higher temperature which is enhanced by poorer heat transfer away into the bulk of the liquid.

The higher temperature will increase the vapour pressure of the free radicals taking place in the liquid phase oxidation reaction in the boundary layer and also increase the concentration of free radicals present in a faster reacting medium; this should give a much higher rate of free radical injection into the gas phase boundary layer than is the case in a properly agitated system.

It is proposed that the rise in oxygen concentration at the air bubble interface combined with the injection of free radicals, presumably at a much higher rate than normal, is the mechanism by which the gas phase can be ignited.

It is assumed that the free radicals generated by the liquid phase oxidation and evaporating into the gas phase will be equally effective in initiating gas phase oxidation as the free radicals normally generated in the gas phase when it is being oxidised. The free radicals may be identical or perhaps the free radical being injected into the gas phase can further react so as to produce the free radicals necessary for the chain reaction in the gas phase. Berezin, Denisov and Emmanuel (1966) consider that the evidence available on the gas phase oxidation mechanism of cyclohexane is not conclusive enough to specify the radicals and steps involved.

Start-up and Shut-down

A typical start up and shut down sequence is now described.

When an oxidiser is brought on line from cold, the oxidiser is firstly purged with nitrogen to remove air and then charged with a suitable quantity of reactants and catalyst. It is then brought up to a temperature at which the liquid phase oxidation reaction will initiate.

A continuous purge of nitrogen is introduced some time during the warming up period. Air is then admitted at a very low rate, the temperature is closely watched to see if initiation of the liquid phase oxidation reaction has occurred and the off gas oxygen analyser carefully noted to ensure that the oxygen concentration stays well below the minimum for combustion. A high oxygen concentration will result from too high an air rate. When a temperature rise indicates initiation has occurred, the air rate can be increased gradually until normal operating conditions are reached. The nitrogen flow is turned off when the reaction has been initiated. In the case of continuous oxidation the feed is brought on gradually as the air feed is increased, and in the case of batch oxidation the end of the cycle is usually determined by an increase in oxygen concentration in the off gas.

The oxidisers are shut down by isolating the air and liquid feeds and re-establishing a nitrogen purge through the air line. An inadvertent shut down occurs every time the air compressor trips out or the air control system fails; the liquid feed is isolated and a nitrogen purge established automatically on low air flow. These isolations are usually made directly from the control room using

remotely operated air powered isolation valves. The isolation valve may not seat properly and the nitrogen may fail to be the correct pressure, in which case either air can leak into the oxidiser when the oxidiser is shut down deliberately, and the air compressor stays on line, or the contents of the oxidiser leak into the air line when the compressor trips out.

Thus it must be accepted that oxidiser contents will leak back into and air line from time to time, when a simple system as described is installed, even though a non return valve is also fitted in the air line.

When the air isolation valve leaks but the nitrogen pressure is correct and the flow sufficient to allow for both a sufficient purge rate and the leak through the valve, then the liquid stays in the oxidiser and does not leak back into the air line or even the sparge pipe.

Manual isolation valves are not much use to improve the system reliability, back flow of liquid will occur in the time interval between the control room operator closing the motorised valves and then the manual valves. If manual isolation valves are used rather than motorised isolation valves, then back flow of reactants will occur every time the compressor trips out.

Eliminating the Hazard

Burning of oxidiser contents in the air inlet line can best be eliminated by stopping the liquid phase reaction from occurring. This can be done by reducing the temperature of the air leaving the compressor so that it will not initiate a reaction. It is usually known by experience what temperatures are necessary to ensure that the reaction will proceed fast enough to exceed the heat losses, initiate the liquid phase reaction and raise the temperature to the normal equilibrium value. The heat losses from the air line will usually be greater in proportion, the initiation temperature should be a little higher in the air line. Allowance should be made for a margin of safety and for variations in temperature control of the air, a figure of 20 - 30°C below the known lowest initiation temperature should give an ample margin. Thus in the case of cyclohexane oxidation an air temperature of 100°C or below will eliminate the hazard. This procedure was adopted on the plant and has been entirely successful in eliminating all incidents due to cyclohexane burning in the air inlet pipe.

An alternative approach is to stop the contents of the oxidiser from flowing back on shut down. Non return valves, automatic block valves, steam purging, an automatic flow of nitrogen have all been tried. These are all subject to random failure; a sufficiently reliable system is fairly complex and usually no cheaper than cooling the air. An automatic flow of nitrogen is recommended as good practice even if it does not always succeed in eliminating back flow.

Certain mechanical details assist in achieving a liquid free air inlet pipe:-

- a) The air line rising from the air compressor to the oxidiser should fall from its highest point right to and on through the oxidiser. No horizontal sections should be used and no upward sloping sections. This will ensure that momentary ingress

of small amounts have a good chance of being completely expelled from the air pipe when the air is re-established.

- b) The air outlet point in the oxidiser should incline downwards if it is a single hole outlet or the holes in the pipe should be on the underside of the pipe if it is a sparge outlet. This will ensure that it is impossible to hold up liquid within the air inlet line at this point.

These points are illustrated in Figure 3.

The incident in which a build up of solid impurities caused the damage illustrated in Figure 1 is not so easy to prevent by simple direct means but fortunately, since the damage is internal, as long as the vessel wall is not affected the damage is an inconvenience rather than a disaster. This sort of incident is prevented by detecting the build up of solids and avoiding process conditions where they build up rapidly. The build up can be detected by a thermocouple on the bottom of the oxidiser. The outside of the oxidiser will cool significantly if solids build up to an appreciable extent; confirmation of the build up can be made by scanning the vessel with a radioactive source.

The air should not be discharged close to the bottom of the vessel in processes where solids are present either normally or are likely to be produced from time to time. A change in the character of the solids, or a reduction in the dispersion efficiency of the agitator, will easily cause the air dispersion point to be engulfed by solids and result in a gas phase burning incident where the oxidiser wall is over-heated. This type of incident can be avoided by raising the air dispersion point close to the agitator.

Gas phase burning can be detected by a change in the CO and CO₂ levels in the off gas. Small amounts of around 1% of CO and CO₂ are normally found in liquid phase hydrocarbon oxidation processes and a knowledge of this level is sometimes valuable in monitoring the process. If all the air to an oxidiser is consumed by burning in the gas phase the combined CO₂ and CO levels in the off gas can be expected to be about 25 - 30%. Not all the air will be used up in this way and if the sensitivity and scale of the instrument allows, an increase of 0.5% over the normal level should be fairly obvious; this represents say 2½ - 5% of the total air flow to an oxidiser being used up in gas phase oxidation. If more than one oxidiser is coupled up to the same off gas system, separate CO/CO₂ analysers should be provided for each oxidiser, otherwise the production of small amounts of CO and CO₂ is likely to be missed because of dilution with the off gases from the other oxidisers.

Oxygen Enrichment

An increase in the plant output can sometimes be achieved by adding oxygen to the inlet air or even by using oxygen instead of air.

Whether processes will be significantly more hazardous, if the air fails in a mixed air/oxygen feed and the oxygen is not turned off, is not a question which can be resolved without experiment. The hazard may not be much worse due to normal auto-ignition. Auto-ignition temperatures quoted by Mullins (1955) and Kuchta, Lambyris and Zabetakis (1962) show that the difference between lowest quoted values in air and in oxygen are lower in oxygen by only 10 - 30°C in general. It is the initiation temperature of the liquid phase oxidation in pure oxygen and its relationship with the oxygen temperature which is of greatest

interest. The liquid phase oxidation initiation temperature in oxygen, or in oxygen/air mixtures, may be significantly lower than the initiation temperature in air and due account should be taken of this possibility.

What happens when oxygen alone enters the oxidiser is not so easy to say. Normal oxidation may take place but perhaps a less extreme deterioration in agitation would lead to ignition of the gas phase.

A consequence of oxidising using pure oxygen is that there will be no concentration gradient of oxygen in the gas phase by mass transfer through nitrogen. If the vapour pressure of the contents of the oxidiser is sufficiently high there will be a concentration of oxygen gradient, through that vapour, but even so, the oxygen concentration at the interface would be higher than with air oxidation. What affect this would have on the ease of initiating a gas phase ignition could only be determined by experiment.

The most reliable way of adding oxygen would be to mix it with the air prior to compression so that when the compressor trips out, oxygen is not fed to the oxidiser. If the oxygen cannot be fed through the air compressor and a separate compressor or a line under pressure has to be used, then a reliable system should be used to prevent oxygen alone from being fed to the oxidiser. Such a system would comprise a ratio control to fix the proportion of air to oxygen, a low air flow trip to shut off the oxygen and an oxygen analyser to trip the oxygen on high oxygen. The system would be designed according to principles of good reliability engineering, so that the probability of oxygen flowing by itself because of an air failure is at a level acceptably low for the risk involved.

Inert Gas Recycle

Some processes employ an inert gas recycle so as to modify the course of the reaction and produce a product of different composition. On the face of it this would be expected to improve the safety of the process but this is not necessarily so.

Off gases from the oxidiser are saturated with flammable vapours from the reaction medium. Part of the gas is recycled via a compressor and the remainder is stripped of its flammable vapour content by condensation or absorption, before being vented to atmosphere. In addition process upsets, or cooling of the off gases being recycled, will inevitably lead to liquid droplets being entrained in the gas.

If the recycle gas is then mixed with air, even if the final gas/air mixture is outside the flammable limits, it will be possible during the mixing process for a flammable mixture to be produced which could be ignited. If entrained liquid droplets can collect and fall or flow back down the air line then there is a possibility of igniting these droplets. Not only would the droplets then burn but the mixed air/recycle gas could also ignite, burn out the recycle line and suddenly release the contents of the oxidiser.

A related hazard of recycle gas is the possibility of a change in the recycle gas to air flow ratio. If the ratio changes because of instrument or machine failure and produces a mixture in the flammable vapour range, an explosion will result if a liquid phase oxidation is initiated at a nearby gas/liquid interface. Other sources of ignition may of course be present but even if they can be eliminated, the risk of an ignition by the mechanism described in this paper will be difficult to exclude if the recycle is taken directly from the oxidiser off-gas.

The easiest way to overcome this hazard is to feed the recycle gas to the oxidiser on its own and rely on bubble coalescence within the oxidiser to provide the mixing required to dilute the oxygen content of the air feed. Alternatively the recycle gas can be stripped of the flammable vapour it contains, down to a fifth of the lower explosive limit for example, and then recycled. This has the disadvantage that a much larger stripping section is required in the plant and a lower heat economy because of the heat needed to warm the recycle gas back up to reaction temperature.

It is probably not possible to remove the hazard completely by other design methods. A vertical pipe in which the air and recycle gas were mixed would prevent liquid from collecting in a pool on the pipe bottom if the pipe were horizontal but it would not prevent the walls from becoming wet when liquid condensed out or entrained. Whether a thin film of liquid could sustain a liquid phase oxidation, which would ignite the vapours, or not is unknown.

Further Work Needed

No experimental work has been undertaken to substantiate this theory since the necessary precautions are now well understood at least in the cyclohexane oxidation process. As existing oxidation processes become modified, by oxygen enrichment of air for example, and as new proposals are developed it may be useful to know more in detail how the process of vapour phase ignition is initiated in order to highlight areas of potential risk.

CONCLUSION

Practical measures such as described in this paper can eliminate or greatly reduce the risk of initiating dangerous fires within liquid hydrocarbon air oxidation processes. Experimental work would be needed to confirm the validity of the two film mechanism proposed to describe the ignition mechanism. Further experimental work may be needed, in developing liquid phase air oxidation processes, to define safe working limits rather than on waiting for an incident and relying upon experience.

REFERENCES

- Berezin, I V, Denisov, E T, and Emmanuel, N M, 1966, "The Oxidation of Cyclohexane", Pergamon Press, Oxford, England.
- Claydon, D A, 1968, I Chem E Symposium Series, No 25, 36
- Hilado, C J, and Clark, S W, 1972, Chem, Eng 79, 75
- Hoot, W F, and Kobe, K A, 1955, Ind Eng Chem, 47, 776.
- Kuchta, J M, Lambyris, S, Zabetakis, M G, 1962, Flammability and Auto-ignition of Hydrocarbon Fuels under Static and Dynamic Conditions, Bu. Mines. Rept. of Invest. Report No 5992.
- Mullins, B P, 1955, "The Spontaneous Ignition of Liquid Fuels", Butterworths Scientific Publications, London, England.
- Sheldon, R A, and Kochi, J K, 1973, Oxid and Comb Revs. 5, 135.

Acknowledgements: Thanks are due to colleagues for their useful comments.

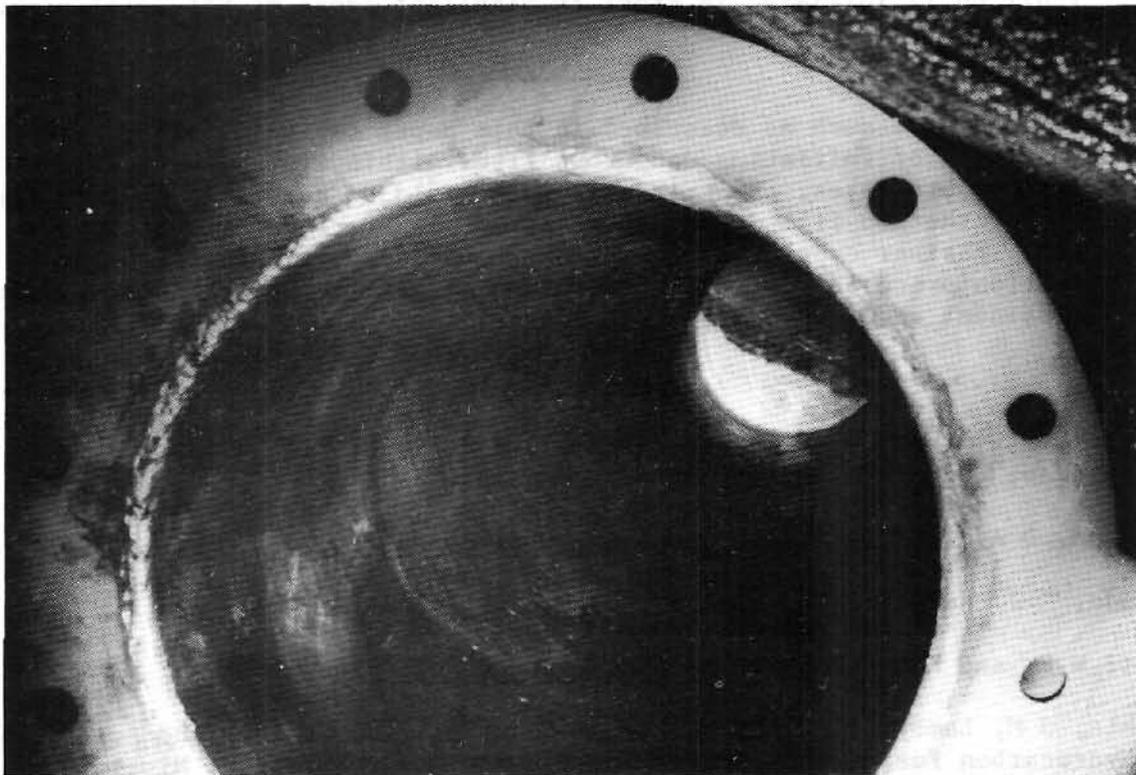
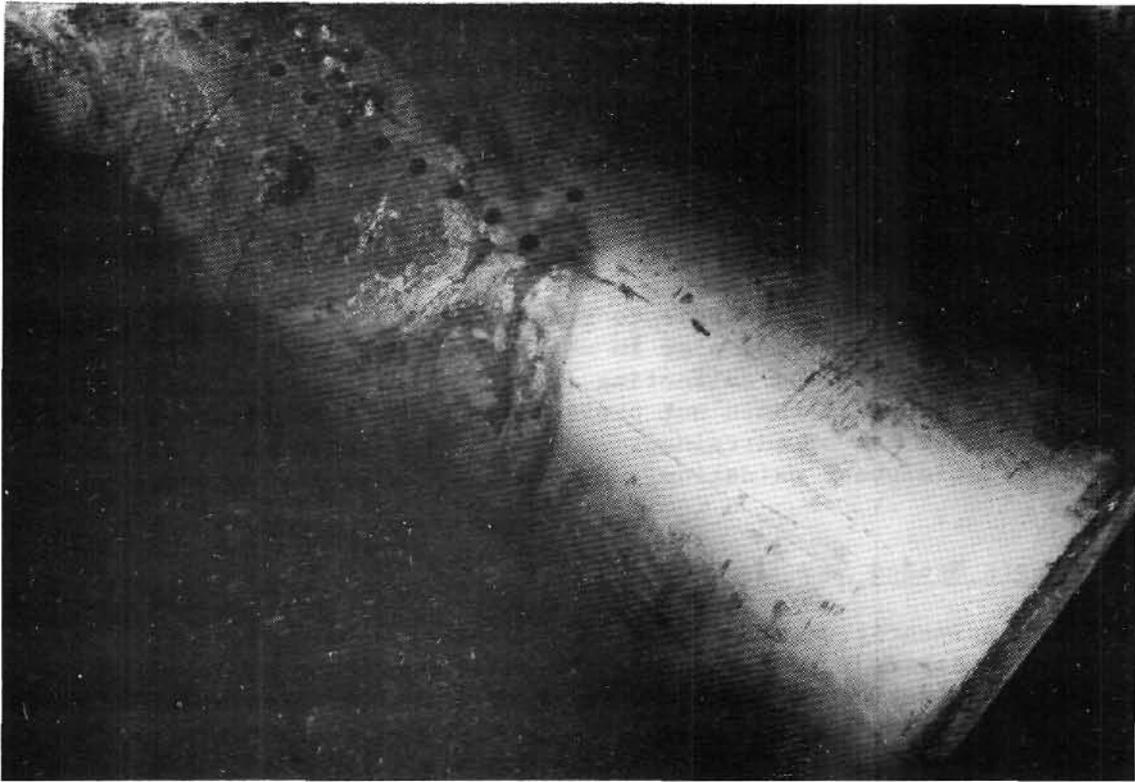


FIG. 1: VIEWS OF DAMAGED AIR DISTRIBUTION PIPE:TOP-THE UNDERSIDE OF THE PIPE WHERE A HOLE HAS BEEN BURNED THROUGH. BOTTOM -THE INSIDE OF THE PIPE

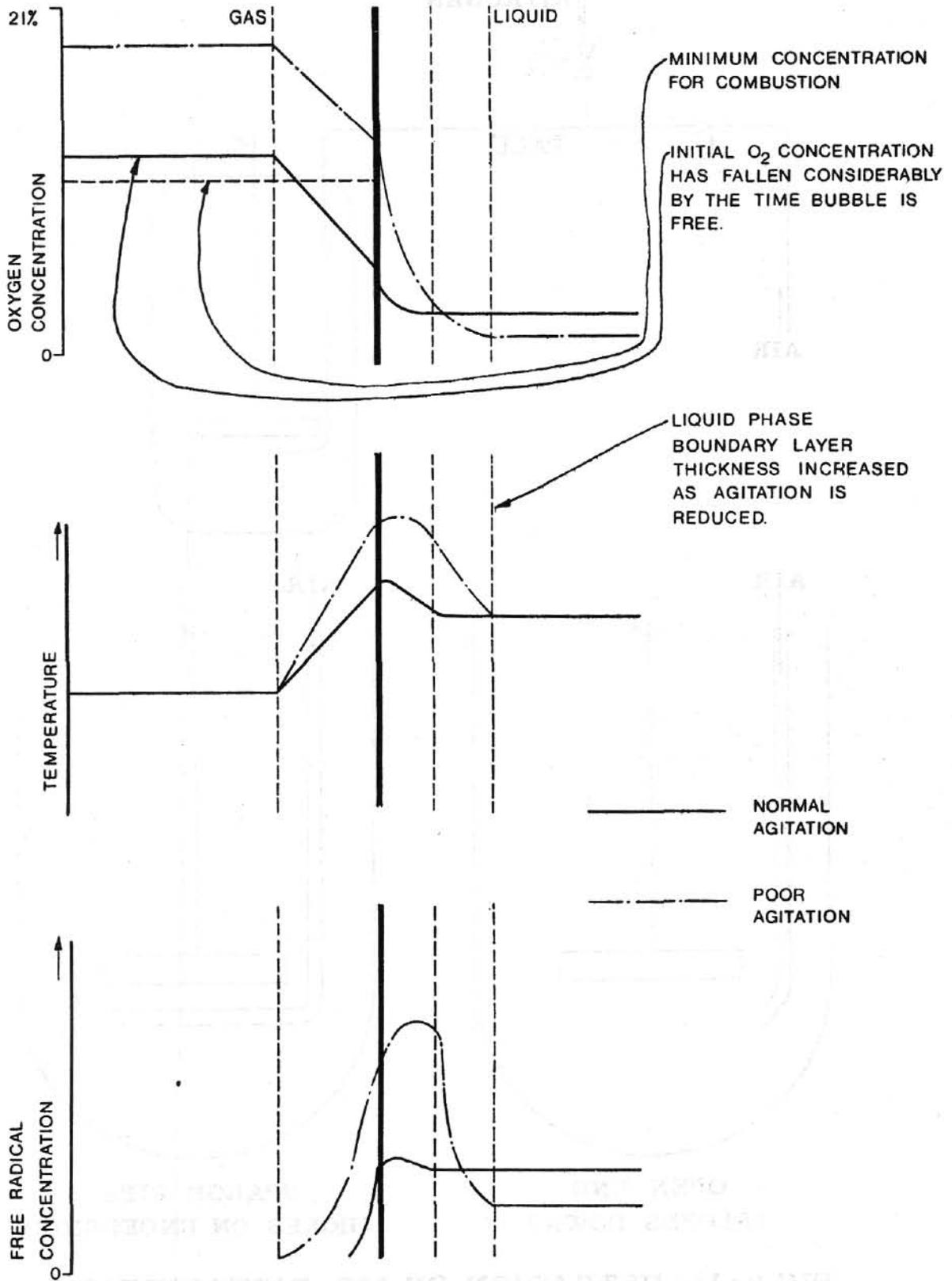
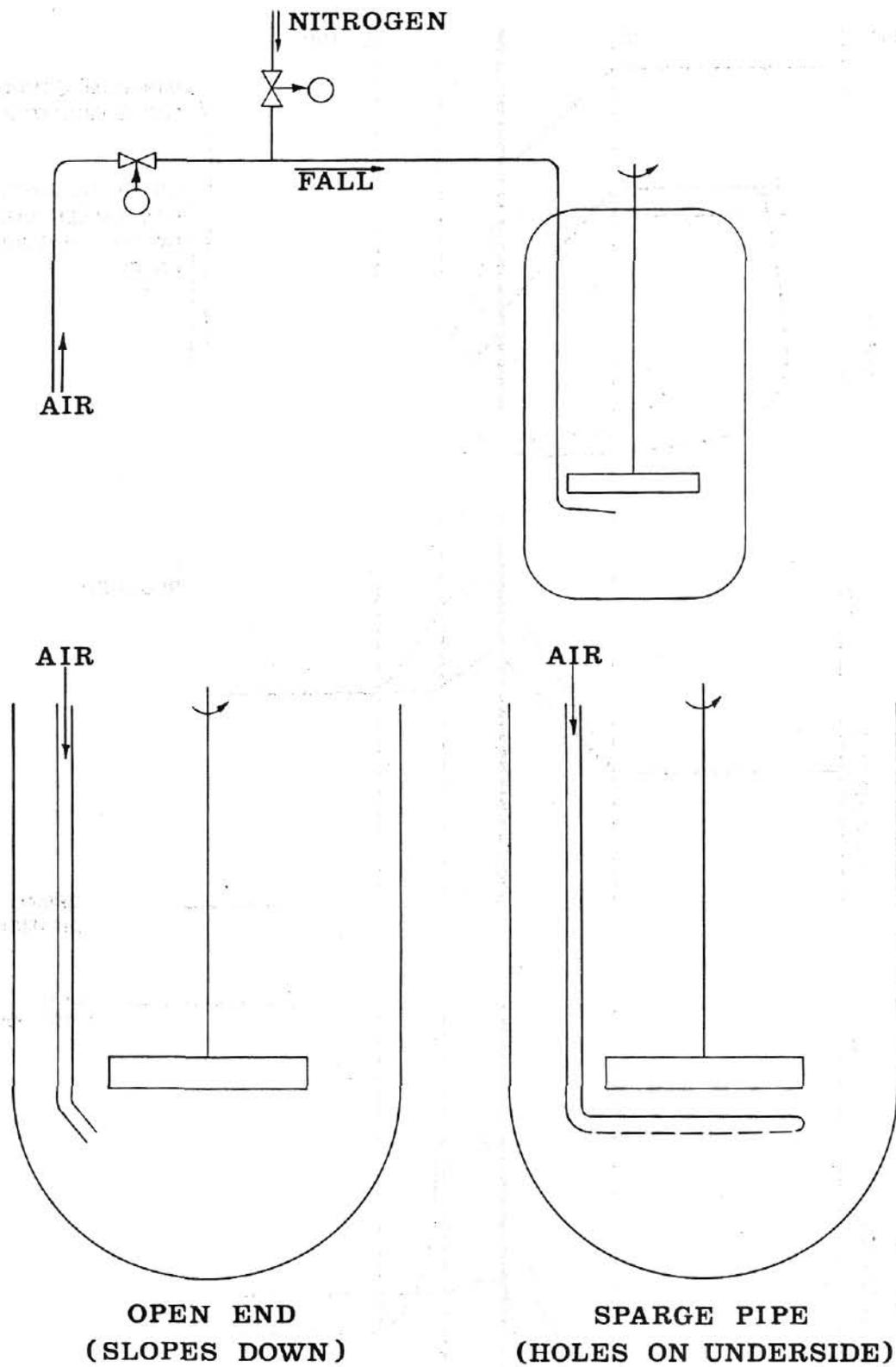


FIG. 2: ILLUSTRATION OF POSSIBLE CONDITIONS AT AIR/LIQUID INTERFACE



**FIG.3: ILLUSTRATION OF AIR DISTRIBUTION
IN AN OXIDISER**