AUTOIGNITION – OCCURRENCE AND EFFECTS

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During the Public Inquiry into the Piper Alpha tragedy, many possible causes were examined. One possible cause of the initial incident was that autoignition occurred in a line leading from a condensate injection pump to the site of its safety valve. After ingress of air when the safety valve was removed, autoignition might have occurred as a result of an attempt to repressurise the pump by rapidly opening its suction valve. It is, however, impossible to predict whether autoignition would have occurred because the standard conditions under which autoignition is assessed are significantly different from those which pertained in the line on Piper Alpha. A review of those conditions which affect the occurrence of autoignition, together with a brief review of one of its effects, is presented here.

INTRODUCTION

The sudden inflammation of a gaseous fuel and oxygen mixture when it is exposed to a particular temperature and pressure is called spontaneous ignition or *autoignition*. The principal ways by which this can be brought about are:

▸ heating in a closed vessel;
▸ flowing through a heated pipe or vessel;
▸ contact with a heated surface;
▸ rapid compression;
▸ heating behind a shock wave.

Except in ideal adiabatic circumstances, there are always specific conditions under which ignition does (or does not) occur. The limiting conditions for a given fuel and oxygen mixture are commonly represented on a pressure–temperature diagram. A typical diagram for the oxidation of an organic gas fuel is shown in Figure 1. The limiting conditions refer quantitatively only to that fuel in a given proportion of oxygen or air in a vessel of specified geometry, volume and wall temperature. The behaviour would be expected to be qualitatively similar but to be quantitatively different in other circumstances. (Note that, in general, the high temperature / low pressure ignition peninsula exists close to atmospheric pressure for an organic fuel in air [1]. Thus autoignition hazards at high pressures are most likely to be associated with the lowest temperature at which spontaneous ignition is possible, which is typically in the range 200 to 250 Celsius.)

Our purpose here is to review the nature and magnitude of these quantitative differences, with particular reference to a possible cause of the initial event on Piper Alpha. This represents one aspect of evidence that two of us (SMR and GS) gave

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to the Piper Alpha Inquiry, in which we examined causation of the initial event associated with the condensate system [2–7] and with hydrate formation [8–10] and also escalation associated with failure of the gas import and export lines [11].

AUTOIGNITION ON PIPER ALPHA

Two reciprocating pumps were used on Piper Alpha to inject condensate (liquid comprising significant quantities of methane, ethane, propane, butane and pentane and small quantities of higher hydrocarbons) into the main oil line for subsequent export along a sub-sea line to shore. The general arrangement of the pumps, their suction and discharge lines and the lines to their safety valves (located about 8 metres above the pumps) is shown in Figure 2.

It appears that, between about 21.45 and 21.50 on 6th July 1988, condensate injection pump 2-G-200B tripped. The other condensate injection pump, 2-G-200A, was depressurised and out of service for maintenance. At the same time, its safety valve, PSV 504, had been removed for maintenance and a blind flange is understood to have been fitted at the site of the safety valve. After removal of valve PSV 504 and before fitting of the blind flange, air could have entered the pipework.

The amount of air which could have entered depends on:
▶ the length of time that the flange at the site of the valve was left open;
▶ whether any other part of the system was open to the atmosphere.
For example, if the manual valve used to vent the pump to the flare was left open, the condensate gas, being denser than air, would continue to stream out of the manual valve, drawing air in through the flange at the site of PSV 504 and filling the pipework with air. On the other hand, if the only opening was at the site of PSV 504, ingress of air would have been much slower. There was a short horizontal section of line leading from the flange at the site of PSV 504 and then the line turned vertically downwards towards pump 2-G-200A. The short horizontal section of the line would have discharged its hydrocarbon contents (and been replaced by air) very quickly but the hydrocarbon in the remainder of the line would have been replaced by air primarily by the slow process of diffusion, although it would have been enhanced by any atmospheric temperature and pressure fluctuations. To an order of magnitude, the penetration distance L is related to the diffusivity D and time t by:

$$L \sim (D\,t)^{1/2} \qquad (1)$$

For propane in air, D is about 0.00002 metres² / second so, for purely diffusive ingress, L is of order 1 metre when t is 1 hour. Although there is, therefore, considerable uncertainty in the amount of air which could have entered the line, it is certain that some air entered the line and that the remainder of the line would have consisted of condensate gas.

When pump 2-G-200B tripped, it is possible that pump 2-G-200A and its associated lines were repressurised prior to an attempt to start the pump 2-G-200A. There were two ways in which this repressurisation could have been carried out. Of these, the only one which might have led to autoignition was by jagging, that is by repeatedly cracking and then rapidly closing, the air-operated suction valve GOV 5005 on the pump; see Figure 2. (The other way was sufficiently slow that most of the heat of compression would have been lost to the pipe wall, so the repressurisation would have been essentially isothermal.) If repressurisation by jagging had been adiabatic, that is without loss of heat, then compression of the condensate gas and air in the line by the incoming condensate would have resulted in a temperature of 420 Celsius.

The repressurisation would not in fact have been adiabatic, however. Heat transfer rates are much higher for high pressure gases than for low pressures ones. Using the computer package BLOWDOWN [12] which we have developed for the simulation of depressurisation and repressurisation of vessels and lines, we have shown [2] that the maximum temperature of the gas containing air in the line after repressurisation would have been about 270 Celsius if the line had originally been completely filled with air and the suction valve had been opened completely once and left open. The maximum temperature would have been rather lower if the valve had been jagged, as Table 1 shows.

Duration of opening and closing phases, assumed to be equal (seconds)	Maximum temperature attained by gas and air in line (Celsius)
0.50	203
0.75	220
1.00	240
TABLE 1	Maximum temperatures attained by gas and air during jagging

The maximum temperature attained by the gas and air would have been considerably less than this (perhaps only 150 Celsius) if air had flowed into the short horizontal section of the line at the site of the safety valve and then diffused into the remainder of the line for a period of order 1 hour. The maximum temperature would have been much lower in this case because the gas and air would have mixed significantly with the incoming condensate during repressurisation, since the volume of the compressed gas and air would have been very low. There would have been relatively little mixing if the line had originally been completely filled with air.

The temperature which could have been attained during repressurisation is within the range of temperatures at which autoignition of higher hydrocarbons with air has been observed at atmospheric pressure [13], as Table 2 shows.

Hydrocarbon	Autoignition temperature (Celsius)
Methane	537
Ethane	515
Propane	466
n-Butane	405
n-Pentane	258
n-Hexane	223
n-Heptane	223
n-Octane	220
n-Nonane	206
n-Decane	208
TABLE 2	Autoignition temperatures

Two questions then arise.
[i] Would the temperature which could have been attained during repressurisation have caused autoignition in the line on Piper Alpha?
[ii] What would the consequences of such autoignition have been?
There is much evidence for the importance of the answers to these questions, some of the earliest of which refers to accidents following autoignition of hydraulic fluid on board ships [14,15].

In attempting to answer these questions, we have noted deficiencies in

understanding both of the occurrence and effects of autoignition in real industrial – as opposed to idealised laboratory – conditions. This is because the standard AITs (autoignition temperatures) make no allowance for:

▸ a mixture of hydrocarbons: AITs are quoted for single hydrocarbon components (the condensate on Piper Alpha would have been a multi–component system, of which about 15 mole% would have been pentane or higher molecular weight hydrocarbons);

▸ a high initial pressure: AITs are quoted for systems initially at ambient pressure (1 bara) (repressurisation on Piper Alpha would have resulted in an initial gas and air mixture pressure of 46.2 bara);

▸ a large line: AITs are quoted for a small volume in a given geometry (the 15 metre long, 0.1 metre (4 inch) diameter line between pump 2–G–200A and the site of safety valve PSV 504 on Piper Alpha had a different geometry and a very much larger volume).

OCCURRENCE OF AUTOIGNITION

As has already been noted, the limiting conditions for autoignition under one set of circumstances give a qualitative indication of them under other circumstances. More generally, AITs give a ranking of reactivity. The ranking itself is relatively insensitive to circumstances but the values of the AITs depend strongly on the circumstances. Different circumstances are now discussed in turn.

Geometry and volume The standard manner (British Standard 4056) in which AITs are determined is in a conical vessel with a capacity of 0.2 decimetres³. With a different geometry and a different volume, the AIT can vary significantly. Thus cyclohexane has a quoted AIT of 255 to 259 Celsius at atmospheric pressure; this drops to 236 Celsius in a spherical vessel with a capacity of 5 decimetres³ [16]. Because a larger volume has a smaller surface area to volume ratio than a smaller geometrically similar volume, heat losses in a larger volume are smaller and so AITs are lower. If the line between pump 2–G–200A and the site of safety valve PSV 504 was full of air before it was repressurised then, after repressurisation, the air would have occupied a volume of about 4 decimetres³. The AIT in such a large volume would thus have been lower than that quoted for a vessel of capacity 0.2 decimetres³.

Fuel to air ratio AITs are very sensitive to the fuel to air ratio. For higher hydrocarbons, the AITs are usually lowest in fuel–rich mixtures. Thus the AIT of n–butane, measured in a 0.56 decimetre³ spherical vessel, is 497 Celsius at the stoichiometric mixture. The AIT falls to 422 Celsius when there is twice as much fuel as in the stoichiometric mixture and to 389 Celsius when there is three times as much fuel as in the stoichiometric mixture [17].

Fuel mixture Higher molecular weight hydrocarbons in a given homologous series have lower AITs than lower molecular weight hydrocarbons. Mixtures of hydrocarbons have AITs which are sensitised by the more reactive higher molecular weight components. Thus a mixture of 90 mole% methane and 10 mole% n–butane has an AIT about 50 Celsius below that of methane in a situation in which n–butane has an AIT 240 Celsius below that of methane [17].

Wall temperature AITs are quoted for a fluid, the initial temperature of which is

the same as that of the wall of the vessel containing it. Repressurisation of line between pump 2–G–200A and the site of safety valve PSV 504 would have resulted in a gas and air mixture, the bulk temperature of which was rather higher than that of the pipe wall. A cool wall would tend to raise the AIT; evidence for n–butane in a 0.02 decimetre³ vessel suggests that it might be raised by of order 40 Celsius.

Fluid motion Motion in the fluid tends to raise the rate of heat loss to the surroundings and hence to raise the AIT. Motion would have been induced in the gas and air mixture in the line between pump 2–G–200A and the site of safety valve PSV 504 during repressurisation; precisely how much and what effect this would have on its AIT is difficult to quantify.

Initial pressure A high initial pressure tends to increase heat transfer rates and hence heat losses to the surroundings. It also tends to increase the species concentrations and hence make the ignition reaction kinetics much faster. The second effect dominates the first, such that the expected overall effect at high initial pressure is to reduce the AIT; see Figure 1. Thus, for propane in air, raising the pressure from 1 bara to 15 bara lowers the AIT in a 0.19 decimetre³ cylindrical vessel by about 250 Celsius [18].

Rapid pressurisation During rapid pressurisation of a vessel, for example in a cylinder of a diesel engine, compression waves are set up at one end of the vessel which reflect off the other end and can double in size if pressurisation is rapid enough. These waves are regions of local excess pressure, and hence of local excess temperature by an essentially adiabatic process. Thus rapid pressurisation can lead to local regions which are at a higher temperature than the AIT while the bulk is at a temperature lower than the AIT.

(Repressurisation of the line between pump 2–G–200A and the site of safety valve PSV 504 would probably not have been sufficiently rapid for local regions which were significantly hotter to have existed. Thus attenuation of finite amplitude compression waves is given approximately by [19]:

$$p = P (1 + \alpha t)^{4/3} \tag{2}$$

where p and P denote the initial and final wave pressures, t denotes time and α denotes a damping coefficient given by:

$$\alpha = 0.002115 \, p^{3/4} \, c \, / \, \Pi \, d^{5/4} \tag{3}$$

where c denotes the speed of sound, Π denotes ambient pressure and d denotes the diameter of the pipe. The equation for α is dimensional: p and Π must be expressed in inches of mercury, c in feet per second and d in feet. For repressurisation of the line between pump 2–G–200A and the site of safety valve PSV 504, $\alpha \simeq 71$. Because jagging would have taken of order 1 second, this means that the local pressure excess would have been reduced by a factor of order 300 (in fact more because this estimate of α makes no allowance for attenuation at elbows in the line). Thus the local temperature excess would have been very small and was almost certainly insignificant.)

Taken together, these considerations imply that the situation in the line between pump 2–G–200A and the site of safety valve PSV 504 would have been so different from one in which AITs can be predicted that it is impossible to determine on theoretical grounds whether autoignition would have occurred. All that we were

able to conclude [4] was that autoignition was certainly a possibility.

These considerations have more general implications, however, since they apply to most if not all situations not just on offshore platforms but also in chemical plants. The only way in which the occurrence of autoignition could currently be determined is through experiments, which would have to be:

▸ full–scale: AITs are sensitive to volume;

▸ geometrically identical to the situation in question: AITs are sensitive to geometry;

▸ thermodynamically identical to conditions in the situation in question: AITs are sensitive to differences in temperature between the combustible fluid and its surroundings and to the temperature of the combustible material, for which reliable prediction methods are rare;

▸ for a range of different initial states (combustible fluid and air compositions and distributions): AITs are sensitive to the fuel and to the fuel to air ratio, which are unknown;

▸ for a range of different processes since these (for example the way of jagging the suction valve on pump 2–G–200A on Piper Alpha) determine the initial temperature. (Note, however, that there has been considerable progress recently in the application of numerical modelling to the prediction of autoignition of alkanes, especially with regard to knock in spark ignition engines [20]. Similar models are applicable to the prediction of industrial hazards provided that heat transfer can be incorporated in a satisfactory quantitative manner and provided that the models can be properly validated.)

EFFECTS OF AUTOIGNITION

As has been shown, it is not possible to determine with certainty whether autoignition could have occurred in the line between pump 2–G–200A and the site of safety valve PSV 504 on Piper Alpha (or more generally in a large system containing a high pressure multi–component fuel and air mixture). It is nevertheless appropriate to consider the magnitude of an explosion resulting from autoignition, assuming that autoignition occurs.

Since an explosion is a rapid event, we may assume, as a first approximation, that no heat is lost to the walls of the pipe containing the explosive mixture. We can also approximate the process on Piper Alpha as taking place at fixed volume since the liquid condensate in the lower parts of the line leading to the site of safety valve PSV 504, which forms one boundary of the confined space enclosing the explosive mixture, would not have time to move significantly.

Explosion, therefore, takes place adiabatically at fixed volume and it is of interest to calculate the explosion pressure resulting when a fuel–air mixture is confined in a fixed volume and ignited. Thermodynamically, the operation is carried out in a closed system in which no work is done on the system (there is no change in volume) and in which there is no heat loss or gain. Thus, from the first law of thermodynamics, the process occurs under conditions of constant internal energy.

The computational procedure involves, therefore, the calculation of internal energy of the premixed fuel and air at the initial pressure and temperature and then a search for the pressure and temperature at which the products of reaction have

the same internal energy and the same mass density as the unreacted material. Since the molecular species undergo a chemical change in going from the initial to the final state, it is essential that the computation of the internal energies of these two states is carried out consistently.

We have used the PREPROP computer package [21] to calculate all thermodynamic properties, in which the elements in their standard states are taken as reference states. This means that all computed thermodynamic properties are automatically thermodynamically consistent, even when chemical reactions take place.

We have checked the calculation procedure by calculating the explosion pressure generated when a stoichiometric mixture of propane and air explodes adiabatically in a vessel of fixed volume. The stoichiometric mixture contains 3.98 mole% propane, taking the composition of air as 20.7 mole% oxygen and 79.3 mole% nitrogen. The predicted conditions after explosion of a mixture initially at 1 bara and 17 Celsius are a temperature of 2577 Celsius and a pressure of 10.24 bara.

These figures differ considerably from those normally quoted [22], based on adiabatic fixed pressure flame temperatures [23], which are a temperature of 1925 Celsius and a pressure of 7.6 bara. The difference arises because of the erroneous method of calculation generally used, in which the adiabatic flame temperature is calculated in a steady state flow system and then, by assuming that the mixtures behave as perfect gases, the explosion pressure is calculated assuming that the pressure increase takes place at fixed volume. This is thermodynamically inconsistent since it mixes steady state flow thermodynamics with closed system thermodynamics. However, using PREPROP to supply the thermodynamic properties for this invalid method, we obtain a temperature of 2087 Celsius and a pressure of 8.13 bara. These values are close to those normally quoted.

We conclude, therefore, that explosion pressures in fixed volume systems are larger than those in fixed pressure systems. The heat of reaction (whether internal energy or enthalpy) differs little for the two systems. The specific heat at constant volume is, however, significantly less than that at constant pressure. Thus, for a given heat of reaction, the temperature rise (and hence the pressure rise) is greater in a fixed volume system than in a fixed pressure system.

Using PREPROP, we calculate that the explosion pressure in the line between pump 2–G–200A and the site of valve PSV 504 on Piper Alpha could have been about 295 bara, assuming an initial pressure of 46.2 bara and an initial temperature of 200 Celsius, and about 270 bara, assuming the same initial pressure and an initial temperature of 270 Celsius. Thus the explosion pressure is slightly sensitive to initial temperature, but not unduly so. (The reason why the explosion pressure decreases as the initial temperature increases is, of course, that the quantity of combustible or explosive material decreases as the temperature increases in a system at constant pressure and constant volume.) There are three main ways in which an explosion resulting from autoignition in the line could have had a significant effect on Piper Alpha:

▸ overpressurisation of the pipework leading to failure of the line;
▸ failure of the flange assembly at the site of safety valve PSV 504;
▸ reactions within the line leading to whipping and hence failure of the pipework.
A discussion of these effects is given elsewhere [4].

CONCLUSION

We have found that deficiencies in understanding mean that it is impossible to predict theoretically whether autoignition would have occurred in the line between pump 2–G–200A and the site of its safety valve PSV 504 on Piper Alpha. Experiments, closely matched in all possible ways to the state and size of the line and the hydrocarbon/air within it, would be needed to resolve the matter.

This has important consequences not only in the particular case of Piper Alpha but also more generally for chemical plants, particularly where rapid valve movements are possible. Although there are methods which claim to be able to predict the occurrence of autoignition [24–26], these methods make three key assumptions which severely limit their practical utility.
[i] The methods all subsume the heat transfer into a polytropic exponent, which effectively masks ignorance of the heat transfer actually occurring. The heat transfer in a high pressure gaseous system is very different from that in a low pressure one and is of crucial importance to the occurrence of autoignition. (Of course, a polytropic exponent can always be fitted retrospectively to experimental data, but this begs the question of prediction of the exponent in a situation for which there are no data.)
[ii] The methods all use an essentially one–dimensional treatment of the fluid mechanics, which ignores the role of mixing of the fuel and oxygen. The local fuel to oxygen or fuel to air ratio is of crucial importance to the occurrence of autoignition.
[iii] The methods all ignore important aspects of the chemistry of autoignition such as the effects of mixtures of different fuels and of high initial pressures which are again of crucial importance to the occurrence of autoignition.

There is, therefore, a need for:
‣ reliable experimental data on autoignition under conditions typical of industrial operations.
These data are essential if more reliable and hence useful predictive methods are to be developed. Until, and even when, such quantitative methods have been developed, there is a need for greater qualitative awareness of the nature of autoignition. Such awareness suggests the need for:
‣ a data bank recording the details of cases where autoignition caused or might have caused particular incidents;
‣ a ranking of factors affecting autoignition.
Provision of both of these would be most valuable for the design and operation of chemical plants.

There is also a need for:
‣ the distinction between confined explosions, which take place at essentially constant volume, and unconfined ones, which take place at essentially constant pressure, to be more generally appreciated.

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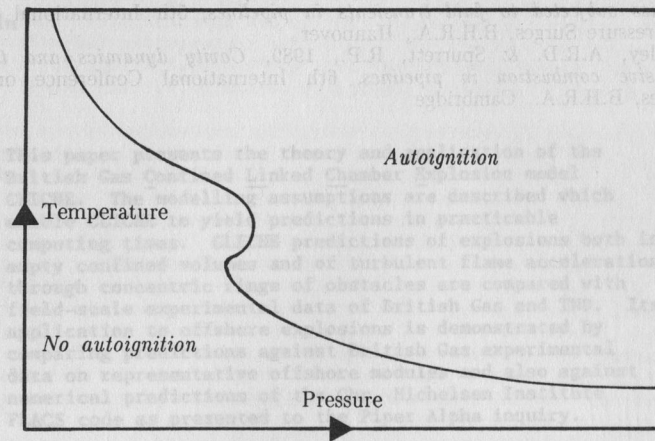
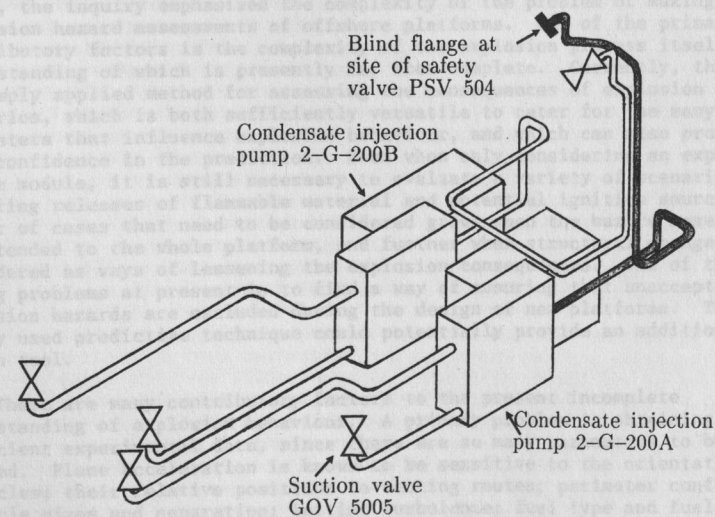FIGURE 1: Schematic pressure–temperature diagram for autoignition

FIGURE 2: General arrangement of condensate injection pumps and associated lines on Piper Alpha: shaded line is one in which possibility of autoignition was examined