INVESTIGATIONS INTO INCIDENTS INVOLVING THE KINDLING CHAIN OF MATERIALS IN HIGH-PRESSURE OXYGEN ATMOSPHERES

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Abstract

This thesis is a thorough examination of high-pressure enriched oxygen system design and analysis focussing on material selection and incident investigation. The aims are to develop a model to predict spontaneous ignition temperatures (SIT), enable the use of more accessible measurement apparatus, and to devise a scientific methodology to investigate oxygen incidents.

Chapter 1 contains examples of incidents in high-pressure enriched oxygen and outlines current methods of material selection and incident investigation. The major flaws with the current systems are explored and the objectives of this work are identified.

Chapter 2 details the current state of the knowledge in relation to oxygen incidents. Materials flammability is explored, and the importance of correct material selection is established. The criteria, standards and test methods currently used to aid this decision are assessed, and the importance of proper oxygen incident investigation is determined.

Chapter 3 shows a programme of experimental work with details on the use of different apparatus for the measurement of SITs. Data acquired from the BS 4N 100 bomb test, and pressurised, and ambient, differential scanning calorimetry are recorded. The use of Thermal Desorption/Gas Chromatography is explored to identify polymer evaporation and degradation products.

In Chapter 4 a simple model is developed to adapt SIT allowing calculation of the SIT of a non-metal in any pressure or oxygen concentration. Data obtained in chapter 3, and from the literature, is used to validate this model. Data on metals is also collected from the literature to be incorporated into a methodology demonstrating the kindling chain.

Chapter 5 covers the development of a ‘tool kit’ for oxygen incident analysis. Understanding of ignition modes, heat transfer modelling, flow diagrams, and the SIT model are used to examine past oxygen incidents, and understand kindling chains.

Chapter 6 examines ‘real life’ incidents and applies the Chapter 5 ‘tool kit’ as a clear scientific methodology, identifying likely incident ignition sources and kindling chains.

Finally Chapter 7 gives conclusions, identifying the successes and limitations of this work, and points where difficulties were encountered. Areas where further scientific investigation is required are identified.

Chapter 1
Introduction to the Use of High Pressure Enriched Oxygen Systems

Oxygen is the second most abundant gas in air (only nitrogen is more plentiful), making up about 21% of our atmosphere with a boiling point of 90K at atmospheric pressure. Oxygen is vital to sustain life and for this reason life support systems or breathing apparatuses are used in a wide number of areas, including civil and military aircraft, medical breathing apparatus and hyperbaric chambers, and diving and mountaineering systems. It is also used in a number of industrial processes, but is most often used for combustion. Combustion is the rapid runaway oxidation of a fuel material. It requires an initial energy input to push the exothermic oxidation reaction rate to pass a critical point, meaning the energy released is then enough to bring about further oxidation of any fuel. This results in a self-perpetuating reaction, which continues as long as there is enough oxygen and fuel to sustain it. The heat produced by combustion is widely used e.g. for cutting and welding in oxy-acetylene equipment.

As oxygen is used so extensively it is often necessary to store and use it at high pressures and concentrations. Where the pressure or concentration of oxygen is increased well above that of atmospheric, oxidation reactions occur more readily, and at a faster rate, relative to those under atmospheric conditions. Certain circumstances can result in unwanted ignition, resulting in the destruction of property and endangerment of life, as illustrated in 1.1.

In order to stop these ignitions (that can result in extremely serious catastrophic failures dangerous to people and property), reduce their occurrence, or reduce their severity, the choice of materials used for the construction of an oxygen system must be made with great care, taking into account the latest information, and ideally involving testing of the materials that are going to be used. The first major aim of this work is to allow the prediction of ignition, and particularly the Spontaneous Ignition Temperature, of materials used in oxygen systems under a range of conditions. It is unrealistic to propose that materials be tested under every set of circumstances, for example under different oxygen concentrations or pressures. This would be both costly in terms of time and money. Thus this work will develop a method of prediction using a single test result. This would advise the suitability of materials to be used in oxygen systems, and also enable the identification of any likely sources of ignition in active systems, or after oxygen incidents.

While the ignition, and first material ignited is key in any fire, it is not the only important aspect of the fire's progression. Being able to predict, or at least to understand the full progression, or kindling chain, of a fire in an oxygen system should expose any design or engineering areas that might be improved to reduce the chance of spread, or reduce the danger an incident might pose to equipment operators. Thus the second major aim of this work is to understand kindling chain reactions, from the ignition source and ignition of the first material ignited to further system components using heat transfer calculations.

After an incident has occurred a number of different groups may be involved in the investigation to find out what happened. There may be a range of methodologies looking at physical and chemical evidence. This work will aim to enable a more effective investigation of oxygen incidents, looking at past incident reports, and identifying areas that could be improved with a deeper understanding of ignition, heat transfer and modern forensic and investigative philosophies and techniques. The following section has some examples of oxygen incidents, demonstrating why understanding and preventing them is so important.

1.1 Illustrative examples of catastrophic failure incidents in high pressure enriched oxygen systems

These are illustrative of the events that have actually occurred and are listed in the British standard for aeronautical oxygen systems BS 5N 100-5 (2006). They not only demonstrate the seriousness of incidents of this type but also that incidents can be classified by their technical root cause.

A fire and explosion occurred at an oxygen filling plant when a valve to a cylinder pack was opened after being connected to a filling hose (BS 5N 100-5 2006). The cylinder pack, a mobile supply for filling aircraft life support systems, was due to be filled with oxygen to 24.8 MPa. The procedure to fill the cylinder pack involved a prior inspection to check for valve contamination, residual pressure, damage and odour. Occasionally cylinders are returned to the filling station with pressures up to that attained at the original filling. If a pack contains a cylinder with a residual pressure the procedure states that the operator should top up this to the fill pressure. The incident occurred when the filling hose was connected to the cylinder pack and the valve to the first cylinder had just been opened. It appears that cylinder no. 1 contained residual oxygen at pressure. Upon opening the valve the filling hose rapidly filled with oxygen. Then, as the filling hose was not pressurized, the flow of oxygen into this closed volume resulted in a rapid rise in temperature caused by the adiabatic compression of the oxygen. It was suspected that this temperature rise exceeded the Spontaneous Ignition Temperature (SIT) of the hose lining material and ignition occurred.

Another incident involved the manufacture of an oxygen pressure-reducing valve (BS 5N 100-5 2006). The valve incorporated a blanking cap over the valve adjusting head. The cap was secured by five screws and sealed by a silicon rubber “O” ring. Its maximum operating pressure was 14.5 MPa. To adjust the reducing valve assembly the cap must be removed, and then replaced again after the adjustment. An incident occurred during this stage of the process. At a pressure of about 11 MPa there was a sudden escape of gas and a drop in pressure. On examination a gap of approximately 1.5 mm was found between the blanking cap and the valve body. The seal had completely burned away. The investigators concluded that the seal had been ignited due to resonance in the cavity between the cap and the body.

In one incident (BS 5N 100-5 2006) an operator “cracked open” the outlet valve of a portable oxygen cylinder assembly momentarily to produce an audible hiss of gas to check its contents and function. As the operator replaced the assembly in its storage area, it burst into flames causing severe facial injury. Examination afterwards showed considerable damage to the operating head with loss by combustion of a sizeable part of the outlet valve housing, seat and seal. The cylinder was designed for use up to 12.4 MPa. It had an aluminium body. The PTFE spindle seat was rigidly attached to the end of the rotating spindle made from austenitic stainless steel. All the assemblies showed particulate contamination of the PTFE (found to be aluminium), presence of grease (found to be a silicone-type), and sharp edges to the cut seat. It was concluded that adiabatic heating of the gas as the valve was closed was the mode of failure, in the presence of a non-compatible lubricant. These incidents demonstrate the importance of being able to identify the cause of an incident. The causes are described in the following section.

1.2 Classification of the causes of oxygen incidents

The main sources of ignition, according to BS 5N 100- 2006 (part 5) in any oxygen system are:

- Pressure shock and rapid adiabatic compression (accumulated oil/ grease often facilitates this method of ignition).

- Impact by contaminant particles
- Mechanical impact
- Friction in valves
- Cavity resonance
- Electric arcing (e.g. short circuit arcing through sheath)
- Kindling chain (initial ignition caused by the combustion of other constituent materials or contaminants resulting in a chain of ignitions)

The accumulation of dust in a system, the contamination by grease not suitable for high pressure oxygen, poor design or inappropriate component material selection resulting in shearing and particle generation can all contribute to the ignition. Yuen et al (1988) suggests that there is usually more than one cause for oxygen related mishaps, and that a combination of factors may be involved.

1.2.1 Ignition by pressure shock and adiabatic compression

When high-pressure valves are opened quickly gas entering the system rapidly can result in heating of materials by two modes. Firstly where high pressure fast flowing gas enters closed-ended components it will be compressed, a process known as adiabatic compression. Due to that compression the gas heats up, and this hot gas can in turn heat surrounding component materials. Secondly this rapid gas flow can result in a supersonic shock wave, referred to as pneumatic shock, as successive compression waves coalesce, and this shock wave further heats materials in the system. In reality it is difficult to determine which of these modes of heating might have occurred, as they generally happen together (Newton and Steinberg 2009).

Yuen et al (1988) stated that at pressures of 40MPa (approximately 6000psi), temperatures produced by adiabatic compression were up to 1773K (1500°C). The theoretical maximum temperature of rapid pressurisation of a gas can be calculated using:

$$\frac{T_f}{T_i} = \left(\frac{P_f}{P_i}\right)^{\frac{1}{\gamma_{cp}}} \qquad \text{Eqn. 1.1}$$

where

T_f = Final temperature

T_i = Initial temperature

P_f = Final pressure

P_i = Initial pressure

$$\gamma_{cp} = \frac{c_p}{c_p - c_v}$$

where

c_p = Specific heat at a known constant pressure

c_v = Specific heat at a known constant volume

γ_{cp} for oxygen = 3.50

This effect has been known to ignite any vapour from accumulated grease and oils in oxygen systems, which then provides the energy for further ignition of the system components. Testing has shown that this force can result in ignition of polymers, and lighter metals/ alloys. Newton et al (2000) reported a case of an aluminium medical regulators igniting due to this cause. In this case an oxygen cylinder valve was opened allowing pressurised oxygen into the regulator, which had the flow control turned to the off position. According to Yuen et al (1988) the chances of adiabatic compression can be decreased by the introduction of slow opening valves and heat sinks. These engineering solutions may however result in an increase in cost that many end users might be resistant to accommodating.

1.2.2 Ignition from impact by contaminant particles

In flowing oxygen any particles, which enter or break off from within the system, can reach sonic velocities. The impact of these particles is capable of igniting both metals and non-metals. The mechanism of ignition varies. Generally it is the particles that ignite on impact and the energy produced by this ignites further materials. Alternatively if the material being impacted upon is particularly flammable (e.g. polymers, aluminium) it may ignite before the particle. This secondary ignition is generally referred to as ‘promoted ignition combustion’ (Stoltzfus et al 1988, Yuen et al 1988) found that bends and valves were likely to be the most critical ignition sites. Newton et al (2000) also reported particle impact had been responsible for igniting a number of aluminium bodied regulators, often indicated by contaminants in the system, or in attached cylinders.

1.2.3 Ignition by mechanical impact

Energy is transferred from kinetic energy, by the impact of an object with a large mass. Testing has succeeded in igniting only polymers and the very light metals and alloys (e.g. aluminium-bronze, titanium) and according to McColskey et al (1991) this type of test has not ignited the majority of bulk metals such as Stainless Steels, or brasses.

1.2.4 Ignition from frictional heating

Continuous rubbing, for example, within a valve can cause a build-up of heat energy. In the case of metals it can also reveal clean metal that is not protected by an oxide layer. The rapid oxidation of this new metal can provide the energy for a runaway combustion reaction. Examples of this are a centrifugal compressor rotor rubbing against its casing, or friction in aluminium valves (ASTM G94 2005).

1.2.5 Ignition by cavity resonance

The ISO standard 14624-2 (2003) states that acoustic oscillations inside resonant cavities can cause a rapid rise in temperature. If particles are present in the chamber, or if gas velocities are high, this resonance can produce much higher temperatures. This type of ignition has been shown to be particularly ubiquitous where gas flows into a tee. Gas flowing into a tee and out of a branch port can form a resonant chamber at the remaining closed port. This has been shown to provide enough energy to ignite polymers, aluminium and stainless steels in testing.

1.2.6 Ignition by electric arcing and sparking

Arcing and sparking are similar but not the same. Arcing is the electrical breakdown of a gas causing an on-going plasma stream, while sparking is a momentary electrostatic discharge (via a plasma stream) from one charged surface to an earthed surface. However they are grouped together in this case because they can both result in very high temperature. The ASTM fire hazards in oxygen systems standards technology training coursebook (2004) stated that they can be an effective ignition source for any flammable material. They can occur from motor brushes, electric power supplies or even lightning.

1.2.7 Ignition by flow friction

This is a relatively newly proposed phenomena Beeson et al (2007) describe this as being caused as a gas flow travels across a polymer, causing erosion and the generation of heat. It is reported by Gallus and Stoltzfus (2006) that a number of fires at NASA have been attributed to this, however Stoltzfus et al (2012) report that it had not been possible to replicate this supposed ignition source, and that other explanations, such as ignition or self-heating of foreign contamination, are more probable. As this is not a credible source of ignition this will not be discussed further in this work.

1.2.8 Kindling chain ignition

Once one material in a system has ignited the temperatures induced by the combustion energy release are often great enough to heat materials inducing further self-sustained oxidation reactions. This is by far the most common cause of ignition of metals in oxygen systems. It should be remembered that these causes often act concurrently, and are in some cases interconnected. One example is friction. Wear on metallic parts can produce enough heat to reach the ignition temperatures, but also produces particles, which can impact on, and ignite, other parts of the system. The complex nature of metal system ignition means that it is not always possible to identify the exact cause.

1.3 Criteria for the selection of materials for use in high-pressure enriched oxygen system devices/ component

The incidents discussed in section 1.2 demonstrate the clear need for careful consideration when choosing materials for use in oxygen systems and apparatus. There are a number of material properties that are relevant to selection for oxygen use. There are also a range of test methods to ascertain flammability information on materials to assess their suitability for oxygen service.

1.3.1 Spontaneous Ignition Temperature (SIT)

The SIT of a substance is defined by Bodurtha (1980) as the temperature at which vapours ignite spontaneously from the heat of the environment. The SIT depends on many factors i.e. ignition delay, concentration of vapours, environmental effects (volume, pressure and oxygen concentration), catalytic material and flow conditions. Clearly if a material ignites at a lower temperature there is a greater risk of it being ignited. This is generally applied to the selection of non-metals.

The most common method for this test is the high pressure bomb calorimeter, or high pressure bomb, test. The bomb (commonly used for non-metals) is a static atmosphere test and comprises of a sealed bomb in which the pressure can usually be changed. A material is inserted into the bomb, and ramp heated under controlled pressure conditions. Thermocouples measure the change in temperature within the bomb compared to the ambient, and results are recorded to allow the SIT to be determined. The SIT of gases can also be tested. A gas is introduced to a test vessel and the vessel is heated in a hot air oven until ignition, identified as any visible flame, is observed via a mirror.

Another method of measuring the effective SIT of a material is Differential Scanning Calorimetry (DSC) which can be done under ambient conditions, or high pressure enriched oxygen conditions (PDSC) depending on the apparatus.

Some work has been done to find the SIT of metals with laser ignition, but thermal testing for metallic materials is generally concerned with the identification of the maximum working pressure (see section 1.3.3).

1.3.2 Combustion mechanism

Ignition occurs when a source provides enough energy to initiate a self-sustaining oxidation reaction in which the heat production exceeds that lost to the external environment. According to Drysdale (1998) to reach a point where most solids will burn they must invariably thermally decompose. The same is true for liquids. The production of combustible volatiles might also occur from melting and evaporation process. Evaporation or decomposition products will then mix with the oxygen in the atmosphere and if enough energy is provided, e.g. by heat, ignition will occur. According to Glassman (1996) there are two mechanisms by which materials are oxidised depending upon their individual characteristics. The most common oxidation mechanism is homogenous oxidation, where materials are vaporised, and combustion takes place in the vapour/ gas phase. The second mechanism is heterogeneous combustion. In this case the materials do not produce volatiles. Instead it is a surface-burning process where the fuel is in solid or liquid form (a different phase to the oxidiser). This is discussed later in section 2.2.3 as it is important to assess the combustion type when trying to calculate the SIT.

1.3.3 Reaction thermodynamics

There are a number of pieces of information that might be used to characterise a chemical reaction. According to Yuen et al (1988) the energy released by the oxidation reaction substantially influences whether the reaction will be self-perpetuating so materials with higher heats of combustion will be more likely to undergo a sustained oxidation reaction. The greater energy release also increases the likelihood of damage to other components. Thus materials are ideally selected with a lower heat of combustion. A careful choice must be weighed over choosing the correct materials based on physical properties versus reducing the possibility of a combustion reaction starting or a catastrophic failure if it does.

Other data that has been looked at in relation to combustion reactions for example Jones and Atkins (2000) state that higher activation energy results in greater reaction temperature dependence thus the higher the activation energy of the oxidation process, the less likely a combustion reaction is to take place. The SIT (BS 4N 100-6 1999) extinguishing pressure and impact sensitivity (Davis 2012) are more commonly used for material selection).

1.3.4 Critical Oxygen Index (COI) and Extinguishing Pressure

The Critical Oxygen Index (COI), also called the Limiting Oxygen Index (LOI), is defined as the minimum percentage oxygen required in the surrounding atmosphere to sustain the oxidation of a material, the critical condition for combustion. Experimental apparatus have been developed to identify this and the tendency of a material to continue to burn once ignited. This test is often used on non-metallic materials, but is not generally carried out on bulk metals, as the majority of these require above 99.5% oxygen. According to Ikeda (1983) COI is one of three criteria used by Air Products and Chemicals Inc. to determine the degree of acceptability of materials for use in oxygen-enriched atmospheres.

High Pressure Critical Oxygen Index (HP COI) has been used for testing metals by Benning and Werley (1986). This test is reportedly similar to earlier COI tests, but has a high pressure vessel capable of measuring the oxygen index as a function of pressure, up to 20 MPa. A thermite pill is used as the ignition source, and again a sustained complete or extensive combustion of the sample was used to identify the oxygen index.

This was also one of the few methods used to explore the possibility of a kindling chain e.g. experiments identified that combustion of nitrile rubber could in turn ignite carbon steel. However the usefulness of this apparatus is questionable as majority of bulk metals require a comparably high percentage oxygen atmosphere for ignition to occur, making differentiation difficult.

As metallic materials require such a high concentration of oxygen for combustion, tests have been devised that instead measure the ‘Extinguishing pressure’ as an alternative to COI. This is the maximum pressure at which promoted combustion of a metal (using a small ignition charge) is not supported. Generally the extinguishing pressure is most commonly used for metal selection (Davis 2012) which is most commonly measured using promoted ignition combustion test. This consists of a sealed pressurised unit with a specimen (usually a rod) held vertically.

Bulk metal thermal behaviour has been tested in a flowing environment. For lighter metals and alloys the oxygen index test can be used. The minimum level of oxygen required to support combustion is recorded. For heavier bulk metals (like those used in the manufacture of oxygen systems) the promoted-ignition combustion test has been adapted with a sample rod in flowing oxygen (Zawierucha and McIlroy 1989).

1.3.5 The reaction of a material to impact stimulus

When an object is impacted upon by another object the kinetic energy possessed by the object is transferred to other forms. Some of it will turn to kinetic energy as the object rebounds from the surface, but much of it will be converted to heat.

A material's impact ignition sensitivity can be tested by a number of different methods. Mechanical impact tests involve dropping a known mass on to a fixed sample from a particular height. Generally the same test will be used as a comparative experiment, with many samples placed in a ranking table. This test is used for non-metals and the lighter metals (e.g. titanium, aluminium). Where one mass, such as a small particle, impacts on a larger mass, such as an oxygen system component surface, the total energy, E_i, available for conversion to heat can be calculated from the mass of the impacting object, m, and the relative velocity it is travelling at, v, using:

$$E_i = \frac{1}{2}mv^2 \qquad \text{Eqn. 1.2}$$

Particle impact tests are used on both metals and non-metals. They involve shooting a particle (either of aluminium or iron) of known size, at a known velocity, on to a material's surface. In both of these tests the atmospheric pressure may be varied to find the maximum working pressure for the material. The original particle impact test, according to Stoltzfus et al (1988), uses a 2mm particle made from 6061 Aluminium placed into a stream at Mach 3.5 (1191.015 m/s). The maximum energy that can be imparted (assuming a spherical particle of mass 3.4mg) is 2.411 kJ, excluding ignition of the particle itself.

Pneumatic impact tests provide energy via a combination of shockwaves and adiabatic compression, simulating conditions similar to the fast opening of valves. A pressure shock, or series of pressure shocks, is applied over a very small period of time by exposure to high-pressure oxygen shock waves. This is often included under the title of impact testing, although it is more akin to a thermal test. This is also only used on non-metals and lighter metals.

1.3.6 Examples of the variation that can exist between different flammability test methods

There is a problem with comparing the results from the various metals' and non-metals' tests. Firstly, due to the different oxygen partial pressures and energy inputs required for auto-ignition, different test methods must be used on the different materials. But even within those groups different test pressures, heating rates, heating regimes, impact heights, or particles for impact are used (see section 2.4 for further details).

One of the best examples of this variation is the promoted ignition test for metals. Table 1-1 shows the large variety of different test pressures used by the various test facilities. Although these tests at different pressures produce rank tables, the numerical data from each cannot currently be compared with the others, or manipulated for other uses.

Table 1-1 The test pressures used in a range of promoted combustion test criteria

Promoted ignition test apparatus	Test pressures MPa
NASA White Sands test facility conducted promoted ignition tests - Stoltzfus et al (1988)	68.9, 55.2, 48.3, 34.5, 20.7, 17.2, 13.8, 6.9, 5.2, 4.1, 3.5, 2.1, 1.4, 0.2, 0.2, and 0.17
Lindé - McIlroy et al (1988)	30.7, 20.7, 6.9
Air Products & Chemicals Inc. oxygen index test - Zabrenski et al (1989)	10.34, 6.20, 5.17, 5, 2.41, 1.90, 0.62, 0.17, and 0.1

1.4 Techniques employed in the investigation of oxygen incidents

Oxygen incident investigation often involves more than one organisation. In the UK fire brigades, Health and Safety Executive, armed services (e.g. Royal Air Force, Royal Navy) private consultancies, insurance companies and interested industrial companies are among those that may be involved. Worldwide, as well as government health and safety groups, and emergency service organisations, a number of standard standards institutions, societies and trade groups are have an interest in this area. These include the American Society for the Testing of Materials, BSI group, the National Fire Protection Association (NFPA) and the Compressed Gas Association (CGA)/ European European Industrial Gas Association (EIGA). There are a number of techniques, which may be employed by the investigators, discussed below.

1.4.1 The use of photography in oxygen incident investigation

This is one of the best ways to document physical information. Recording the environment a system is kept in, the system design and assembly, and the condition of individual components is imperative at a scene in case evidence might be lost. Any photographs taken should be in colour to show all of the fire damage in the most detail and notes should accompany them to describe what they depict. Although many reports include photographs, they are not always well explained and a scale is rarely used.

1.4.2 Interviews in oxygen incident investigation

Any witnesses, persons involved with the incident, and persons involved in the use and maintenance of the system involved should be interviewed to identify normal practice, and the exact circumstances of the moments leading up to the incident. Even small details from these interviews may provide the investigator with key information on the cause, or results of the incident. They are used by organisations like the HSE to develop a chain of events leading up to the incident, and to help identify the root cause of the incident, the conclusions of which are summarised by investigators in their final report (used in this thesis).

1.4.3 Component examination in an oxygen incident investigation

Probably the most important part of the investigation is the examination of the physical evidence, i.e. a full examination of the system components involved in the incident. A schematic diagram of the system design should be used to identify the components, and assess whether the system had been constructed correctly and in accordance with safety considerations.

An in-depth examination of the system’s constituent parts and components must be carried out to identify the damaged areas and the seat of the ignition. Comparison with new or undamaged components will help to identify damage and any missing component parts, the existence of which an investigator may be unaware. The dimensions and constituent part materials should be recorded. The damage should be measured, ideally by the measurement of dimensions and mass loss.

Added to the physical evidence there may be chemical evidence. In some cases, such as where there is no obvious cause, or where the materials identification is in doubt, it may be necessary to do further experimental testing. This is especially important if the material is in a position, which may have been in, or close to, the site of ignition. There may be evidence of a residue. Most oils and greases are highly flammable and if present in oxygen systems greatly increase the chance of ignition. Although fire will generally destroy any residue inside an oxygen system it may be left between thread seals or other more protected areas. Using a technique such as a non-invasive variety of Infra-red spectroscopy (IRS) to identify polymers may be useful as, on top of not destroying your sample, it is a fast and reliable way to check correct materials were being used. Swabbing internal surfaces and then analysing the combustion or pyrolysis deposits may also allow identification, or confirmation, of the materials used in the system that have been burned away, using IRS or Gas Chromatography (GC) techniques. It may also reveal evidence of oils or greases not suitable for use in oxygen systems that might have been part of the ignition process.

It may be necessary to determine the thermal characteristics of materials using, for example e.g. Differential Scanning Calorimetry (DSC). Physical examination details (for example component dimensions), GC and DSC have all been used in this work to explore the flammability of materials, to predict the SIT of materials, and try to understand the kindling chain reactions that can occur in oxygen systems.

1.5 The problems with the current system of material selection and investigation of incidents in oxygen systems

There is a need for predicting the performance of materials under a variety of conditions. Crude guidance is available from league tables and from experimental data obtained from various methods and equipment, but these only apply to particular environmental conditions. They do not take into account changes in oxygen concentration, or pressure. They also do not take account of sample configuration, and the effects that changing these can have on the rank order of materials. It is impossible to look at these results and to accurately predict the behaviour of the same materials in new circumstances.

Because of this, there is a need to be able to establish mathematical relationships using experimental data and to apply these to any conditions:

- employed in new designs
- involved in an incident

Also, currently there is no comprehensive system or set of guidelines available to examine incidents after they have occurred. It is essential to ensure as much information as possible can be gleaned from the debris of an incident to help identify inappropriate materials, aid in the design of oxygen system components, and most importantly, to prevent similar incidents occurring in the future. Because of this, road maps and guidelines for the investigation of incidents are also required.

1.6 The objectives of this work

Based on the information in this chapter the main aims have been determined. These are to develop a universal model to predict materials spontaneous ignition temperatures (SITs), to enable the use of more accessible measurement apparatus, and to devise a scientific methodology to investigate oxygen incidents and better follow the kindling chain. In order to achieve these, the following objectives will need to be met;

a) To review literature on the oxidation of materials in high pressure enhanced/ pure oxygen atmospheres in order to understand the fundamentals of flammability and to review the results of current ignition and flammability tests.
b) To combine data bases relating to both metals and non-metals, which will provide scope to improve oxygen system designs, operations and incident investigations
c) To continue the development of mathematical models, incorporating the pressure of an environment, the oxygen concentration, the pressure differential and system flow rate, and the sample mass, to predict ignition (oxidation) temperatures in scenarios involving single substances, using small scale testing
d) To combine heat transfer models with databases to permit the prediction of sequential ignitions and oxidations prevalent in kindling chains, involving contaminants, non-metallic material decompositions and metals' oxidation.
e) To predict the SIT for non-metals in a defined scenario based on experimental measurements and theoretical/ empirical relationships.
f) To form more structured and robust methodology for the investigation of oxygen incidents relating to the collection and analysis of information, incorporating a systematic procedure.
g) To analyse past oxygen incidents using experimental data to validate the use of the heat transfer models for the prediction of ignition/ oxidation and thermal behaviour of materials within oxygen systems.
h) To develop tools to enable the selection of safe materials for use in assemblies/ components (e.g. valves) based on spontaneous ignition data and a risk analysis procedure.

Chapter 2

A literature survey on the problems associated with high pressure enriched-oxygen materials selection and incident investigation

This chapter will detail the current state of knowledge in relation to oxygen incidents, and show the seriousness of these incidents, the worldwide problem they cause, and the need for the optimum safe operation and a methodology for the investigation of oxygen incidents. The following sections illustrate the many ways in which compatibility of materials within oxygen systems can be (and are) assessed, and demonstrate the lack of comparability of these methods. They also report the frequency and type of oxygen incidents that have occurred, as well as detailing the varying way that these incidents are investigated and reported.

Information in this section has been sourced from a wide variety of sources including

- Industrial contacts at Meggitts PLC, Honeywell Aerospace, Marshalls Aerospace & Defence Group and BOC Ltd.
- Government contacts at the Ministry Of Defence (Defence Logistics Organisation)
- Reports and safety advice from National Aeronautics and Space Administration (NASA), European Industrial Gas Association (EIGA) and the USA Compressed Gas Association (CGA).
- Incident investigation reports by the Health & Safety Executive (HSE), NASA white sands facility staff, and the Health & Safety Laboratory (HSL).
- BSi, ASTM and ISO Industrial standards
- The seminal fire text books by Glassman and Yetter (2008a) and Drysdale (2011)
- A range of applied and theoretical journals, and similar publications, including ‘Combustion and Flame’, ‘Fire Safety Journal’, ‘Loss prevention in the process industry’, and ‘Flammability and sensitivity of materials in oxygen enriched atmospheres’.

A large range of journal, book and similar sources have also been found, searched and viewed at the British library, the libraries of University College London and Imperial College London, and using the online directories ‘ScienceDirect.com’, ‘OnlineLibrary.Wiley.com’, and ‘Scholar.Google.co.uk’.

2.1 Illustrative incidents of catastrophic failure in high pressure enriched-oxygen due to combustion

Section 1.1 detailed incidents for the purpose of showing their technical root causes. The following section demonstrates the number of serious incidents over the course of a relatively short period of time, both nationally in the UK, and internationally.

Dicker and Wharton (1988) reported 28 high pressure oxygen incidents between 1982 and 1985. Fowler and Baxter (2000) detailed the occurrence of several incidents in the UK involving pressurized oxygen in the period 1996 – 1998. Gregson (2008) recorded that between 1996 and 2002 158 oxygen incidents had been reported to the HSE, including 59 minor injuries, 25 major injuries and 5 fatalities.

An oxy-acetylene cutting equipment incident, mentioned by Fowler and Baxter (2000), occurred when the operator lit the torch there was a flashback and the single storey workshop was completely demolished in the resultant explosion. There was over one million pounds worth of damage, but fortunately no one was injured.

Fowler and Baxter (2000) reported seven incidents involving the ignition of oxygen regulators (generally following connection of full, high pressure cylinders) causing injury. In one case the operator’s clothes caught fire and he was seriously injured. The hazards of high-pressure oxygen can be demonstrated here by two other incidents.

In the first, oxygen was used instead of nitrogen to pressure test an air conditioning unit. The oxygen reacted with the mineral oil present in the unit. There was an explosion causing extensive damage. The cause of oxygen incidents is often attributed to contaminants, such as greases or oils.

The second incident was at a filling facility where calibration gas mixtures (methane/ oxygen) were being prepared. It was thought that the pressurised oxygen was added to the methane. The methane ignited, and the cylinder was blown apart. The equipment layout and procedures for use were found to be at fault and allowed a single mistake, which resulted in the death of the operator. The report recognises that high gas velocity (when valves are opened) can result in combustion due to adiabatic compression and that contaminant particles, such as rust or dust, can be pushed through a system causing frictional heat, resulting in ignition.

According to Bradley and Baxter (2002), there were several incidents in the UK in the period 1998–2000 involving the use of high-pressure oxygen. Oxygen can be supplied in cylinders at pressures up to 23MPa. This article recommends that equipment for oxygen use must be specifically designed for that purpose and should be cleaned rigorously. In four of the most serious incidents oxygen was used to pressurise or "blow through" equipment (instead of Nitrogen or compressed air). This resulted in the system igniting, either due to pneumatic impact/ adiabatic compression or contaminant particle impact.

Bradley and Baxter (2002) also found that one of the main dangers of oxygen-enriched atmospheres is that clothing can catch fire more easily and burns very rapidly. One incident occurred in a sewage treatment plant where three workers were upgrading equipment. Sparks from an angle grinder ignited the clothes of a worker, who died very shortly afterwards. The investigation revealed that they had been working in an underground chamber, close to an oxygen point. Although the area had been assessed for confined space working and oxygen depletion, oxygen enrichment had not been considered.

This is not just a problem in the UK, but internationally. The NASA Oxygen-Enriched Fire Incidents reporting site (2013) records 119 documents on oxygen incidents between 1984 and 2009, primarily in the USA armed forces, hospitals or similar commercial establishments. The vast majority of these are reports pertaining to actual oxygen incidents, while some are documents on testing in relation to simulated or proposed incidents. The site also lists 30 further incidents occurring prior to 1992 in Boeing establishments. One of the most recent incidents on the register is investigated by Lewis et al (2010) The register also includes a short report on a factory explosion in 2003 where an oxygen pipe ruptured causing a fire/ explosion which killed 3 people. This is a voluntary recording system and is not therefore indicative of the total number of incidents in the USA, but does show there is in continuing problem.

Ahrens (2008) shows the scale of the incidents involving oxygen usage stating that between 2002 and 2005 the US Fire Service attended and average of 182 fire incidents per year, where medical oxygen had been the cause of the fire, with an average of 46 deaths per year resulting. He also states that in the USA between 2003 and 2006 there were an average of 1190 thermal burns per year due to oxygen usage. These are primarily from home usage. The NFPA (2014) medical oxygen incident document also lists a selected 40 serious incidents, primarily in the home, involving significant death, injury or financial damage, where medical oxygen was involved, including 2 reports of fatal fires from 2014. The EIGA Safety Advisory Group (2009) give examples of oxygen incidents that have occurred, without giving numbers, but stating there have been many more similar incidents. The recording of industrial incidents in other European countries varies, and is often missed due to the variation in Occupational Health and Safety Legislation, for example in Germany an incident need only be reported if it caused an employee to take 3 days or more off work (Bergman et al 2007).

These incidents not only show how oxygen systems and their use can cause serious incidents, they support the information in section 1.2 on the various types of ignition sources. The ignition sources are foremost in the minds of incident investigators. They are also the main problems system designers have to contend with when designing operating procedures for oxygen systems. Some compatibility criteria have been developed to aid in the material choices to prevent or reduce the chances of ignition.

2.2 Theoretical basis for materials’ flammability

Combustion in its simplest terms requires 3 things, oxygen, fuel, and energy, often referred to as the ‘fire triangle’. Combustion is an exothermic reaction between some form of fuel and an oxidant, usually oxygen, which generally requires some initial form of energy input to begin. Some sources have expanded this illustrative triangle to a tetrahedron, with the final side being a self-sustaining reaction. The following sections will explain the mode of these reactions, and the effect reacting species and energy input have on the development of a self-perpetuating reaction.

Different objects burn differently depending on a number of factors including their chemical and physical properties but the majority of solids and liquids must be converted into a vapour or gas in order to be part of a combustion reaction (Drysdale 2011). Although some oxidation may take place before this, a full oxidation combustion reaction will generally take place homogenously, completely in the gas phase (excluding some materials such as denser metals).

The production of volatiles is generally the result of an energy input (e.g. an electric spark, or a rise in temperature) causing evaporation or thermal decomposition. A combustion reaction can be written simply as a one-step global chemical equation, for example,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{Eqn. 2.1}$$

but as a number of authors, such as Glassman and Yetter (2008a) and Drysdale (2011) have noted this hides much greater complexity. What is written in a single equation is actually representation of a large number of different reactions happening one after the other, and simultaneously. The interim reactions can involve the initial reactants, and other atomic and molecular species in various states.

In essence then a combustion reaction can be expressed in three stages; Initiation (with the creation of propagating species), chain propagation/ branching (where those radicals etc. beget more propagating species), and finally chain termination (where all species have reacted (radicals joined) and formed the final ‘product’). These phases are by no means distinct from one another in time, and reactions from all of these stages may well happen at once. Glassman and Yetter (2008a) describe a situation where ignition might be said to occur, where the rate of chain carrier (the atom or radical propagating the reaction) generation exceeds that of chain termination. This results in an ‘ever increasing’ reaction rate. For most liquids and solids that burn homogenously the major rate limiting step has been identified as the development of volatiles and gases as this limits the creation of those chain carriers. Volatiles must reach the lower flammability limit (minimum atmospheric percentage) for combustion to be supported.

This is not the only consideration however that influences the likelihood of a self-sustaining reaction. There are also thermal effects that must be considered. Drysdale (2011) refers to Semenov’s theory which describes ignition as a thermal runaway or thermal explosion process which occurs where heat production exceeds heat loss. In actuality it is likely that both thermal, and chain branching/termination rates, play a role (Glassman and Yetter 2008a). Because of this complexity and dual way of seeing any combustion reaction (or indeed any reaction) there are a number of constants, and processes that are used to assess the suitability of materials for use with enriched oxygen atmospheres.

2.2.1 The effect thermal decomposition on material flammability

When materials are exposed to higher temperatures they receive heat energy, and thus become energised. In the case of non-metals this can cause evaporation of some species, but with larger more complex molecules such as polymer chains it can initially bring about a breakdown, or scission, at the molecular level which is referred to as thermal decomposition/ degradation. Small sections of molecule can break away, and then evaporate to form a gas or vapour. With great enough energy input ignition may occur, and the combustion of the polymer might then continue in the vapour phase (homogenous combustion). Thus the ignition temperature of a polymer is directly dependent on the vapours and gases released by thermal degradation, on the ignition temperatures of those substances, and the rate at which they are produced.

Non-metals can degrade in a number of ways when exposed to heat. This decomposition mechanism depends upon the unit structure of the molecules. According to Cullis and Hirschler (1981) the most common degradation mechanisms are random chain scission, end-chain scission, chain stripping, and cross-linking. They also state that only one per cent of bonds in a polymer backbone need to be broken in order for catastrophic changes to occur. In general polymers will decompose to their original monomers, but often, this process results in the release of other smaller molecules as well. Many tests (see section 2.5.8) have been done to identify the thermal degradation products of non-metals, specifically polymers.

If we know the gases or vapours released from a particular polymer, and the SIT of those substances, it may be possible to simply approximate the SIT of the polymer. The current literature lists SITs measured under idealised standard conditions, however it is unlikely that the gases or vapours from degraded polymers would ignite in the same manner as those conditions, and we would therefore expect some differences in the real life oxygen incidents. Also the rate of gas production by the decomposition process will have a significant influence on this.

2.2.2 The effect of the oxidation activation energy on the flammability of materials

The activation energy must be reached for a reaction to start, and therefore directly affects materials' ignition. Once overcome, polymer thermal degradation products react as part of a self-perpetuating oxidation reaction (combustion), fuelled by the exothermic process. For most hydrocarbons this activation energy does not vary a great deal (see Table 2-1). As discussed in section 1.6 there is no single system for assessing the suitability of materials for oxygen use, or the analysis of a system following an oxygen incident. The following sections aim to show the range of criterion and tests currently used, and to further demonstrate the need for a model to enable investigators to calculate the SIT of any material, under a variety of conditions.

Table 2-1. Literature information on activation energies

Author	Hydrocarbon	Conditions	Energy kJ/ mol
Bonner and Tipper (1965a)	Cyclohexane	Air. 503 – 623K. 0.027 MPa	167
Bonner and Tipper (1965b)	n-Heptane	Air. 503 – 623K. 0.027 MPa	179
Cheng and Oppenheim (1984)	Methane	1600 – 2200 K. 0.101 – 0.303 MPa	193.7
Chung and Sandler (1963)	n-Pentane	Oxygen (5 to 50%) and air. 0.009 – 0.027 MPa. 503 – 573K.	217
Egerton et al (1957)	Methane	0.013 – 0.053 MPa. 723 – 773K	163
Griffin and Pfefferle (1990)	Methane	800 – 1100 K	188
Murty Kanury (1975)	Propane	Oxygen and air	130
	n-Octane	Oxygen and air	167.36
Melvin (1966)	Methane	Air and 60 – 90% Methane. As low as 623K. 5.8-1.1 MPa	188
Penner and Mullins (1959)	Methane	1246 – 1646K	121.3
	Iso Octane	1246 – 1646K	135.6
	Cyclohexane	1246 – 1646K	194
	n-Heptane	1246 – 1646K	253
	n-Hexane	1246 – 1646K	212
Petersen et al (1999)	Methane	Highly diluted methane: oxygen mixtures. 1175 to 1880 K	196
Slack and Grillo (1981)	Methane	Oxygen and air. 1640 – 2150 K	218.8
Trimm and Lam (1980)	Methane	Stoichiometric Methane: air mixture. Below 800K	172
Vandenabeele et al (1960)	Methane	Methane (10 – 25%), Oxygen (10% to 40%) and Nitrogen; 300 – 700 K	158

2.2.3 The effect of combustion mechanism on material flammability

As discussed in section 1.3, Glassman (1996) stated that there are two mechanisms of combustion. The most common oxidation mechanism is homogenous oxidation. In this mode the energy (in the form of heat) causes thermal decomposition of the main fuel load to form a vapour or gas layer on its surface. The vapour or gas mixes with the oxygen in the atmosphere and if the energy input is enough, ignition will occur. A combustion reaction then follows totally in the gas or vapour phase. Both fuel and oxidiser are in the gas phase, hence the reaction is said to be homogenous. Non-metals generally oxidise via this mechanism. Under these circumstances the rate of production thermal degradation products (volatiles) is generally the rate limiting step (Lyon 1996, Glassman and Yetter 2008a).

The second mechanism is heterogeneous combustion. In this case the materials do not produce volatiles. Their combustion process is therefore very different to that of the volatilisation process and, according to Glassman (1996) is more akin to that of coal char combustion. This is a surface-burning process where the fuel is in solid or liquid form (a different phase to the oxidiser). In the case of oxidation through liquids a higher oxide is formed in the molten layer and then the surface below is oxidised from this. The surface burning rate, and accessibility to the oxidiser, determines how much of the material is consumed. It generally takes far more energy for this type of oxidation/ combustion to occur. Under these circumstances Ward (2007) reports for metals that the rate limiting factor will be the heat transfer rate, as no gasification of the metal is occurring.

Some metals oxidise heterogeneously, while others oxidise homogeneously. This makes calculation of a material's SIT problematic. An indicator of a metals' mode of oxidation is Glassman's criterion and burn ratios.

2.2.3.1 The use of Glassman's criterion and burn ratios to indicate flammability

Glassman (1996) stated that if the boiling point of the metal oxide is greater than that of the parent metal then combustion occurs in the vapour phase. Glassman used the burn ratio as a way to determine whether a metal will undergo phase transformation, and in which phase it will burn.

The burn ratio is defined as the ratio of enthalpy of combustion at inlet conditions to the total enthalpy change of the reactant metal at either, its boiling point (BR_{bp}), or melting point (BR_{mp}), shown in Table 2-2. The equations for these terms are:

$$BR_{mp} = \frac{\Delta H_c}{\Delta H_{rt-mp} + \Delta H_{fusion}} \quad \text{Eqn. 2.2}$$

$$BR_{bp} = \frac{\Delta H_c}{\Delta H_{rt-mp} + \Delta H_{fusion} + \Delta H_{mp-bp} + \Delta H_{vap}} \quad \text{Eqn. 2.3}$$

Where

ΔH_c = Heat of combustion

ΔH_{rt-mp} = Heat to increase metal temperature from room temperature to melting point

ΔH_{fusion} = Heat of fusion

$\Delta \mathrm{H}_{mp-bp}$ = Heat required to heat material from melting to boiling point

$\Delta \mathrm{H}_{vap}$ = Latent heat of vaporisation

Gordon et al (1968) agreed with this principle, stating that if the surface temperature of self-sustained metal burning configuration is near the boiling point of the metal at least part of the combustion will occur via metal vapour transport from the surface to the reaction zone. According to Keeping (1971) if the equilibrium combustion temperature is below the vaporisation temperature of the metal and its oxide the combustion process is kept going by the formation of a higher oxide on the molten slag. Steinberg et al (1992) disagreed with this approach saying that within the literature there is disparity between boiling points and inconsistency in concept (sometimes boiling, decomposition or sublimation). So clearly, other thermodynamic principles must also be taken into account. Monroe et al (1983) calculated many (see Table 2-2) of these and stated that they are very satisfactory for determining whether a material will ignite or not.

2.2.4 Spontaneous Ignition Temperature

As stated in section 1.3, Bodurtha (1980) defined the Spontaneous Ignition Temperature (SIT, also referred to as the Auto-Ignition Temperature, or AIT) of a substance as the temperature at which vapours ignite spontaneously from the heat of the environment. Clearly if a material ignites at a lower temperature there is a greater risk of it being ignited. Bodurtha also lists a number of factors, upon which the SIT depends, and that should, in some way, be included into a spontaneous ignition model. These, some of which have already been discussed in this chapter, are shown in the Table 2-3 below. The British Standard BS 4N 100-2 (1999) supports Bodurtha, adding that the rate of production of combustible volatiles, not just the concentration, will affect when the material reaches the Lower Flammability Limit, and thus can undergo spontaneous ignition.

Table 2-2 The BR_{bp} and BR_{mp} of selected metals

Metals	BR_{bp}[a]
Copper	0.2
Nickel	0.5
Iron	0.5
Tin	0.8
Lead	0.9
Titanium	1.7
Aluminium	2.2
Zinc	2.4
Magnesium	3.6
Metals	BR_{mp}[b]
Silver	0.4
Copper	2.0
CIDA 938 Tin bronze	2.8
Monel 400	3.0
Monel K 5008	3.6
Nickel	3.7
Ductile iron	5.1
Iron	5.1
304 stainless steel	5.4
Titanium	13.1
Lead	18.6
Zinc	19.3
Magnesium	22.4
Aluminium	29.0
Tin	44.8

a Monroe et al, (1983). b American Society for Testing and Materials G94-05 (2005)

Table 2-3 Factors which influence the SIT according to Bodurtha (1980)

Factor	
Vapour concentration	The level of gases or vapours released by the material on heating must be between the flammability limits. There must be a good ratio and mix of the vapours and oxygen. As it is the vapour that burns, it should be possible to calculate the SIT by combining the SITs of the thermal degradation products.
Environmental effects	The environment volume, pressure and oxygen concentration will affect the ignition. Firstly the production thermal decomposition products must be great enough to reach the Lower Flammability Limit of that material. Materials in 'lower' oxygen atmospheres ('low' pressure/ concentration) will require a greater energy input for ignition to occur, theoretically to encourage collision of reaction molecules.
Ignition delay	This time delay may be due to heat transfer within the system, and to the external surroundings, assuming the system is not adiabatic (thus, as Janoff et al 1997 states, it is important to consider factors like the thermal inertia, thermal conductivity and specific heat), to phase changes such as vaporisation, or may be the time lag due to pre-combustion chemical reactions (Lakshminarayanan and Aghav 2010).
Flow conditions	Increased flow will provide fresh oxygen for oxidation, however initially it will also remove heat.

Table 2-4 The thermal properties of selected materials

Material	Specific Heat, J/g-K	Thermal Conductivity W/m-K	Thermal Inertia (thermal effusivity) (calculated) J m^{-2} K^{-1} $s^{-½}$
Metals			
Monel 400	0.427	21.8	9066
Silicon brass	0.38	26	8995
304 stainless steel	0.5	14.6	7594
Inconel 600	0.444	14.8	7438
Inconel 625	0.41	9.8	5823
Red brass	0.38	159	22992
6061 aluminium	0.89	180	20846
Naval brass	0.38	116	19288
Nickel	0.456	70	16845
Tin bronze	0.376	74	15650
Aluminium bronze	0.375	57	12929
Ductile cast iron	0.461	37	10930
Non-metals			
Nylon 6,6	1.4 – 2.75	0.24 – 0.49	990
PTFE Moulded	1.4	0.27	910
PEEK Victrex	2.13	0.25	830
Silicone rubber	1.46	0.31	800
Vespel SP1	1.13	0.346	750
Polyurethane	1.58	0.245	740
Aflas	1.67	0.2	720
PES Radel A	1 .09	0.24	620
Rulon polycarbonate	1.2-1.3	0.19-0.22	560
PCTFE	0.9	0.135	510
PVC	1.046	0.15	470
Viton AH-V	0.95		

Properties from www.matweb.com (2013). Properties defined at room temperature.

BS 4N 100-2 also provides a definition for the Statistically Defined Spontaneous Ignition Temperature (SDSIT). This is defined as the mean of several measured SIT values, minus twice the standard deviation. It was used historically as a safety measure, as results obtained from Bomb tests prior to the 4N100 Bomb (see section 3.1) had particularly large standard deviations. The advantage of the SIT is that it is one number that, under prescribed conditions of containment and gradual heating, which can be used to compare materials without the need to understand the decomposition, and ignition processes.

2.2.5 Heat release

Heat release of material due to oxidation is regarded to a key part of influencing whether a reaction will be self-sustaining, and thus advance to becoming a full combustion reaction. In terms of measuring a material’s flammability Glassman and Yetter (2008a) place a great emphasis on the adiabatic flame temperature, which is related to the enthalpy of combustion and heat capacity of the material, while Babrauskas and Peacock (1992) state that this is less important than the rate at which energy is released. When comparing the flammability of materials it seems more logical to initially compare the energy output of material combustion to understand the danger they might pose in a high pressure enriched oxygen environment particularly as, as Yuen et al (1988) states, the heat of combustion has a great influence on whether the combustion reaction will start at all.

2.3 Current compatibility criteria used to select materials for oxygen service

This section describes the main criteria that can be used for assessing the flammability of materials. They include criteria created by industry bodies, and engineering companies.

2.3.1 The Air Products and Chemicals Inc. Acceptability Index for comparing materials’ suitability for use in high pressure enriched oxygen systems

At Air Products and Chemicals Inc. experts discuss and review experimental data and the scenarios in which materials are to be used, undertaking a risk assessment. As part of this process Lapin (1973) established an ‘’Acceptability Index’’ and an “Equivalence Concept’’ to be used as a basis for approving non-metallic materials for Oxygen service. Lapin decided that the Oxygen Index of a material would be the most important since it was desirable that a material should not burn at all, or require the highest concentration of Oxygen to burn. It was also decided that the SIT should be as high as possible in order to prevent ignition and the Heat of Combustion be as low as possible reducing the effects cause by initial ignition.

In order to use the Acceptability Index, Lapin introduced the Equivalency Concept. With this, two materials with equivalent oxygen compatibility have equal Acceptability Indices. Lapin measured the Acceptability Index of a wide variety of materials. He devised a scale of minimum Acceptability Indices for specific end use materials, evaluated from known oxygen compatible materials in such end use configurations but emphasised that the Index should only be used to compare different materials and should be used alongside other test methods that assess the end use compatibility of the system as a whole. Lapin devised the numerical Acceptability Index (i) as:

$$i = \frac{O^2 T_{AI}}{\Delta H_c} \qquad \text{Eqn. 2.4}$$

Where

O = Oxygen Index, % Oxygen

T_{AI} = Auto-Ignition Temperature in 100% at 100kPa Oxygen, in °R

ΔH_c = Heat of combustion, cal/g

Note: Non S.I. units part of the industry standard Acceptability criteria

This is a thorough measure but is complex, requiring the use of 3 different test procedures.

2.3.2 The BOC group Ltd (Linde) method of assessing a material's suitability for use in high pressure enriched oxygen systems

According to Irani (2004) the most commonly used calculations at BOC group Ltd are those using heat of combustion and mass to simply work out the maximum energy produced by an oxidation reaction in the system. This can be used for any material, metals or non-metals. The heat of combustion allows the reaction to self-perpetuate. The higher the heat of combustion is, the more violent the oxidation reaction. This results in a greater chance of further ignition chain reactions and greater damage to the system. The total energy released by a component can be calculated by using the equation,

$$\Delta H = m \Delta H_c \qquad \text{Eqn. 2.5}$$

Where

ΔH = Total energy release

m = Material mass

ΔH_c = Heat of combustion of material

It is possible to use this value to calculate the temperature a component, or system, might reach if it absorbed such heat, using:

$$\Delta H = mc_p \Delta T \qquad \text{Eqn. 2.6}$$

Where

c_p = Specific heat at constant pressure

ΔT = Change in system temperature

Multiple items can be incorporated into this equation using:

$$\Delta H = (m_1 c_{p1} + m_2 c_{p2} + ...m_n c_{pn}) \Delta T \qquad \text{Eqn. 2.7}$$

This would give the possible uniform temperature a system could reach when exposed to the specific energy release, and BOC group Ltd have used this to identify the hazard posed by a material in an oxygen system. However this does not indicate the probability of a material's ignition.

2.3.3 The use of pre-existing ignition test rank tables for assessing the suitability of material use in high pressure enriched oxygen systems

Often rather than doing expensive and time consuming testing of materials at high temperatures in pure oxygen, industry will choose to use existing data to assess the suitability of materials for oxygen service. There are a number of published tables ranking materials by their flammability in particular circumstances for both metals and non-metals for various test methods (see section 2.4). There are a number of problems with this method of assessment. Firstly the formulation of alloys and particularly those of polymers can vary significantly. Ingredients in alloys are usually defined by a range, rather than a specific value, while in order to maintain or improve particular properties, polymer manufacturers will change ingredient levels, meaning that materials may be different from batch to batch. The flammability may very well be affected by these alterations/ variations, rendering any previous ranking tables meaningless. The following section will attempt to explain the reasons for this variability in flammability by exploring the theoretical factors affecting ignition and sustained oxidation reactions.

2.4 Standard test procedures for assessing bulk metal flammability

Metals are used as the main structural materials in all oxygen systems. Although not generally the first materials in oxygen incidents to ignite, their oxidation is generally the most violent of the system components. It is therefore important to understand their flammability. The variety and number of different tests for metals' flammability are shown in Table 2-5.

Table 2-5. Metal flammability testing areas

Test class	Description	Tests
Thermal	These tests assess the metals' behaviour when a rapid amount of heat is applied to the surface. This can be done in a variety of configurations. The pneumatic impact test can be regarded as an impact test but ignition is likely caused by thermal effects of the shockwave/ adiabatic compression	Promoted combustion Limiting oxygen index Hollow vessel Auto-ignition test Pneumatic impact
Impact	These may test resistance to ignition when the oxide layer is broken, by impacting various objects on the samples.	Particle impact Mechanical impact
Abrasive	These tests generally involve a stationary piece and a moving piece touching, with the ignition energy being generated by friction.	Frictional heating
Fracture	These test the likelihood that a material (often in pipe configuration) will fracture under high-pressure conditions.	
Configurational	These will be designed for a very specific configuration and set of environmental conditions, for use in a particular apparatus.	

The majority of these tests are designed for one specific application, and this makes it difficult or often impossible for the data from each to be compared to the other. Details of the main tests employed for the determination of flammability characteristics of metals compound the view that there is a need for a clearer system.

2.4.1 Promoted ignition testing

This is the most commonly used test apparatus for metals. It involves a pressurized chamber in which the test specimen is fixed. A promoter, fixed to the specimen, can be ignited electrically to encourage combustion. Thermocouples and pressure transducers take measurements. The majority of tests measure upward combustion, however downward combustion has also been investigated. The results of this test method are regarded to be the most important contained in the ASTM G94 standard with a number of significant characteristics being identified, including:

- Highest No-Burn Pressure (HNBP) historically called the threshold or extinguishing pressure.
- Burn length
- Highest No-Burn Temperature (HNBT)
- Burn/ propagation rates and characteristics including the Regression Rate of Metal Interface (RRMI), the interface between solid and molten liquid metal.

This is one of the only standardised test for metals' flammability with oxygen-enriched environments (described in the ASTM G124 standard 2010) and is meant to mimic the ignition of a contaminant, such as oils, greases or particles. The standardisation of this test was important to obtain comparable data. However, the comparability of the data is limited to the pressure used in the individual tests, the materials selected for testing and the criteria applied to the results. Generally the apparatus is used to provide a rank order, however, testing can sometimes result in vague results, as the results in Table 2-6 show, and do not necessarily allow discernment between materials. A similar thermal test, which can also be used to find the HNBP of a metal, is the limiting oxygen index test. The upward directional version of ASTM G124 (2010) is used in ISO 14624-1 (2003), and has been adopted into NASA technical standard NASA-STD-(I)-6001A (2008).

The test also involves paper beneath the sample to test for danger of ignition from debris, and can be used with ultrasonic transducers to measure 'real-time' regression rate data (RRMI). A similar test is used for evaluating electrical wiring insulation in ISO 14624-2 (2003) but this is not relevant to oxygen systems.

Table 2-6 Promoted ignition test results from 2 different apparatus displaying the extinguishing pressure for several alloys

Materials	NASA WSTF[a] HNBP, MPa	Linde[b] HNBP, MPa
Monel K-500	>68.9	>30.3
Inconel MA 754	>68.9	
Monel 400	>68.9	>30.3
Brass 360	>68.9	
Nickel 200	>55.2	>30.3
Copper 102	>55.2	
Red brass	>48.3	
Tin bronze	>48.3	>30.3
Yellow brass	>48.3	
Naval brass		>30.3
Hastelloy C22	34.5	
Inconel 600	20.7	>30.3
Stellite 6 (B)	20.7	>30.3
Hastelloy C-276		20.7
Inconel 625	20.7	20.7
Ductile Cast Iron	<3.5	
Inconel 718	6.9	6.9
Invar 36	<6.9	
304 SS	6.9	<6.9
17-4 PH		<6.9
316 SS	3.5	<20.7
Nitronic 60	<3.5	
9% Nickel Steel	<3.5	
Aluminium bronze	1.4	<6.9
Aluminium 1100	<0.7	<6.9
Ti-6Al-4V	<0.007	

a NASA NSS 1740.15 (1996). b McIlroy et al (1988). Shaded areas denote materials not tested.

Promoted combustion tests have been conducted using different sample configurations (geometry and thickness). A number show that changing this can impact on the HNBP of a metal. Most noteworthy are Schadler and Stoltzfus (1993) and Zabrenski et al (1989). Zabrenski et al compared the HNBP of solid rods (6.4 mm thick) and tubes (6.4 mm thick wall) for a number of steels. Despite the same thickness, they found that while the HNBP did not vary for, inter alia, stainless steel 430, 9% nickel steel, it did for aluminium 6061 and stainless steel 316 showing that rank order could be changed. Schadler and Stoltzfus (1993) compared the HNBP of Monel 400, stainless steel 316, and some tin bronzes. Solid rods and sintered filters were compared for all three materials. While tin bronze was relatively unaffected by the change in configuration, both the stainless steel, and surprisingly, the Monel were dramatically affected. The stainless steel rod and sintered filter had a HNBP of 6.9 MPa and 82.0 kPa respectively. The Monel rod HNBP of over 68.9 MPa fell to 0.69 MPa for the sintered piece. Again this demonstrates that varying the shape of a material changes its flammability.

2.4.2 Auto-ignition of metals

This is used to measure the SIT. This test is far more common for powdered metals than for the bulk variety, due to the high temperatures and pressures necessary for the bulk metals to ignite. The bulk metal test requires an extremely powerful heating source, for example a continuous wave carbon dioxide laser, as used by Bransford (1986). No method has been standardised for this test.

2.4.3 Particle impact testing

One or more particles enter an oxidant stream and impinge on a sample. Generally this tests flammability when fresh, un-oxidised metal is exposed to the oxygen stream. This is apparently a rare test for metals, despite the relatively high likelihood of ignition resulting from ignition by particles in a system. It has been used on polymers, such as by Forsyth et al (2000), but is not a common test method for these materials. The high-velocity particle impact test system at WSTF (Bryan et al 1993) consists of three major sections,

i. The gas inlet and flow straightener,
ii. The particle injector and converging nozzle, and
iii. The diverging nozzle and test specimen holder.

Particles are carried in an accelerated oxygen stream. The particles released into the oxygen can be varied. In the initial experiments, NASA employed a single 2000µm particle made from 6061 aluminium, (later 5g samples of an iron powder/inert particle mix). Samples are configured as a cylinder and positioned to expose the end to the impacting particle. The system inlet pressure is kept constant at 28MPa, and temperature of the sample is varied from 220 to 700K.

Table 2-7 NASA WSTF particle impact ignition results (Stoltzfus et al 1988)

Material	Sample temperature above which ignition did not occur K
Monel 400	> 630
Tin bronze	> 580
Yellow brass	> 620
Inconel 600	> 605
Inconel 718	475
Ductile cast iron	475
Incoloy 800	470
316 SS	325
304 SS	320
Nitronic 60	310
6061 aluminium	240

2.4.4 Mechanical impact

A plummet (weight) is dropped on to a sample down a sliding carriage. This is only used to ignite the lighter aluminium and titanium alloys, and is therefore not very useful in the context of oxygen service flammability.

2.4.5 Pneumatic impact

This test replicates adiabatic compression/ shockwave ignition. Like mechanical impact, it also only ignites the lighter metals and alloys and has restricted use when assessing flammability in oxygen service.

2.4.6 Frictional heating

These tests can take a variety of forms, but there is always one stationary and one moving component. The two pieces are placed in contact with each other and the contact pressure is increased until ignition of the metal occurs. They can be used to test the likelihood of ignition of a number of samples due to frictional heating (reaction to heat and disruption of the oxide layer).

Table 2-8 NASA WSTF Frictional heating results for selected similar and dissimilar pairs (ASTM G94-05 standard 2005)

Similar pairs	'PV product' [a] at ignition	Dissimilar pairs		'PV product' [a] at ignition
Stationary and Rotary	W/m^2 x 10^{-8}	Stationary	Rotary	W/m^2 x 10^{-8}
Inconel MA 754	3.96-4.12	Ductile cast iron	Monel 400	1.28-1.45
Nickel 200	2.29-3.39	Monel 400	Nitronic 60	1.03-1.69
Tin bronze	2.15-2.29	Tin bronze	304SS	0.97-1.25
Hastelloy C-22	2.00-2.99	Monel K-500	Incone1 625	0.93-2.00
Inconel 625	1.63-1.73	Monel K-500	304SS	0.92-1.13
Monel 400	1.44-1.56	Inconel 718	304SS	0.90-1.18
Monel K-500	1.37-1.64	Monel 400	304SS	0.85-0.94
Hastelloy C-276	1.21-2.82	Ductile cast iron	Stellite 6	0.84-1.16
304 stainless steel	0.85-1.20	Monel K-500	17-4 PH SS	0.80-1.00
Aluminium 6061	0.061	Tin bronze	Aluminium bronze	0.77-0.84
		304 SS	17-4 PH SS	0.75-1.09
		Monel 400	17-4 PH SS	0.66-1.53
		17-4 PH SS	Inconel 625	0.64-1.09

[a] Where the 'PV product' is the product of the contact pressure (N/m^2) and the surface speed (m/s) at ignition

The most commonly used example of this test is the NASA Frictional heating apparatus. Useful for testing pairs of materials, NASA has two examples of this test. NASA has carried out extensive testing with the WSTF Frictional heating apparatus, which consists of a high-pressure test chamber, an electric motor and transmission assembly, and a pneumatic actuation cylinder. The apparatus chamber contains a rotating shaft that extends the length of it. The shaft is attached at one end to the drive motor-transmission assembly and at the other end, to the pneumatic actuation cylinder. The rotating test specimen is mounted on the shaft and the stationary test specimen is affixed to the test chamber via a sample mounting housing. The rotating test specimen has a surface velocity of approximately 20 m/s when the shaft turns at 17,000 rpm.

2.5 Standard test procedures for non-metals

The variety of tests for the compatibility of non-metals with enriched oxygen (demonstrated in Table 2-9) is just as extensive. Again the comparability of the data depends upon the materials and the test pressure selected.

Table 2-9 Non-metals' flammability testing areas

Test class	Description	Tests
Thermal	These methods test for ignition from heating. The pneumatic impact test is in this group as ignition is likely caused by thermal effects of shockwave and adiabatic compression.	Bomb test Pot test Critical oxygen index Differential Scanning Calorimetry Pneumatic shock (impact)
Impact	Energy imparted to sample by a weight, (or pneumatic shock/ adiabatic compression). Can be in liquid or gaseous oxygen.	Mechanical Pneumatic shock
Vapour analysis	Sample is heated, and resulting vapours are analysed.	Thermal Desorption/ Gas Chromatography
Configurational	Designed for a very specific configuration, and set of environmental conditions.	These tests do not apply to this research.

2.5.1 Bomb tests

As discussed in section 1.5.1 this method covers the determination of the temperature at which liquids and solids will spontaneously ignite. The current UK standard is the BS 4N-100 – 1999 (Part 2) bomb test (discussed later in section 3.1). A 100 ±2 mg sample is taken, and split into 20 equally sized blocks, and exposed to high pressures and temperature in the bomb. The temperature is ramped at a rate of 10K/ min. The test is terminated at ignition, or at 773K, whichever is earlier. The data from these tests would be collated in a league table, enabling comparison of the materials. Table 2-10 shows the maximum working pressures (MWP) of a number of selected non-metals. Court (2001) defines the MWP as the greatest pressure at which a material is bomb tested six times, with no ignition occurring. The SIT at 13.2 MPa for component selection is used as it is approximately 25 °C below the SIT at the maximum working pressure. Another proposed safety margin is proposed by BAM, who use a figure 100 °C below the SIT for a working temperature. These enable comparison in specific circumstances. Table 2-11 shows some types of bomb, and Table 2-12 some results.

Table 2-10 Maximum working pressure based upon new bomb results (Court 2001)

SIT at 13.2 MPa, °C	Maximum working pressure (MPa absolute) up to 363K
> 200	0.4
> 230	1.1
> 250	2.1
> 300	4.1
> 350	10.1
> 375	15.1
> 400	20.8
> 500	34.6

Table 2-11 Other bomb tests

Test	Pressure, MPa	Sample size, g	Other information
ASTM G72 Bomb (ASTM G72/ G72M – 09 2009)	2.1 — 20.7	0.2 +/- 0.03	Heat rate 5 +/- 1 °C min. Maximum 425 °C.
BAM (Wegner et al, 1988)	5 & 10	0.4 +/- 0.1	Heat rate 120 °C/min. 5 tests per material.
Linde	≤ 25	0.5	Heat rate 5-6 °C /min. Maximum 500 °C.
L'Air Liquide (Vagnard et al 1991)	12	-	Heat rate 10 °C /min.
Nihart & Smith (1964)	≤ 70	-	Maximum 823 °C.

Table 2-12 SIT data from some selected polymers at 13.2MPa in 99.5% oxygen.

Polymer	SIT (°C) at 13.2 MPa
PTFE	490
Fluorel	336
Vespel SP1	410
Viton	325
Poly (vinyl)chloride	272
Aflas	318
PEEK	350 [a]
Silicone Rubber	310
Polycarbonate	320
Chloroprene	193
Nylon 6,6	219
Polystyrene	250 [a]
Polypropylene	170 [a]
Nitrile	268.5
Butyl rubber	200 [a]
PB	187
Polyurethane	230 [a]

SIT values from LSBU database (see table 3-2 for further results).

[a] Additional values from Wendell Hull & Ass. Inc. Oxygen compatibility materials database (2013)

2.5.2 Pot test

These tests are designed to replicate the conditions in low pressure flowing systems. The BS4N100- 2 test was developed to simulate the dynamic conditions found in oxygen hoses or masks, with pressures below 0.69 MPa, and a maximum temperature of 673 K (400 °C). This test is described by Keeping (1971). A sample (60 mg) is placed into a glass tube and heated by a furnace (to the desired temperature, sustained for 15 minutes) while the oxygen flow is maintained at $2\text{x}10^{-3}$ m^3/min at atmospheric pressure. The sample is examined for signs of ignition. A material is regarded as suitable for use up to 0.4 MPa if the highest temperature recorded (before ignition) is not less than 523 K. According to Wegner et al (1988) another example of this type of test is the BAM ambient pressure test. Hilado and Clark (1972) do not recommend this test alone for determination of materials' suitability as it always gives higher values than the Bomb test.

2.5.3 High Pressure Critical Oxygen Index (HPCOI)

A standard COI test is used to determine the minimum concentration of Oxygen in a flowing mixture of Oxygen and Nitrogen that will support combustion, generally at 1 atm but can be performed at higher pressures depending upon the application of the material under test. HPCOI is used by Air Products and Chemicals Inc. as part of their materials' selection criteria for non-metals for use in high pressure oxygen systems. Described by Benning and Werley (1986) this apparatus increased the previous maximum pressure limit of 2 MPa to 20 MPa. The sample is exposed to a thermite igniter, using a particular configuration that enables the heat to be transferred from the pill, before the molten pill could run through the base. A solder plug is used to prevent the loss occurring too early, while a sample with a thinned wall and tapered length at one end allow smooth transition of the flame to a thicker walled section. The pressure vessel is constructed in stainless steel, with brass plates to shield the bulk from the reaction spatter. Copper exhaust vents also prevent hot gas exposure. A copper pipe contains the test specimen, around which is wound a thin brass pipe, through which water is circulated to remove heat. The test gas (variable mixture of oxygen and argon) flows through the vessel at 1.67 x 10^{-5} m^3/s. This test was designed to allow the testing of metallic materials, which have a far higher oxygen index value than non-metals, but practically provides limited capacity for differentiation between the large varieties of metals used in oxygen system manufacture. Table 2-13 shows some examples of results from an oxygen index test

Table 2-13 Oxygen index results from Benning (1983) at approx. 2MPa

Polymer	Oxygen Index %
Fluorel	31.0
Neoprene	25.5
Nylon 6,6	21.5

2.5.4 Differential Scanning Calorimetry (DSC)

The DSC measures change of enthalpy with time versus temperature. The DSC uses a method of differential heat flow measurement based on the power consumption of a reference sample to that of the test sample. A more detailed description of this is in section 3.2.

2.5.4.1 Pressurised Differential Scanning Calorimetry (PDSC)

Some DSC instruments can be pressurized (PDSC), and operated in oxygen atmospheres to determine the SIT. A more detailed description of this device can be found in section 3.3.

2.5.5 Mechanical impact

Mechanical impact tests involve a sample being placed in liquid oxygen and subjected to an impact from a plummet (the plummet providing a known energy amount). The UK standard is the BS4N100 – 2 Liquid oxygen mechanical impact test. The test involves dropping a plummet of a known weight from a known height on to a striker pin, on a sample imparting energy. The sample (normally mixed with an abrasive ignition-enhancing powder, e.g. carborundum) is immersed in liquid oxygen in a Nickel foil cup. The material is considered to have passed the test if no audible detonation occurs in a set number of trials. Further details of these are shown in Table 2-14.

Table 2-14 Standardised and industry mechanical impact tests

Test	Plummet mass	Drop height	Impact Energy	Other
BS4N100 – 2	9.1 kg	1.37 m	122 J	Tested at 4.0 MPa or 20.8 — 34.6 MPa (used alongside bomb test at higher pressure). No audible detonation to occur in 10 successive tests. If visual detonation occurs, a further 10 successful tests must be performed for material to pass.
ASTM G86 (2011) test (pressurised)	9.04 kg	1.1m	98 J	Elevated pressure in cryogenic, ambient or elevated temperature oxygen environments
B.A.M. Test	76.5 kg	Variable	127 J	Test is terminated if a material still reacts at a drop height of 0.17 m
L'Air Liquide Test (Vagnard et al, 1991)	9 kg	1.1 m	97 J	No audible detonation to occur in 20 successive tests. If one test fails, a further 40 successful tests must be performed for material to pass.

2.5.6 Pneumatic shock

The tests described in this section provide energy via pneumatic impact and adiabatic compression. They simulate conditions similar to the fast opening of valves, and are of a pass/fail nature. A sample is exposed to heated high-pressure oxygen via a series of cyclic pressure shocks. The test sample must not burn or suffer any internal damage to be considered compatible. There are two standardised methods (shown in Table 2-15).

Table 2-15 Pneumatic shock tests

Test	Temperature		Other
	°C	K	
BS EN ISO 2503:2009 Pressure shock test	60	333	20 MPa. 20 10s pressure shocks (20ms pressure rise time) at 30s intervals. (Used by B.A.M with 0.2-0.5 g sample)
ASTM G74 Gaseous oxygen impact test (2008)	21	294	Configurational 5 cycles per minute

2.5.7 SIT test for gases and liquids

Also discussed in section 1.5.1 this covers the determination of the temperature at which gases and liquids will spontaneously ignite, according to BS EN 14522:2005 “Determination of the autoignition temperature of gases and vapours”. A 200 ml narrow-necked Erlenmeyer flask made of borosilicate glass is used as a test vessel, and gaseous or liquid samples are injected into it. The Test vessel is placed into a hot air oven, and the temperature is raised at a ramp rate of 5 °C/ minute. The test vessel can be viewed by using a mirror. The sample is judged to have ignited when there are visible flames.

2.5.8 Identification of polymer thermal degradation products

A number of different techniques described in the literature analyse the thermal degradation products of polymers. A popular technique is Thermal Desorption (TD) and pyrolysis. In this analysis the non-metal is exposed to high temperature, by pyrolysis (heated in the absence of oxygen), followed by analysis of the gaseous materials released. Most researchers conduct this analysis using Gas Chromatography (GC), which is sometimes twinned with Mass Spectrometry (MS) or Infra-Red (IR) analysis. Some results are shown in Table 2-16.

Table 2-16 Current literature decomposition results

Material	Author	Analysis	Atmos.	Temp. °C	Released
Acrylonitrile Butadiene Styrene (ABS)	Herrera et al (2003)	Py	Nitrogen	330-490	Butadiene and styrene etc.
Butyl rubber	Dubey et al (1995)	Refers to Mamadov	-	600	CH_4 0.4%, C_2H_6 7.5%, C_2H_4 2.9%, C_3H_6 4.5%
Chlorinated alkanes	Bergman et al (1984)	GC-MS	Helium	300 – 700	Benzene, toluene and chlorinated alkanes
Poly-chloroprene	Fuh and Wang (1998)	Py GC MS HP 5	-	50 – 280	Chloroethene, 1,3 butadiene, 2 chloro 1,3, butadiene, benzene, toluene, chlorobenzene
	Gardner and McNeill (1971)	Py TLC		270 – 400 and 400 – 500	Methane, propene
Low Density Poly-Ethylene	Hajekova and Bajus (2005)	Pyrolysis	Nitrogen	450	Mainly alkanes and alkenes produced
Nylon 6,6	Morimoto et al (1976)	Py – IR	Nitrogen		Methane, ethane, ethene
Poly-Butadiene	Chen and Qian (2002)	Py-GC Ov101 50m	Nitrogen	25 – 300	Methane, C2 – 4, cyclohexene, vinylcyclohexene, xylene, Methylnaphthalene, Fluorine
Poly-Ethylene	Marimoto et al (1976)		Air		Methane, ethane, ethene
Poly-Ether-Ether-Ketone	Day et al (1990)	Py – GC/MS	Nitrogen	1000 – 1500	Mainly phenol, some benzene and small volatile components
Poly (n butyl methacrylate)	Ettre and Varadi (1963)	Py-GC	-	400 –950	Methane, ethane, methanol, ethanol, propanol

Polycarbonate	Jansen et al (1988)	TD — GC (Tenax)-FTIR-MS	Nitrogen	350	chlorobenzene, phenol, p-alkylphenol
Polyester-urethanes	Jansen et al (1988)	TD -GC (Tenax)-FTIR-MS	Nitrogen	350	aliphatic diols/ esters, cyclopentanone, tetrahydrofurane
Polystyrene	Shappi and Hesso (1990)	Pyrex pyrolysis, GC (SE54 25m) and GC-MS	Air and Nitrogen	300	C7 – C36 alkanes, toluene, benzene, styrene, phenol for both atmospheres, but with a greater variety in air.
	Cascaval et al (1979)	Py-GC	Argon	420 – 790	C1-C3 aliphatic, benzene, toluene, etc.
	Morimoto et al (1976)	Py – IR	Nitrogen		Methane, ethane, ethene
Polypropylene	Fardell (1993)	-	-	-	Alkanes, Alkenes, Benzenes
	Buchalla et al (2000)	TDS-GC (Tenax, 1701)-MS	Irradiation in air	160	Simple alkanes
	Hajekova and Bajus (2005)	Pyrolysis	Nitrogen	450	Mainly alkanes and alkenes produced
Polyurethane	Morimoto et al (1976)	Py – IR	Nitrogen		Methane, ethane, ethene
Poly-Vinyl-Chloride	Boettner et al (1969)	GC/ MS	Air	25 – 580	Basic aliphatics, propene, benzene, toluene
	Buchalla et al (2000)	TDS-GC (Tenax, 1701)-MS	Irradiation in air	160	Simple alkanes
	Andersson (1988)	TD-GC-MS	Helium	160	Aliphatic hydrocarbons, alcohols, aldehydes, ketones

	Aracil et al (2005)	Horizontal quartz reactor	Nitrogen	500-1000	Methane, propane, Pentane, Hexane, benzene, toluene,
Natural Rubber	Chen and Qian (2000)	Py-GC Ov101 50m	Nitrogen	200 –600	C1-6 aliphatics, benzene, toluene

2.6 Oxygen system hazard analysis and risk assessment

There are two main standards for the selection of materials for use in oxygen enriched environments. In the UK the main set of standards are the British Standard BS N100 series. In the USA, the ASTM G88-05 (2005) (compiled mostly by NASA) incorporates a number of other standards to give an overall picture of oxygen system risk assessment and materials' selection.

2.6.1 The BS N100 series of standards advice on the design and testing of high-pressure enriched oxygen systems and their component parts

This standard covers the design, installation and testing of oxygen systems and the materials used in their construction. It also deals with the investigation of incidents. In terms of system hazards the most important sections are:

a) BS 4N 100 – Design and installation (1999)

This section specifies that the oxygen systems be separated from all other potentially hazardous systems, such as electrical systems, and clear of any moving parts. The couplings and connections should prevent excessive pressure charging and be accessible so as to prevent cross contamination. Replenishment points should have filters to prevent foreign particulates from entering the system, and system seals should not be directly exposed to the oxygen stream. Finally all materials used, including soldering, brazing, welding and cleaning materials should be compatible with enriched oxygen environments.

b) BS 5N100 – 5 Guide to fire and explosion hazards associated with oxygen, including handling, storage and replenishment (2006)

Part 5 states that, with a few exceptions, both metallic and non-metallic materials continue to burn in oxygen-rich atmospheres once ignited. BS 5N 100-5 also deals with the common causes of oxygen incidents, as covered in section 1.2, and includes case studies demonstrating them.

c) BS 4N100 – 6 Guidance and recommendations on the selection of materials for use with oxygen (1999)

In this part the selection of metallic and non-metallic materials is discussed. Table 1 of this standard is a smaller version of column 1 in Table 2-6 (in section 0 of this work) showing the Promoted ignition-combustion test results. Non-metallic materials must be proven to be compatible with the temperatures and pressures likely to occur in use, by bomb test.

2.6.2 The ASTM G88- 05 (2005) Standard guide for designing systems for oxygen service

This document applies to the design of systems, but rather than being a comprehensive document, refers to the G63-99 (2007) and G94-05 (2005) standards that deal with the selection of materials. Section 5 of G88 does, however, define thermal ignition as the heating of material in an oxidizing atmosphere to a temperature sufficient to cause ignition, and describes the major factors leading to it (covered by section 1.2 of this document). One of the most useful elements in G88 is a graph showing the potential velocity of an oxygen stream resulting from a pressure differential, enabling designers to check the flow-rate within a component or a system.

Section 7 of G88 specifies oxygen system design. It insists that a system must avoid unnecessary elevated temperatures and pressure. Heat, radiation, electrical sources, and contaminants should also be avoided. The standard details the use of filters and the top-wards orientation of bypass valves to prevent the accumulation of contaminants. Enriched oxygen compatible materials should also be used.

Neither BS N100, nor ASTM G88 standards detail how an oxygen incident investigation should be carried out. Forsyth et al (2003) have constructed a method to assess hazards in oxygen systems using the ASTM G88 standard guide, shown in Table 2-17. This encourages a step by step approach, looking at a system as a whole, as well as each individual component and their constituent parts. A similar process can be applied to incident investigations. This guide is useful to investigators who are very familiar with oxygen systems however it still does not go into the sort of forensic detail that might be required to be collected in order to fully assess a system, or an incident. In this approach a series of ranking criteria are used to assess the ignition likelihood, based on the different physical factors (0 being almost possible, and 4 being highly possible), but no true numerical analysis is carried out. Although it can be adapted to incident investigation, this approach does not directly cover oxygen incident investigation. Section 0 briefly demonstrates the information that is sometimes missed by investigators.

Table 2-17 Hazard assessment of oxygen systems (Forsyth et al 2003)

1. System level analysis	
a. Component listing	- Composing schematics and list
b. Component severity and compliance ranking	- Analyse system schematic and perform a visual inspection. - Assess the maximum working conditions, design for cleanliness and possibility for ignition.
c. Component priority listing	- Create a list of components requiring in-depth ignition hazard analysis
2. Component level analysis	
a. Component priority listing	- Compile component cross section drawings
b. Component hazard analysis	- Analyse each part - Evaluate materials' flammability - Explore possible ignition mechanisms - Predict reaction effects - Evaluate overall likelihood of an incident occurring

Rosales et al (2007) have added to this in the NASA document TM-20070213740 stating that the worst case operating conditions must also be identified.

2.7 Incident investigation

This section contains the details from 2 investigation reports for oxygen incidents. They will demonstrate the sort of incidents that can occur in oxygen systems and the variation in the way that these incidents can be reported.

2.7.1 The catastrophic failure of a charging panel and connective hose

In 2007 an oxygen incident occurred in Tidenham, Gloucestershire. This was investigated by the HSE and further investigated by HSL. While gauging the gas contained within two 7-litre cylinders connected to a gas charging panel an explosion occurred. The gas charging panel was extensively damaged and the tubing (connecting the panel and cylinders) was destroyed.

In the report the investigator notes that the outlets attached to the cylinders did not contain non return valves and therefore allowed any contamination in the cylinders to enter back into the charging system. They also note that a Viton ‘O’ ring on one of the cylinders (at outlet 1) had a section missing (not due to fire damage). The Viton is judged to be a likely source of ignition, probably ignited by adiabatic compression. Many system and environmental details are recorded. Photos and schematic diagrams enable the identification of the components involved, although a scale is not used in the photographs.

2.7.2 The catastrophic failure of an oxygen system regulator

In 1987 an oxygen incident occurred in Boston, Lincolnshire. This was also investigated by the HSE. An empty cylinder was being replaced by a new full cylinder. The new cylinder was opened briefly to clear the neck and then closed again. The regulator was then put on to the new cylinder, and the cylinder valve was opened. At this point the regulator exploded, bursting into flames.

In the report the investigator judged the fire to have started in the high-pressure section of the valve however no reason is given for this. The initial material was judged to have been organic.

The missing components from inside the regulator (i.e. the components that comprised a significant portion of the kindling chain) were not identified, nor were the materials from which they were made. It is possible that this information was not available to the investigator at the time. The environmental pressure and percentage of atmospheric oxygen in the system are not listed. The lack of description in relation to materials makes this incident practically impossible to fully analyse. This is an example of an incident report that contains no, or little, technical or useful scientific information. As these two summaries show, there can be a great difference between incident investigations. Some are investigated fully, with all the relevant and useful information being recorded, whilst others provide insufficient detail to learn from the incident. Sections 2.2 – 2.6 have all demonstrated that the environmental conditions, component mass and material of construction all affect the SIT of materials and subsequently the kindling chain of an oxygen incident. It therefore follows that any incident report should contain as much of this information as possible.

2.7.3 Investigation principles

As mentioned in section 1.4 there are a number of interested parties concerned with oxygen incidents however there is no one way to investigate incidents. The process can be confined to one organisation, for example an insurance company consultant, or collaborative. The more serious the incident, the more institutions may have to be involved e.g. an injury or death will result in the involvement of police and, in the UK Health and Safety Executive (HSE) or in the USA the Occupational Safety and Health Administration (OSHA) or one of the organisations they oversee. It is expected that the most serious of events will have substantial resources applied to them, but this may be too late, and there is no strict process applied. The philosophy behind having a safety culture and regulations/ regulatory organisations is to identify problems before they happen, or before they cause serious harm (HSE "Investigating accidents and incidents" guide 2004). Thus the recording of all scientific information possible for minor incidents as well as major should help to identify problems sooner. This may be especially true if the cause of the incident is not clear. The use of science and scientists' knowledge has been invaluable in gaining greater understanding of events that occurred at crime scenes (forensic meaning pertaining to law), and principles developed to accompany its use have changed the nature of criminal investigations. Evidence handling, scene and activity recording, and general evidence integrity have all aided the knowledge gathering process (Cobb 1998). Incorporation of these principles, and specifically details of materials, dimensions, atmospheric conditions and similar data/ information into recognised incident investigation methods, such as fault trees and root cause analysis, might similarly aid health and safety investigations.

This chapter has detailed the current technology and standard status for the assessment of materials used in high pressure enriched oxygen systems. It has demonstrated that events can be catastrophic, resulting in equipment damage, and loss of life, and that they are a worldwide problem. It has demonstrated how important it is that materials are suitable for this highly specialised environment, and that should they fail, the incident is fully investigated, maximising the information obtained for both the current, and possible retrospective, investigations.

Chapter 3
The determination of non-metal spontaneous ignition temperatures under a range of conditions

A scheme was devised to gather further information from experimental work (and the existing literature) to enable the accurate analysis of a kindling chain combustion reaction, with particular reference to oxygen service, i.e. incorporating data from high pressure environments with oxygen enrichment.

The first stage of this process was an experimental programme to test the SIT of selected non-metals used in high-pressure oxygen systems. Initially this was done using a Bomb apparatus, in 99.5% oxygen at pressures ranging from 3 – 40 MPa. Further SIT tests were then conducted on the same or similar materials using differential scanning calorimetry (DSC) at ambient pressure, in air, and using pressurised differential scanning calorimetry (PDSC) in 99.5% oxygen at pressures ranging from ambient to 3.4 MPa. Secondly thermal desorption (pyrolysis) – gas chromatography has been used to identify the gases evolved when non-metals used for oxygen service are heated. Using SIT data for these individual gas components of the volatiles it might be possible to estimate the SIT of the polymer from which the vapours have been released. The results from these tests are to be used to derive a mathematical relationship, which will allow the approximate prediction of a SIT for any material, under a range of typical working conditions.

3.1 Measurement of the SIT of a number of selected polymers at a range of pressures using the high pressure bomb test

The high pressure bomb apparatus was used as part of the programme to identify the SIT of non-metals. Tests were conducted on a large number of polymer samples. The environment consisted of 99.5% oxygen and the pressure was varied from 5 to 40 MPa. The London South Bank University bomb is an example of the BS 4N-100-2 (1999) bomb test. It improved the previous (BS 3N 100 1985) design for the bomb criteria, allowing test pressures up to 45 MPa and a maximum temperature of 550°C (823 K). The newer BS 4N-100 bomb test has a greater accuracy, repeatability, and reliability than its forerunner (which produced series of results with high standard deviations adding the need to statistically define the SIT). It is also capable of testing materials over a greater range of temperatures, and pressures, and accommodates larger samples (see Table 3-1 below).

Table 3-1 Comparison of BS 3N- 100 and 4N-100 bomb tests

	3N- 100	4N-100
Maximum temperature	673 K	823 K
Maximum test pressure	13.8 MPa	45 MPa
Maximum sample mass	60±2 mg	100±2 mg
Heating rate	Not less than 20 K/ min (maintaining constant linear rise problematic)	Uniform heating rates from 2 to 100 K/ min

3.1.1 Description of apparatus

The apparatus consists of a stainless steel containment vessel, which contains a thin walled Monel K500 combustion vessel. The internal vessel is filled with oxygen, while the external vessel is filled with Nitrogen, maintaining pressure equalisation. This allows the inner vessel's Monel wall to be thinner, thus minimising the thermal inertia of the apparatus. The thermal inertia of the system can be represented by:

$$\frac{m_r c_{pr} + m_b c_{pb}}{m_r c_{pr}}$$

where:

m_r = Mass of sample

c_{pr} = Specific heat of sample

m_b = Mass of bomb apparatus

c_{pb} = Specific heat of bomb apparatus

This apparatus allows the heater to be mounted on the external wall, so not in the oxygen environment (as in the earlier BS 3N 100 version) reducing the chance of an oxygen incident from electric arcing or short-circuits. Three Inconel thermocouples are used to monitor the temperature changes and to provide information for the feedback control. Two are above the sample to measure the sample temperature, and temperature on ignition. A third is beneath the sample, and is buffered from minor temperature fluctuations by the combustion boat. This is suitable for the heater controller feedback temperature. The ideal gas law states that

$$PV = nRT \qquad \text{Eqn. 3.1}$$

where

P = Pressure

V = Volume

n = Number of gaseous moles

R = Universal gas constant

T = Temperature

As the temperature of the system is raised, so is the pressure (as it is a constant volume), so a buffer is used to maintain a constant system pressure via a manually operated high pressure vent valve. The heater is a standard 1 Kilowatt mineral insulated band heater, which is contained in a nitrogen atmosphere. The system also has a buffer vessel, into which vented gases can be released up to the maximum vessel pressure of 69 MPa. Strain gauge type pressure transducers are used to monitor gas pressures in both vessels. A Monel 400 high-pressure filter is fitted in line with the combustion vessel. The vent line is fitted with a brass flame arrester. The environmental oxygen content is 99.5%.

Figure 3-1 BS 4N100 Bomb apparatus

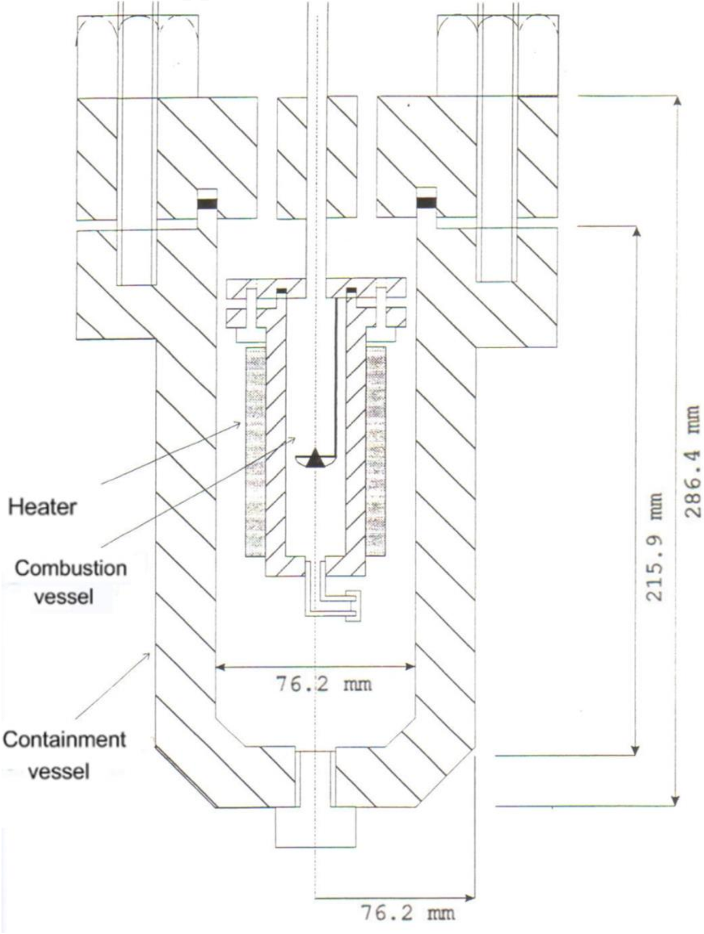

Diagram from McGuire (1993)

3.1.2 Experimental procedure for the BS 4N 100 Bomb test

A 100 ±2 mg sample was taken, and split into 20 equally sized blocks, and then cleaned (with an aqueous solution of ‘Today & Beyond’ Beyond-2001® in accordance with BS 5N 100 – 7). The samples were then inserted into the combustion boat, and the combustion vessel was lowered into the containment vessel. The combustion vessel was purged, and filled with oxygen, while the containment vessel was filled with nitrogen (maintaining the equilibrium), (See appendix A for full procedure).

The standard test conditions use a heating rate of 10°C/min at a constant pressure of 13.2MPa (chosen due to the large amount of results available in databanks at this pressure due to its historical use in BS 3N 100 1985 and BS 4N 100 1999). Ignition tests were also conducted at a range of other pressures between 5 and 40 MPa. After completion the oxygen was vented at the same time as the nitrogen. After the test was complete and all gases were removed, the containment vessel was opened and allowed to cool.

3.1.3 BS 4N 100 Bomb test results

Table 3-2 below shows Spontaneous Ignition Temperature (SIT) test results acquired in 99.5% oxygen for a number of polymers, in a range of test pressures.

Table 3-2 High Pressure bomb test results

Material	Pressure, MPa	SIT	
		K	°C
Aflas [a]	9	609	336
	13.2	591	318
	15	585	312
	25	575	302
	29	573	300
	33	568	295
Bromo-Butyl Rubber [b]	5	480	207
	13.2	464	191
	30	457	184
	40	449	175
Fluorel [a]	8	623	350
	13.2	609	336
	16	605	332
	31	601	328
	35	600	327
	40	600	327
Makrolon [b]	5	615	342
	13.2	593	320
	30	583	310
	40	577	304
Nitrile [b]	5	563	290
	13.2	542	268
	30	529	256
	40	520	247
Noryl [b]	13.2	474	201
Nylon 6,6 [a]	6	498	225

	13.2	478	205
	15	475	202
	27	468	195
	35	463	190
	40	463	190
PCTFE [a]	6	728	455
	13.2	708	435
	19	708	435
	27	698	425
	35	695	422
Polybutadiene [a]	8	473	200
	12	461	188
	13.2	460	187
	16	452	179
	29	441	168
Polychloroprene [a]	10	473	200
	13.2	466	193
	25	450	177
	39	443	170
Polyisoprene [b]	13.2	411	138
Polyurethane [a]	5	495	222
	6	503	230
	13.2	495	222
	13.2	493	220
	15	491	218
	27	482	209
	38	478	205
PTFE[a]	5	773	500
	9	768	495
	13.2	763	490
	22	763	490
	35	763	490
PVC [b]	13.2	475	272
Rulon Tape [b]	5	740	467
	13.2	718	445
	30	698	425
	40	690	417
Silicone Rubber [a]	5	587	314
	9	588	315
	13.2	583	310
	30	553	280
	36	557	284
	40	548	275
Vespel SP1 [b]	5	698	425
	13.2	683	410
	30	670	397
	40	665	392
Vespel SP21 [a]	8	691	418
	13.2	673	400
	17	673	400
	25	663	390

	29	660	387
	35	660	387
	39	660	387
Viton [a]	6	628	355
	12	602	329
	13.2	598	325
	16	596	323
	33	584	311
	35	573	300
	37	573	300
Viton A [b]	5	607	334
	13.2	591	318
	30	582	309
	40	574	301

[a] McGuire (1993) [b] Rahman and Nolan (2000).

It should be possible to develop a relationship between these data for a given material i.e. devise an equation, incorporating all of the pressure and temperature variations. It may also be possible to take into account the system flow, resulting in an equation that enables us to predict the SIT of a material under any conditions. Predicted values will have to be compared to values measured under varying conditions in other apparatus. There may be a problem comparing polymers though. Even if the polymer is from the same manufacturer or has the same trade number it may not actually be the same. Polymer manufacturers change the chemical make-up from one batch to the next to alter the physical characteristics, or maintain characteristics in desired conditions (also depends on the chemicals' availability). Although this may change the outward polymer behaviour only a little, altering the materials composition can significantly alter the flammability. For this reason within one polymer group, the SIT can vary a great deal.

3.2 DSC – Mettler Instruments DSC12E[1]

The Differential Scanning Calorimeter, as the name suggests, calculates the energy released or absorbed by a material by comparing it to an empty reference sample holder. The instrument heats both on a ramp, grading how much energy needs to be provided to each to keep them the same temperature. The Mettler DSC12E was utilised as part of the experimental programme using Flynn and Wall's (1966) method. The detected exothermic onset temperature can be considered to be the ignition temperature of the test sample. This value has been used for comparison with SIT values at higher pressures (see Chapter 4).

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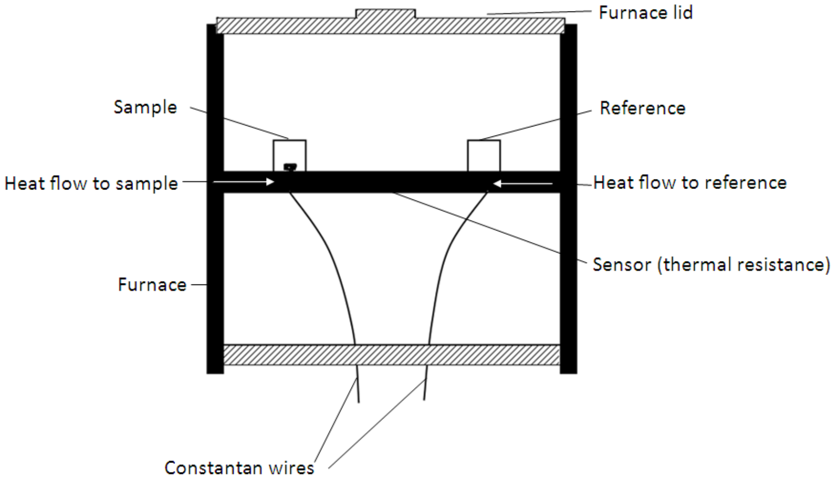
[1] Mettler-Toledo Ltd., 64 Boston Road, Beaumont Leys Leicester, LE4 1AW

3.2.1 Description of apparatus

This apparatus compares a sample in a crucible with an empty reference crucible as heat flows from the furnace across the defined thermal resistance (sensor) to the sample and reference side. If the heat capacity of the sample does not equal the reference it results in a net heat flow to or from the sample, leading to a temperature difference. It is capable of heating up to a rate of 20 K/ min, with a maximum temperature of 673K. The Mettler system software TA89E was used for data collection and recording. The Sample holders used were high-pressure gold plated (inert material), steel crucibles measuring 7 mm in diameter and 5.9 mm high.

Figure 3-2 DSC sample chambers



3.2.2 Experimental procedure for the Mettler DSC12E

See appendix B for full method. A sample material was selected and a 5 – 10mg section was cut, weighed, and cleaned. This was then inserted into a Mettler high-pressure crucible and sealed shut using a press. The crucible was placed into the DSC sample chamber, on the left plate, with an empty crucible (of the same type) on the right heating plate to act as a reference, for comparison. The chamber lid and DSC lid were replaced, and the water supply was switched on (in order to cool the machine's electronic components). The sample was heated at a rate of 5 K/ min, from 323 K – 673 K (50 – 400°C), with a thermogram being recorded by the Mettler TA89E software. The 5 K/ min ramp rate was the optimum specified by the manufacturers for this apparatus. Work by Bryan and Lowrie (1986) states that this should show essentially no variation from results obtained at a ramp rate 10 K/min. This is supported by results in Wharton et al (1989) and section 6.2.1 of BS 4N100-2. Analysis was conducted on the thermogram to determine the onset temperature of the main exothermic peak, which can be equated to the ignition temperature.

3.2.3 Experimental results from the Mettler DSC12E

Table 3-3 shows ignition temperatures for selected polymers. A number of materials tested were found not to ignite below the 673K (400°C) maximum test temperature. These are Aflas, Makrolon, Nylon 6,6, PCTFE, Rulon, Silicon rubber 2451, Silicon rubber S87, Vespel SP21, and Viton A. An example thermogram can be found in appendix B.

Table 3-3 Atmospheric Differential Scanning Calorimetry results

	Ignition Temperature, 5 K/ min	
Polymer	°C	K
Polychloroprene	266	539
Noryl	306	579
Polybutadiene	315	588
Polyisoprene	185	458
PVC	264	537

3.3 PDSC – TA Instruments 2910[2]

The TA 2910 is a pressurized DSC. A similar method has been employed, as with the atmospheric tests, but with necessary differences due to the pressurised conditions. This apparatus was also utilised as part of the experimental programme using Flynn and Wall's (1966) method, with the exothermic onset temperature (considered the ignition temperature) being recorded. As the exothermic onset temperature can be approximated with a material ignition temperature the results can be compared with results obtained using the DSC and Bomb test apparatus (See Chapter 4)

3.3.1 Description of apparatus

Like the Mettler DSC, this apparatus also compares a sample in a crucible with a reference crucible (see 3.3.2). These are placed in pans on a raised constantan disc. It is capable of heating at up to a rate of 50K/ min, with a maximum pressure of 7 MPa and maximum temperature setting of 873 K (600 °C). The pressure DSC cell (contained beneath a small silver lid, and cover) is enclosed in a steel pressure cylinder, capped with a pressure cover, to allow pressurisation. The cell has two pressure control valves (inlet and outlet), a pressure gauge on the front, and a pressure relief valve at the rear.

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[2] TA instruments Ltd., Block D, The Fleming Centre, Fleming way, Manor Royal, Crawley, W. Sussex, RH10 9NB

As the samples must be exposed to the enriched oxygen environment, the non-metal samples are tested in an open aluminium crucible.

3.3.2 Experimental procedure for the TA Instruments 2910

(See appendix C for full procedure)

In this case a sample material was selected and a 2 – 5mg section was cut, weighed and cleaned (in accordance with BS 5N 100 – 7). The sample was then placed in an aluminium crucible. This and the reference crucible were then inserted into the high pressure cell on the reference plates. The chamber was sealed, and purged using Nitrogen. The chamber was then filled with oxygen and pressurised to 3.4 MPa. The chamber was then heated from ambient (well below the exothermic onset temperatures) to 873 K (600°C) at a ramp rate of 10 K/ min. The pressure was maintained by continual 'bleeding off' of hot gas using the purge valve. TA instrument's Thermal analysis software was used to calculate the exothermic onset temperature of the samples. This process was then repeated at the same ramp rate, to assess the repeatability. The method was also employed at a pressure of 2.1 MPa.

3.3.3 Experimental results obtained using the TA Instruments 2910

Table 3-4 Pressurised Differential Scanning Calorimetry TA Instruments 2910 results

Material	SIT 2.1 MPa		SIT 3.4 MPa	
	K	°C	K	°C
Aflas 100S	628	355	607	334
Polychloroprene	688	415	626	353
Nylon 6,6	636	363	628	355
Polybutadiene	436	163	431	158
Silicone rubber 2451	611	338	605	332
Silicone rubber S87	585	312	578	305
Vespel SP21	782	509	761	488

An example thermogram can be found in appendix C. These data were acquired using the TA Instruments 2910 PDSE at Honeywell Aerospace, Yeovil.

3.4 Thermal Desorption – Gas Chromatography (TD/GC)

This experiment was used as part of the programme to find out whether it would be possible to identify, or at least simply approximate, the SIT of non-metals from the identification of the thermal decomposition products. Tests were conducted on a selected group of polymer samples. The materials were subjected to pyrolysis using a

Perkin Elmer ATD50 Thermal desorber[3] and the resulting vapours and gases evolved from the evaporation of additives and polymer pyrolysis were analysed using an AMS Model 93 Gas chromatograph[4]. Based on preliminary experiments it was decided to carry out the thermal desorption at approximately 50K below the SIT of the test sample material (though in some cases this value is increased due to the maximum temperature of the apparatus). This was to allow easier identification of the volatiles being expelled by the material without the chance of ignition.

3.4.1 Description of apparatus

The Perkin Elmer Thermal Desorber ATD50 has a sampler section (with 50 sample places), a desorption oven for heating, and a secondary cold trap for the collection of evaporation and thermal degradation products. The oven can be set to temperatures from 323K (50°C) to 523K (250°C), and can be on for between 3 and 30 minutes. The secondary cold trap temperature can be set between 243K (-30°C) and 303K (30°C). The sample tubes are sealed at both ends, raised into position, and each sample tube undergoes a test sequence including carrier test, carrier purge blocked tube test, leak and pressure tests (to check that no products will be lost) before desorption. The AMS Model 93 Gas Chromatograph was used for separation. A 25m 1701 column was used with a flame ionisation detector (Figure 3-3).

3.4.2 Experimental procedure for the use of Perkin Elmer ATD50 Thermal desorber and AMS Model 93 Gas Chromatograph

(See appendix D for full procedure)

A small sample of the chosen polymer was cut (approximately 30 – 40 mg) and placed in the sample holder wrapped in glass wool. The sample was then subjected to thermal desorption. The desorption temperatures were entered (see Table 3-5) with an initial desorption time of 10 minutes and secondary time of 30 minutes. A cold trap temperature of 303 K (30°C) and a carrier gas pressure of 0.28 MPa (approximately 90% of the column pressure) were also entered. For the Gas Chromatography the single ramp program was used. The materials were held at 323K (50°C) for one minute followed by a 15K/minute program to 523K (250°C), which was then held for 30 minutes.

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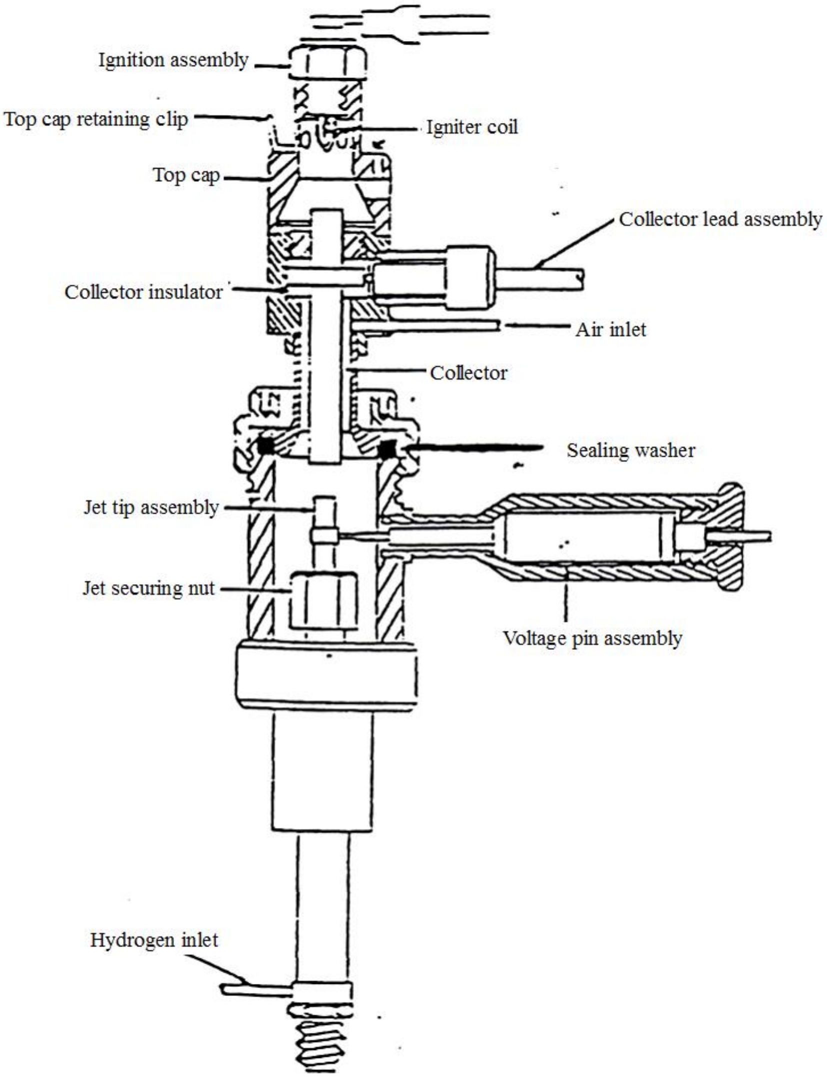
[3] Perkin Elmer Instruments, Chalfont Road, Seer Green, Bucks, HP9 2FX.

[4] Analytical Measuring Systems, London Rd, Pampisford, Camb, CB2 4EF

Figure 3-3 Flame ionisation detector (from AMS 93 manual)



3.4.3 Experimental results obtained from the thermal desorption – Gas Chromatography analysis of selected polymers

Table 3-5 Identification of degradation products of selected polymers at atmospheric pressure

Butyl Rubber – Desorbed at 483 K (210 °C)					
Peak No.	Time	Area	Conc.	Kovats	ID
1	4.382	18852	54.8843	410	2 Methyl propane
2	4.515	598	1.742	475	
3	5.118	624	1.8166	598	Hexane
4	8.104	535	1.5575	773	3-methyl heptane
5	9.607	355	1.0326	825	Toluene
6	21.802	718	2.0912	1164	
7	22.956	10236	29.8008	1196	Dodecane
TOTAL		31918	100		
Polychloroprene – Desorbed at 523 K (250 °C)					
Peak No.	Time	Area	Conc.	Kovats	ID
1	4.343	1044	4.7223	438	
2	4.467	242	1.0965	481	Methyl butane
3	4.565	484	2.1895	499	Pentane
4	5.095	428	1.9355	594	Hexane
5	5.375	477	2.1554	621	
6	5.558	478	2.1637	636	1,1-Dichloroethene
7	6.744	290	1.3123	716	Chloroform
8	8.601	3784	17.1109	791	1,2 Dichloropropane
9	9.483	1199	5.422	821	2-Pentanone
10	11.645	651	2.943	883	1,3-Dichloropropane
11	20.508	433	1.9563	1125	
12	22.058	956	4.325	1171	1,2,3-Trichlorobenzene
13	23.069	2482	11.2244	1199	Dodecane
14	23.3	1313	5.9358	1207	
15	27.163	1631	7.375	1335	
16	27.351	1994	9.0164	1342	
17	27.808	1027	4.646	1360	Xylenol
18	29.486	2888	13.0599	1421	
PP – Desorbed at 523 K (250 °C)					
Peak No.	Time	Area	Conc.	Kovats	ID
1	4.34	467	5.14	437	
2	4.473	1501	16.5304	474	
3	4.563	601	6.6159	499	Pentane
4	5.074	489	5.385	590	
5	9.366	3154	34.7388	817	Dimethyl Heptene
6	9.583	796	8.7646	824	

PVC – Desorbed at 523 K (250 °C)

Peak No.	Time	Area	Conc.	Kovats	
1	4.375	4576	1.7838	410	Butane
2	4.601	2774	1.0811	506	Pentane
3	6.808	17220	6.7123	719	Chloroform
4	8.272	4503	1.7645	779	Dichloropropane
5	8.935	8789	3.4257	803	Octane
6	21.148	196324	76.5255	1144	Trichlorobenzene
7	21.559	5074	1.9777	1157	Benzyl chloride [b]

SBR — Desorbed at 523 K (250 °C)

Peak No.	Time	Area	Conc.	Kovats	ID
1	4.408	718	1.2143	456	
2	4.547	980	1.658	494	Pentane
3	4.617	644	1.0902	509	
4	5.062	951	1.6084	588	
5	5.159	2006	3.3942	602	Hexane
6	5.245	604	1.0228	610	
7	5.434	17414	29.4668	626	Methyl cyclopentane or Propanol
8	8.775	3969	6.7161	798	Octane or diethyl hydroxyl amine
9	14.561	642	1.0864	963	Isopropyl benzene
10	16.25	677	1.1456	1005	Decane
11	16.4	1048	1.7738	1010	
12	17.85	603	1.0203	1051	Methyl branched alkane
13	19.297	1304	2.2072	1090	Octanal or Benzaldehyde
14	19.542	705	1.1928	1096	
15	19.954	705	1.1936	1108	
16	20.107	997	1.6872	1113	
17	20.215	817	1.3826	1116	
18	20.51	839	1.4189	1125	
19	20.733	635	1.0748	1132	
20	21.253	1020	1.7258	1148	
21	26.233	331	9.5597	1299	
22	27.608	1928	3.2616	1352	
23	27.914	6230	10.5422	1364	
24	28.008	1320	2.2341	1367	
25	29.674	2337	3.9549	1428	
26	29.753	1215	2.0564	1431	

[a] Pacakova and Feltl (1992), [b] Safarova et al (2004), Otherwise HSE MDHS 88 (1997) Only materials making at least 1% of released degradation products are shown. Materials constituting less than 1% have been removed as they are not deemed significant towards ignition. [c] Where Kovats are the constituent compound retention indices normalised against a reference standard of alkanes (C2 – C16) for comparative purposes. An example chromatogram can be found in appendix D.

Chapter 4
Development of Spontaneous Ignition Temperature results and combustion models

In an oxygen system once one material has ignited, a kindling chain is often quick to develop. For this reason prediction of the ignition, and particularly the Spontaneous Ignition Temperature (SIT), is the most important factor when considering the flammability of materials in such a system. Various factors and test methods are currently used to assess polymer use in oxygen systems (see section 2.2).

Development of a model to predict the ignition of materials is a complex process due to the number of different parameters affecting the mechanism of ignition. Some of the theoretical parameters were discussed in section 1.3. The fire triangle demonstrates the three major factors in combustion; fuel, oxygen, and ignition energy. Assuming that ignition energy is supplied (by one of the modes mentioned in section 1.2) the determinative system parameters are those that affect the levels of fuel vapour and oxygen available to react. These are:

- Environmental pressure
- Oxygen concentration
- Environment flow
- Material configuration (e.g. size, shape, thickness etc.)

A simple relatively simple model is derived here, and the data obtained in chapter 3 is used to demonstrate the applicability of that model, in order to calculate the SIT of a non-metal at a given pressure, and oxygen concentration. The effects of flow, and scale are also dealt with. Finally, further data on metals have been collected from the literature, due to the specialist equipment required for bulk metal SIT testing, to be incorporated into a model demonstrating the kindling chain.

4.1 Variation of polymer SIT with pressure

Due to reaction kinetics, increasing the amount of reactants available for collision increases the rate of the reaction. It also means that initially the chance of collision between reactants and products increases, increasing the chance of ignition, with a lower energy input (assuming a one-step global reaction for simplicity). Often in combustion reactions the major limiting factor is oxygen. Increasing the pressure of an environment increases the concentration of oxygen within a given volume, resulting in a lower SIT, as noted by Kishore and Sankaralingam (1986).

4.1.1 Kinetic modelling – Critical gasification of polymers

The ignition of the thermal decomposition products of polymers has been shown to occur when the surface of the polymer reaches a critical temperature, at which intense gasification is possible.

Glassman and Yetter (2008a) report hydrocarbon reactions have orders ranging between 1.5 and 2, and thus to develop a single overarching equation assuming a reaction order of 2 is not unreasonable. If we assume second order reaction the rate equation states:

$$-r = \vartheta C_A C_B \qquad \text{Eqn. 4.1}$$

Where

$-r$ = Rate of reaction (mol L^{-1} s^{-1})

ϑ = Rate constant (L mol^{-1} s^{-1})

C_A = $C_{A0}(1- \omega_A)$ (mol L^{-1})

C_B = $C_{B0}(1- \omega_B)$ (mol L^{-1})

C_{A0} = Initial concentration $_{\text{A (polymer)}}$ (mol L^{-1})

C_{B0} = Initial concentration $_{\text{B (oxygen)}}$ (mol L^{-1})

ω_A = Conversion of polymer volatile reactant to product (mol L^{-1})

ω_B = Conversion of oxygen reactant to product (mol L^{-1})

Thus;

$$-r = \vartheta C_{A0}(1-\omega_A)C_{B0}(1-\omega_B) \qquad \text{Eqn. 4.2}$$

The Arrhenius equation is:

$$\vartheta = Ae^{-\frac{E}{RT}} \qquad \text{Eqn. 4.3}$$

Where

A = Pre-exponential factor (L mol^{-1} s^{-1})

E = Activation energy (J mol^{-1})

R = Universal gas constant (J mol^{-1} K^{-1})

T = Temperature (K)

Also, using the ideal gas law the concentration of oxygen can be defined:

$$C_B = \frac{n}{V} = \frac{P}{RT} \qquad \text{Eqn. 4.4}$$

Where

n = Number of gaseous moles

V = Volume (cm^3)

P = Pressure (MPa)

If we assume that at auto-ignition (at temperature T_{ig}) the conversion of reactants to products is 0, and that C_{A0} is a constant (as only a small fraction gasifies prior to ignition and we only require the lower flammability limit to be reached) then we can use equations 4.2, 4.3 and 4.4;

$$-r = Ae^{-\frac{E}{RT}} C_A \frac{P}{RT_{ig}} \qquad \text{Eqn. 4.5}$$

$$\ln -r = \ln A - \frac{E}{RT_{ig}} + \ln C_A + \ln P - \ln RT_{ig} \qquad \text{Eqn. 4.6}$$

$$\ln P = \frac{E}{RT_{ig}} + \ln RT_{ig} - \ln A + \ln(-\mathrm{r}) - \ln C_A \qquad \text{Eqn. 4.7}$$

$$\ln P = \frac{E}{RT_{ig}} + \ln \frac{RT_{ig}(-\mathrm{r})}{\mathrm{A}C_A} \qquad \text{Eqn. 4.8}$$

This can be written as

$$\ln P \approx \frac{a}{T_{ig}} + b \qquad \text{Eqn. 4.9}$$

McGuire (1993) comes to a similar conclusion, however he does so by replacing the Concentration, C_B, with a pressure term. Lewis and Von Elbe (1987) state that for many material explosions a number of experimental observations appear to agree with

$$\log P = \frac{a}{T_{ig}} + b \qquad \text{Eqn. 4.10}$$

Where a and b are constants (assuming the effect of T_{ig} on b is negligible):

$$a = \frac{E}{R} \qquad \text{Eqn. 4.11}$$

$$b = \ln \frac{RT_{ig}(-\mathrm{r})}{AC_A} \qquad \text{Eqn. 4.12}$$

The relationship derived in equation 4.9 might enable smaller scale test data to be used to predict the SIT of non-metals at far higher pressures.

A major factor hindering the prediction of ignition at higher pressures can be the presence of flame retardant materials, such as halogens, in the chemical makeup of the material. On thermal decomposition the evolved halogens form a chemical acid gas, which interferes with the combustion mechanism by trapping other radicals, interrupting the supply of energy.

4.1.2 Hydrocarbon activation energy

Equations 4.8 and 4.9 show a constant *a* defined as the combustion reaction activation energy, *E*, divided by the universal gas constant, *R*. The thermal decomposition products of polymers, shown in section 2.5.8, are generally the smaller alkane and alkene molecules. The activation energies for the combustion of hydrocarbons are shown below in Table 4-1. They have a spread from 162 to 217 kJ/mol (taken from Table 2-1 in section 2.2.2). It can be expected to see values for E/R of between approximately 19000, and 24000 K (where R = 8.314 J/ mol. K), however given the large range of hydrocarbons released by polymers by the process of thermal decomposition this may vary significantly.

Table 4-1 Selected hydrocarbon oxidation activation energy (see Table 2-1 for full details)

Hydrocarbon	*E*, kJ/mol
Methane	188^{a}
Ethane	191^{a}
Propane	162^{a}
Butane	167^{b}
Pentane	217^{b}
Hexane	212^{b}
Heptane	216^{a}
Octane	167^{a}
Cyclohexane	180^{a}

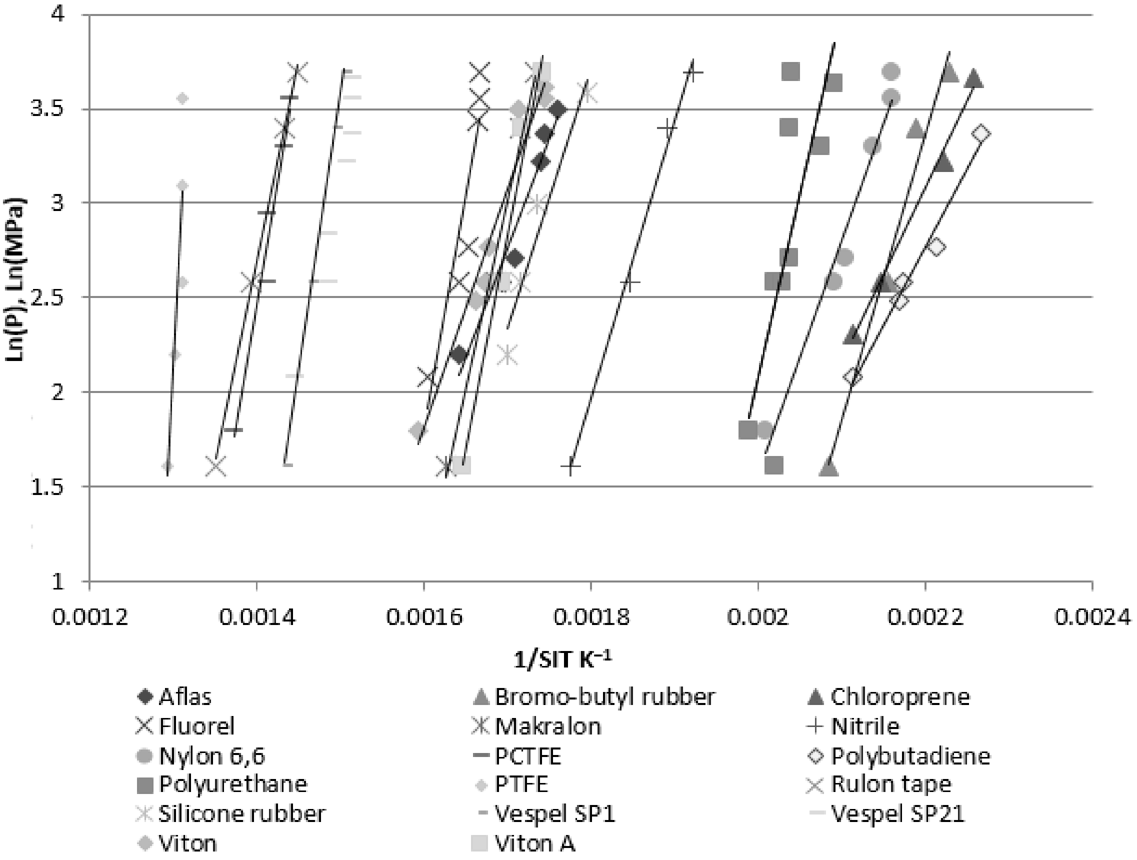
a Average of a number of values from various literature sources (see Table 2-1)
b Value from a single source only (see Table 2-1)

Studies, such as that of Vandenabeele et al (1960), have shown that these values remain relatively unaffected (within 40 kJ/ mol) by changes in concentration of reactants, temperature, or pressure.

4.1.3 Development of bomb test results

Figure 4-1 below shows the combined data from the LSBU polymer bomb tests (Obtained from Rahman and Nolan 2000 and McGuire 1993). The trend-lines on the graph show a clear relationship between the natural logarithm of the pressure and the reciprocal of the SIT for all of the materials. The gradient of the lines is extremely similar supporting the hypothesis that one relationship might be used for the calculation of a SIT of any polymer, at any pressure.

Figure 4-1 Showing the relationship between the reciprocal of the SIT, and the natural logarithm of the environmental pressure



The average gradient of all the trend lines was calculated for the combined bomb data, and was found to be 20934 K (similar to that predicted in section 4.1.2 based on the activation energy for the combustion of hydrocarbons). It may be possible to use this gradient where no real value of E/R has been obtained to give an approximation. Using this relationship, it should now be possible to predict the SIT of the materials at any pressure.

4.1.4 Calculation of SIT at a variety of pressures

The relationship derived from the rate equations and bomb data (equation 4.9) can be applied for a polymer at any pressure. Assuming the constant B is the same for each material this can be rearranged to form:

$$\ln P_1 - \ln P_2 = \frac{a}{T_{ig1}} - \frac{a}{T_{ig2}} \qquad \text{Eqn. 4.13}$$

Therefore:

$$\frac{1}{T_{ig2}} = \frac{1}{T_{ig1}} - \frac{\ln(P_1 / P_2)}{a} \qquad \text{Eqn. 4.14}$$

This equation should allow the use of 1 data set to calculate the approximate data for new conditions, resulting in eliminating the need for the intercept, *b*. Ideally the specific value for *E/R* (*a*) for that polymer should be used.

Example:
At 3.4 MPa the lowest SIT of silicone rubber 2451 was measured as 605 K in a pressurised DSC. Using this result and equation 4.14 it is possible to calculate the SIT for silicone rubber at a pressure of 13.2MPa (matching measurements carried out in the bomb test, with a value, *a*, of 12706). This calculation gives an SIT value of 568 K (295 °C). The SIT of Silicone rubber at 13.2 MPa is listed as 583 K in BS 4N-100 bomb test results from McGuire (1993).

The results in Table 4-2 and Table 4-3 compare PDSC results (see section 3.3.3), and calculated predicted results for 13.2 MPa using these, with Bomb test results at 13.2 MPa (see section 3.1.3). For both pressures, the predicted results for Aflas 100S, Polybutadiene and the 2 varieties of Silicone rubber are all between 15 and 63 K below the measured ignition temperatures. At 2.1 MPa the calculated SIT for Vespel SP21 is 5 K below the measured valued, while at 3.4 MPa the calculated value is 5K above the measured. The results for Polychloroprene, and Nylon 6,6 are well above. This may be due to a number of reasons.

Table 4-2 A Comparison of PDSC SIT values from 2.1 MPa Oxygen and Bomb test results

Material	SIT, at 2.1MPa in Oxygen		Calculated SIT, at 13.2 MPa 99.5% Oxygen		SIT, Bomb test results at 13.2 MPa 99.5% Oxygen		Difference
	K	°C	K	°C	K	°C	
Aflas 100S	628	355	571	298	591	318	-20
Polychloroprene	688	415	616	343	466	193	150
Nylon 6,6	636	363	569	296	478	205	91
Polybutadiene	436	163	397	124	460	187	-63
Silicone rubber 2451	611	338	562	289	583	310	-21
Silicone rubber S87	585	312	539	266	583	310	-44
Vespel SP21	782	509	668	395	673	400	-5

Table 4-3 A Comparison of PDSC SIT values in 3.4 MPa Oxygen and Bomb test results

Material	SIT, at 3.4MPa in Oxygen		Calculated SIT, at 13.2 MPa		SIT, Bomb test result at 13.2 MPa		Difference
	K	°C	K	°C	K	°C	
Aflas 100S	607	334	566	293	591	318	-25
Polychloroprene	626	353	580	307	466	193	114
Nylon 6,6	628	355	578	305	478	205	100
Polybutadiene	431	158	403	130	460	187	-57
Silicone rubber 2451	605	332	545	272	583	310	-38
Silicone rubber S87	578	305	568	295	583	310	-15
Vespel SP21	761	488	678	405	673	400	5

The properties of polymers can vary to a large degree, from batch to batch. Additives to alter flame retardancy, elasticity and other physical properties can impact on the ignition temperature variation. Although widely used in oxygen systems, polychloroprene rubber is one such example. Literature listed in the Wendell Hull & Associates Inc. oxygen compatibility materials database (2013) show that various samples of this materials tested using the ASTM G72 test at 10.8 MPa auto-ignited at temperatures ranging from 423K to 593K (150°C to 320°C). Nylon is known to be capable of absorbing water. How it is stored, and how long for, can dramatically affect the SIT. Results can be extremely variable (e.g. Swindells et al 1988). Variations in this data may also be explained by another factor affecting material's flammability. Swindells identified that the ignition temperature of Vespel decreased dramatically with increasing surface area, with 60mg samples being divided into 4, 8, 12 and then 16 pieces. Variation in surface area between different test methods might account for the figures being different from expected, calculated ignition temperature values.

NASA staff has tested a large number of non-metallic materials at a variety of pressures, however it is not known if the materials in the different studies are exactly the same so are not best for comparison purposes, although they may be used to show batch variation. Bryan and Lowrie (1986) tested the same materials at both 3.4, and 6.8 MPa. The results are shown below in Table 4-4.

Table 4-4 The NASA Bryan and Lowrie (1986) results of the G72 test

	SIT at 3.4MPa, K	SIT at 6.8MPa, K
Polychloroprene (Neoprene)	464	457
Polyimide (Vespel SP-21)	625	610
Fluorel A-2160	599	596
Nylon 6,6	520	475

From Bryan and Lowrie (1986)

If we apply the relationship to these results it should be possible to see if these values match the calculated values. The values measured at 3.4 MPa have been used to calculate values at 6.8 MPa using equation 4.14. The values for *a* have been taken from LSBU experimental testing. These may not be exactly the same as for the materials tested by NASA. The results are shown in Table 4-5.

The calculated SIT values for all materials are similar to those measured using the NASA G72 apparatus. The calculated results for Polychloroprene, Vespel and Fluorel are within 16 K of the measured values. The calculated result for Nylon 6,6 is 26 K from the measured value. This may be due to the fact that the ignition temperature of Nylon 6,6, can vary dramatically due to varying water content within the material. If this relationship can be used to compare SIT at different pressures, it might also be possible to use them to compare data from different experimental apparatus.

Table 4-5 Comparison of Bryan and Lowrie (1986) results with calculated SIT values

	a	Measured SIT value (6.8 MPa, 99.5% oxygen) from Bryan and Lowrie (1986), K	Calculated SIT for 6.8 MPa, 99.5% oxygen, K
Polychloroprene	9263	457	448
Vespel SP-21	8415	610	594
Fluorel E-2160	25001	596	589
Nylon 6,6	9958	475	501

4.2 Variation of polymer SIT with oxygen concentration

All of the bomb tests were conducted in 99.5% oxygen. It should be possible to calculate the SIT of the polymers in any environmental condition by calculating the oxygen concentration and using the partial pressure of the oxygen in that environment as the pressure value in the relationship.

If we take the bomb test results for Polyisoprene as an example;

At 13.2 MPa the bomb test result for Polyisoprene was 411 K. This was conducted in 99.5% oxygen, making the partial pressure of the oxygen in the bomb test environment 13.13 MPa. DSC tests carried out on the same material were conducted in air (21% oxygen) at atmospheric pressure (0.101 MPa) resulting in an ignition temperature of 458 K, making the partial pressure of the oxygen in the atmosphere 0.0213 MPa. Although the DSC used a ramp rate of 5 K/min, work by Bryan and Lowrie (1986) states that this should show essentially no variation from results obtained at the 10 K/min ramp rate used in the bomb test. Results in Wharton et al (1989) support this. If oxygen partial pressures are used in place of atmospheric pressure in equation 4.14 then the SIT values for a range of oxygen atmospheres can be calculated. In the case of this example T_{ig} at a partial pressure of 13.13 MPa was calculated as 401 K. 9 K lower than the measured value.

The results from the DSC test (see section 3.2.3) have been adapted using equation 4.14 and the environmental partial pressures, and compared with results measured in the bomb test at 13.2 MPa in 99.5% oxygen (see section 3.1.3).

Table 4-6 Comparison of DSC SIT values and Bomb test results

Material	SIT, at ambient pressure, in air		Calculated SIT, at 13.2 MPa 99.5% Oxygen		Bomb test SIT at 13.2 MPa 99.5% Oxygen		Difference
	K	°C	K	°C	K	°C	
Aflas	673[a]	400	488	215	591	318	-103
Makrolon	673[a]	400	551	278	593	320	-34
Polychloroprene	539	266	408	135	466	193	-58
Noryl	579	306	421	147	492	219	-72
Nylon 6,6	673[a]	400	468	195	478	205	-10
Polybutadiene	588	315	402	129	460	187	-58
Polyisoprene	458	185	402	129	411	138	-9
PCTFE	673[a]	400	578	305	708	435	-130
PVC	537	264	461	188	475	202	-14
Rulon	673[a]	400	559	286	718	445	-159
Silicon rubber 2451	673[a]	400	501	228	583	310	-82
Silicon rubber S87	673[a]	400	501	228	583	310	-82
Vespel SP21	673[a]	400	443	170	673	400	-200
Viton A	673[a]	400	565	292	591	318	-26

a - Difference where samples did not ignite below 673 K (400°C) under atmospheric conditions

Validation of this method proved problematic as few studies involve varying the oxygen concentration level, while some that do (e.g. 11th STP 1497 comparing 30 – 60% oxygen environments) are unreliable showing inconsistencies (even compared with their own past results), and lack of repeatability. Some work has been done by Court (2001) to compare SIT results in different oxygen concentrations.

4.2.1 Comparison due to changes in oxygen percentages

Research by Court (2001) compared the SIT of polymers with different ratios of oxygen to nitrogen at 13.2 MPa. The results are shown in Table 4-7.

Table 4-7 Comparison of SITs at different oxygen and nitrogen levels (Court 2001).

Material	SIT, K, 100% O_2	SIT, K, 60% O_2	Calculated SIT, K, 40% O_2
Bromo-butyl rubber	464	472	474
Nitrile rubber	542	558	555
Viton A	591	601	607
Makrolon	593	602	609

From the results in 100% oxygen, the SITs for 60%, and 40% oxygen were calculated, and compared with the measured values. This comparison is shown in Table 4-8. Apart from one result for Nitrile rubber in 60% oxygen, all of the calculated SITs are within 3K of the experimentally measured SITs, and most are virtually identical. These results are consistent with the $\ln P \propto 1/T_{ig}$ relationship in equation 4.14, demonstrating this can be applied to the data from the bomb tests and other oxygen auto-ignition test results.

Table 4-8 Comparison of calculated and measured SITs at different oxygen concentrations

Material	Oxygen %	SIT		Calculated SIT	
		K	°C	K	°C
Bromo-butyl rubber	100%	464	191		
	60%	472	199	469	196
	40%	474	201	474	201
Nitrile rubber	100%	542	269		
	60%	558	285	549	276
	40%	555	282	555	282
Viton A	100%	591	318		
	60%	601	328	600	327
	40%	607	334	607	334
Makrolon	100%	593	320		
	60%	602	329	602	329
	40%	609	336	609	336

4.3 Variation of polymer SIT with oxygen flow rate

All of the tests mentioned previously have been done in a static environment. Although there will be some movement in the system due to convection, they do not test the effect of a flowing oxygen stream on the SIT. An increase in oxygen flow will affect the reaction kinetics by constantly providing fresh oxygen for the reaction. However it will also affect the reaction due to the removal of volatiles, and heat, by the passing gas stream. Balendran (1999), and Wolf et al (1993) reported far higher SITs for polymers in oxygen at 0.12 MPa, flowing at 100 cm^3/min, than would have been expected in static oxygen at the same pressure. However the work in this area is very limited. Given that the static temperature appears to be lower the static SIT still operates as a good safety margin.

4.4 Effect of size (scale), and shape on polymer ignition

Swindells et al (1988) tested the effect of mass and sample size on auto- ignition. Fluorel was found to be affected to a small extent (with a variation of up to 20°C). No reliable pattern was identified for the other materials tested. Wharton et al (1989) conducted similar tests with Polychloroprene where a 60mg sample was split into varying number of pieces. Where pieces weighed between 5 and 20mg the SIT values did show some relationship but varies little (within 11 K of each other). Where pieces were greater than 20 mg there was significant drop in the measured ignition temperature.

4.5 Analysis of TD/GC results

A number of polymers were analysed using thermal desorption/ gas chromatography. The temperature heating limitation of the TD apparatus was 250°C, thus polymers with relatively low SITs were analysed. The results were examined to see if the SIT of the decomposition products could be directly linked to the SIT of the polymer. The polymers degraded to release a number of chemicals, most constituting below 5% of the products. Table 4-9 below shows the materials with 1 dominant decomposition product detected by the GC analysis, and compares the ignition temperatures of these materials, with the SIT of the polymer. Even for these 3 materials the low temperature and complex mechanisms involved mean that only 2 of the materials have substantial identified decomposition products with an SIT in air at atmospheric pressure in the region of the polymer SIT under similar conditions.

Table 4-9 Current literature decomposition results

Polymer	SIT K	Main thermal decomposition product at 523 K (250°C)	% of decomposition products	Ignition temperature K	Disparity
Butyl rubber	550	2 Methyl propane	54%	733[a]	183
PP	510	Dimethyl Heptene	35%	503[b]	-7
SBR	510	Methylcyclopentane	29%	531[c]	21

[a] Air Liquide, [b] propylene trimer : 90 – 99%, [c] NFPA

Also tested were Polychloroprene and Polyvinylchloride. The main chemicals emitted from these materials were 1,2dichloropropane, and trichlorobenzene respectively. These are well known ignition inhibitors. The results for polychloroprene and PVC were thus, not close (both over 100 K above) the measured SIT.

One of the most important factors in material flammability is the degradation temperature. For example, PTFE is known to decompose to release primarily C_2F_4, which has an auto ignition temperature of 513 K (240°C) in air. However it doesn't begin to degrade as a material until 623 K (350°C). Added to this the lower flammability limit of the gas must then be reached, raising the polymer SIT again. Polychloroprene and PVC molecules release chlorine when heated. Halogens such as chlorine and bromine are often added to other polymers as a flame-retardant and their release may be affecting the decomposition temperature, and thus, the SIT of the polymer. Other additives are likely to be affecting these temperatures too. As mentioned previously polymers are rarely comprised of just the material monomer. Although they generally have a main chemical base (of linked monomers) they will also have a variety of additives included in the mix to change the material's characteristics. Stabilisers, plasticizers, cross-linkers, surfactants and other property modifiers might all be added to a material composition. Thus there is usually a range of thermal degradation products, beyond those of just the base molecule, which can result in a completely new reaction mechanism. The new degradation products may raise the degradation temperature of the main polymer molecule (particularly halogens), and in turn the SIT of the polymer. Alternatively they may catalyse the oxidation of other degradation products, lowering the SIT of the polymer. Thus, prediction of the polymer SIT becomes far more complicated than understanding the release of degradation products from one polymer molecule.

4.6 Metals SIT relationship

The main challenge for this section of the work is to construct a relatively simple model (e.g. able to be used quickly in real life investigation situations), which is also capable of calculating metal SITs to a reasonable level of accuracy. Calculation of the SIT of metals has been attempted in the past with mixed results. Reynolds (1959) proposed a relationship:

$$e^{-1/T_{ig}} = \left(\frac{{T_{ig}}^{5}}{X}\right) + Y{T_{ig}}^{2} \qquad \text{Eqn. 4.15}$$

Where

T_{ig} = SIT

$X = \frac{A\Delta H_c}{8\sigma\varepsilon\delta\rho_{oxide}\gamma_{mo}}\left(\frac{R}{E}\right)^4$

$Y = \frac{2h\delta\rho_{oxide}\gamma_{mo}}{A\Delta H_c}\left(\frac{E}{R}\right)$

A = Arrhenius pre-exponential constant

ΔHc = Heat of combustion

σ = Stefan Boltzmann constant

ε = Emissivity

δ = Thickness of Oxide film

ρ_{oxide} = Density of Metal oxide

γ_{mo} = Ratio metal: oxide (by mass)

R = Universal Gas constant

E = Oxidation activation energy

h = Heat transfer coefficient

Metal oxidation is distinctly different from that of other materials due to the oxidation mechanism being highly dependent on the oxide layer formed at the metal's surface. It is also dependent upon the heat transfer coefficient. Although the Reynolds equation is recognised as being capable of calculating the SIT of the metals which burn homogenously with accuracy, it is far less accurate when trying to apply it to the metals that oxidise heterogeneously, through a molten oxide layer. The most reliable method of determining whether a material will burn heterogeneously or homogenously is using Glassman's burn ratio (see section 2.2.3). This incorporates not only the heat of combustion, but also the energy required to raise the temperature of the metal to its autoignition point. Such calculations would only be possible for pure metals due to the availability of data.

In a series of studies Bolobov et al (1990, 1998, and 1999) found the SITs for a number of metals and alloys. They state that generally, if there is no damage to the metal surface, the SITs practically coincide with the temperature at which the material begins to melt, and that this is independent of pressure. The findings of Abbud-Madrid et al (1993) matched these, but added a special case. They state that the SIT of aluminium is far higher than the melting point of aluminium and is instead around the temperature at which aluminium oxide melts. Bolobov (1999) found that ignition temperature of metals is independent of oxygen pressure, and shows that past work suggesting that it is dependent on oxygen pressure is down to systematic errors in measuring surface temperature.

Chapter 5

High-pressure enriched oxygen ignition mechanisms and associated models

Incidents in high pressure oxygen enriched environments can be extremely difficult to understand. The large array of components, materials and varying atmospheric properties, not to mention the high degree of damage that results from combustion in gas with a high proportion of oxygen, all contribute to the complexity.

The illustrative incidents in section 2.1 demonstrated the great variation in the information collected in investigations. Added to this, section 2.7 shows that there is no well-defined scientific process to assess or confirm the kindling chain followed by a fire within an oxygen system. The collection of oxygen system and component information is essential to be able to fully understand an oxygen incident.

Although a small catastrophic failure event, or relatively minor oxygen incident may not seem significant enough for a full scientific investigation at the time it occurs, the information on the system environment and makeup must still be collected. One reason for this is it is possible that subsequent to the initial investigation the event might need to be revisited in greater detail. For example, if further similar incidents occur investigators might need to go back through past incident reports to identify if there is a recurring problem e.g. a particular component or material use, or if there have been recurring health and safety failings. In this circumstance there might need to be extremely detailed analysis and therefore knowing information, such as material identification and thermal properties, would be absolutely necessary for thorough understanding. This would be particularly important where the possibility of a crime having been committed, such as criminal damage or criminal negligence, is explored.

This chapter will demonstrate why the collection and recording of this information is so important. It will construct a ‘tool kit’ using knowledge of ignition modes, SITs and ignition/ heat transfer models to examine the past analysis of oxygen incidents, and identify better ways to follow and understand a kindling chain.

By looking at the position of each of the system components and the thermal properties of the materials they are made of, as well as investigator’s observations, it should be possible to determine a simple understanding of the kindling chain which can then be compared with the incident investigator’s original deductions. The kindling chain event is an extraordinarily complex issue, and to completely accurately analyse it would take a considerable amount of computational power and time, not to mention a large body of research work on the behaviour of materials in this specific environment. However, this would not be suitable or feasible for every incident investigation particularly where time is a key issue. Here there is a need for a simple methodology which, while less accurate, should provide an investigator with useful approximate path information to aid their investigation and to ensure the recording of detail that would enable more thorough investigations later. Based upon this research into current incident investigations, the modes of ignition (see section 1.2), and the materials' ignition information and test data, a relatively simplistic procedure has been developed to follow, and perhaps identify, the most probable kindling chain reactions in an oxygen system incident.

For any system designer, and system user, the main aim related to fire safety is to prevent that ignition. For oxygen incident investigators, as with all fire investigation, identification of the site of ignition and identifying the material first ignited can lead to the cause of ignition, and help to prevent similar incidents occurring in future. The major modes of ignition have been discussed in section 1.2. These are:

- Pressure shock and rapid adiabatic compression
- Impact by contaminant particles
- Mechanical impact
- Friction in valves
- Cavity resonance
- Electric arcing
- Kindling chain

Using the information discussed in section 1.2, and the information on standard flammability test methods discussed in section 2.5 it should be possible to define criteria to recognise ignition events (a key part in understanding initial, and subsequent kindling chain ignitions) which should aid the modelling and prediction of oxygen incidents and scenarios. The most common causes of ignition of materials in oxygen systems are identified by Gallus and Stoltzfus (2006) as adiabatic compression and shockwave, particle impact, and onward kindling chain ignition. This work will therefore concentrate on these.

At the BOC group Ltd (Irani 2004) a simple method for determining material flammability involved using equation 2.6 (see section 2.3.2):

$$\Delta H = mc_p\Delta T \qquad \text{Eqn. 2.6}$$

Where ΔH is the total energy release, m is the material mass, c_p is the specific heat at constant pressure and ΔT is the change in system temperature. In very simplistic terms this relationship can also be applied to materials to calculate the energy required to raise a component part to its ignition temperature. However, while this simplistic steady state approach might be appropriate for smaller metal components (with relatively high thermal conductivity), for many materials in oxygen systems, such as those made of polymeric materials this is not accurate enough. The extremely low thermal conductivity of these components means that it is very unlikely that an entire component will approximate to a single temperature.

Under most ignition conditions (excluding a very gradual temperature rise of the whole system) these materials will have a significant temperature gradient. It is far more likely therefore that at a critical point (surface temperature, critical depth, ignition time, heat flux) part of that material will be ignited, causing the rapid onset of a combustion reaction in the whole component (assuming exposure to the high pressure oxygen). To fully understand the ignition, and subsequent ignitions of materials, it is therefore necessary to understand at what point, in time and temperature, these critical values are reached. It may be possible to develop a simple system incorporating the more critical factors, while still enabling a relatively simplistic approach. This would be useful, not only as a workable tool, but also because much of the data that might be required for a far more sophisticated method is not available for high pressure oxygen atmospheres.

5.1 Ignition mechanisms in high-pressure enriched oxygen environments

A high pressure enriched oxygen environment is defined by the EIGA safety information document (2008) as pressures of over 3 MPa, with a concentration of more than 23%. These high pressures are understood to affect a number of the measurable phenomena associated with ignition (McAllister et al 2010, Swindells et al 1988).

Under ‘normal’ circumstances, i.e. atmospheric pressure in air, the ignition mechanism of a solid polymer, while it may be complex, is relatively well understood. As described in section 2.2.1, heating of a hydrocarbon solid causes the material to decompose (and possibly melt) causing the release of volatiles and gases which at a key concentration will mix sufficiently with oxygen to provide the right environment for ignition to occur. With sufficient energy added to the mix this will result in a self-perpetuating oxidation reaction. This form of combustion is called homogeneous, or gas-phase, combustion. While extensive work has examined the combustion of simple hydrocarbons to better understand the behaviour and kinetics of the reactions in this unique environment (such as that by Slavinskaya 2007 [air up to 6 MPa], and Healy et al 2008 [methane/ propane/ ethane in air up to 50 MPa]) much of the research conducted on polymers in high pressure enriched-oxygen has been focused on identifying materials (Swindells et al 1988, Bryan et al 1993) that are safe to use and hazards from particular ignition mechanisms (Dees et al 1995, Hirsch et al 2003) in this challenging environment. It has not focused on the fundamentals.

Some attempts to understand the gas phase burning mechanisms of polymers and apply it mathematically to the ignition in high pressure enriched oxygen have been made by McAlevy et al (1960) and Hermance et al (1966) in shock tube conditions, however at higher pressures (above 4 MPa) the relationship starts to lose accuracy, significantly over-estimating time to ignition. The models are also relatively complex (Kashiwagi et al 1973). At higher pressures work by Shelley et al (1993) demonstrates the propensity of some engineering polymers to burn at the surface, rather than burning with a diffusion flame.

Research on the ignition of solid propellants for use in aeronautical and space applications has led to alternative ignition mechanisms being proposed (Price et al 1966). The propellants used in this work consist of a mixture of solid polymer (e.g. Polybutadiene) and a solid oxidiser embedded at their surface (e.g. Ammonium Perchlorate). This mixture is extremely vulnerable to surface oxidation (Price et al 1966), and upon addition of a strongly oxidising gas will automatically ignite, with no added external energy source required for a runaway chemical reaction to occur. This led scientists to examine reaction mechanisms where ignition occurs without the need for thermal decomposition and gasification, with the oxidation reaction starting directly at the solid surface.

The first attempt to understand this process was made by Hicks (1954) who proposed a purely solid state ignition mechanism however this was soon rejected as it did not take into account the variation of time to ignition with atmospheric oxygen concentration.

Work by a number of researchers has led to another alternative to the homogenous ignition mechanism theory. That is the heterogeneous ignition mechanism. This was originally described by Anderson et al (1963) and applied to the hypergolic situations described, where ignition of materials occurs upon the addition of an oxidising gas. Rather than ignition occurring in a thin gas layer above the surface, the proposed mechanism involves a reaction at the solid/ gas interface. On exposure to an oxidising gas, as Price et al (1966) describes, the solid oxidiser starts to degrade. This causes oxidation directly at the surface, which in turn causes the surface temperature, and thus the oxidation reaction rate, to rise, leading to runaway reaction and ignition.

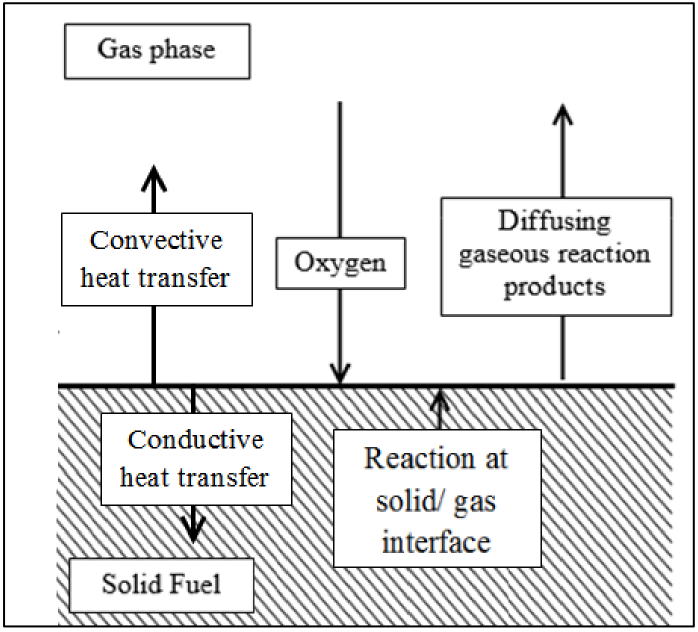
This hypergolic ignition idea has been developed by Williams (1966) and Waldman and Summerfield (1969) and adapted to the exposure of polymer surfaces to high pressure oxygen environments, under shock tube conditions, with no added external heat flux.

The Williams (1966) model assumes diffusion of high concentration, high pressure oxygen (or a gaseous oxidiser) at the solid/ condensed phase surface, causing oxidation to occur at that interface, rather than in a gas layer above the surface. A simple representation of the mechanism is shown in Figure 5.1. The rise in the oxidation reaction rate causes an exponential rise in surface temperature and ignition is judged to occur at a critical point where the interface temperature reaches the ignition temperature. Using computer modelling Williams identifies an empirical formula to represent 'most' results, without the need for the ignition temperature (see equation 5.4), and finds that where E/RT_i is greater than 30, there is less than a 20% error compared with more fully modelled results. The advantage of William's approach for oxygen environment analysis is that it incorporates a function dependent on the oxygen concentration.

Williams (1966) treats the propellant as a one dimensional time dependant system, modelled as a semi-infinite slab. Chemical heating is regarded as starting instantaneously and heat is judged to be produced only at the solid surface, being transferred outwards by conduction and natural convection. The material properties are assumed to be temperature independent, and isobaric conditions are assumed. As Harrland and Johnston (2012) note, no phase change is accounted for.

Waldman and Summerfield (1969) develop the Williams model, rightly pointing out that a hot gas will cause a change in the solid/gas interface temperature. Thus they use the pressure-dependent gas temperature value, and calculate a higher surface temperature using classical heat transfer. This makes the model applicable to environments undergoing adiabatic compression.

Figure 5-1. Heterogeneous combustion reaction mechanism proposed by Waldman & Summerfield (1969) to apply to shocktube condiitons in high pressure oxygen.



The Waldman and Summerfield model is inaccurate at pressures below 2 — 3 MPa (see section 5.2) however it does however find reasonable agreement for a number of polymers above this pressure (Kashiwagi et al 1973). Shelley et al (1993) examined the burning behaviour of 4 polymers from high flammability. HDPE, Polyimide (PI), graphite-filled PI and PTFE were attached to the base of aluminium rods and ignited using a fuse in between 3MPa – 69MPa 100% oxygen. Shelley et al found that the HDPE burned entirely with a diffusion flame, while the other less flammable polymers had some (or in the case of PTFE complete) surface burning characteristics. This supports the idea that in high pressure enriched oxygen environments some engineering polymers may burn partially, or completely, heterogeneously. This makes the significance of the surface temperature even greater.

5.2 Time to ignition models for piloted and auto-ignition

A number of models have been developed for the analysis and calculation of time to ignition in air under a range of circumstances for non-metals.

Many models have concentrated on piloted ignition (generally with an electrical spark igniter). For example Mikkola and Wichman (1989) propose a relationship between time to ignition in seconds, t_{ig}, and the heat flux in kW/m^2, q:

$$\sqrt{\frac{1}{t_{ig}}} \propto q \qquad \text{Eqn. 5.1}$$

and North (1999), referred to in Babrauskas (2003), suggests a similar relationship based around

$$t_{ig} \propto \frac{\rho}{q^2} \qquad \text{Eqn. 5.2}$$

will provide an approximation of the time to piloted ignition. However Babrauskas (2003) states that although typical errors are approximately 20%, errors can be as much as 200% with this method. Janssens et al (2003) describe a number of the relationships in relation to time delay and thermal depth for materials ignited in a piloted ignition process, and Mowrer (2003) summarises and compares a number of commonly used analytical relationships (including those by Quintiere 1990, Delichtasios et al 1991, and Tewarson et al 2000) to numerical results for piloted ignition, finding the relationship proposed by Tewarson et al to be the most accurate. Mowrer (2003) does identify some overestimation of times, but states this become less significant with increasing heat flux, and is still the most pessimistic model, which in terms of safety will be the most suitable.

Shi and Chew (2013) unusually conducted experiments to measure time to ignition under autoignition circumstances testing 6 polymers; 3 thermosets, and 3 thermoplastics. Their autoignition results fit the relationship in equation 5.48 best. This is especially true for samples of 20mm thickness or less, where an approximation can be made:

$$t_{ig} \approx 151\frac{\rho}{q^2} \qquad \text{Eqn. 5.3}$$

Although this carries an average error of 32%, this becomes less significant with increasing heat flux (as ignition times decrease). For a heat flux of 75 kW/m^2 the average error is approximately 6 seconds (28%), compared with 22 seconds (36%) for test data for 50 kW/ m^2.

Although these models allow some approximation of times they do all carry inherent error, but there is a far more problematic issue when adapting them for oxygen systems. That is the very limited amount of work in enriched or high pressure oxygen environments, and the identification of the effect of oxygen pressure and concentration on time to ignition of these materials. McAllister et al (2010) looked at the effect of reducing the air pressure below ambient, and compares air with Oxygen/ Nitrogen mixtures (21%, and 30% oxygen) up to 120 kPa (0.036 MPa partial pressure). Kashiwagi and Ohlemiller (1982) explored the effect of oxygen concentration (0 – 40%)

at 1 atm (a maximum oxygen partial pressure of 0.041MPa), and identified a distinct increase in mass flux at higher concentrations of oxygen, and for Polyethylene (the only samples to ignite) a reduction in ignition time with increasing oxygen concentration. However without testing in 100% oxygen, and at much higher pressures with comparable heat flux exposures, it is impossible to use, or apply, this accurately.

However, the time to ignition of polymers in high pressure enriched oxygen has been examined under adiabatic compression/ shock conditions. A number of researchers have explored the possibility of the use of solid polymers as propellants for aeronautical applications. Shock tube experiments were conducted exploring the ignition of those materials in high pressure enriched and heated oxygen environments, both theoretically and experimentally. A range of relationships based around gas phase (McAlevy et al 1960, Hermance et al 1966, Price et al 1966) and heterogeneous (Anderson et al 1963, Williams 1966, Waldman and Summerfield 1969, Price et al 1966) ignition modes have been explored mathematically.

Kashiwagi et al (1973) conducted a serious of shock tube experiments to identify ignition time delay involving polymers including polyurethane and polybutadiene, both alone and combined with an additional oxidising agent. The materials were tested in high pressure oxygen with partial pressures ranging from around 10 to 47atm, with the partial pressure of oxygen being controlled by both varying the concentration and the overall pressure. Kashiwagi et al (1973) found general agreement between their results for Butarez (Polybutadiene) and both the gas-phase and heterogeneous models although at higher pressures (above 25 atmospheres) results were closer to the heterogeneous example shown by Waldman and Summerfield (1969), and the addition of an additional solid oxidiser at the surface has little effect.

The Williams (1966) model (described in more detail in section 5.1) proposes that where a forced external heat flux q is small the ignition delay, t_{ig}, can be calculated using the ambient temperature of the solid mass, and current temperature of the surrounding gas, T_0 and T_g respectively, the thermal inertia (also called the thermal effusivity) of the oxidising gas and fuel, I_g, and I_A, respectively, and the heat produced by any oxidation written:

$$t_{ig} = \frac{\pi}{4}\left(T_0 - T_g\right)^2 \left[I_g^{\frac{1}{2}} + I_A^{\frac{1}{2}}\right]^2 \left(\Delta H_c\, A C_B{}^n e^{-\frac{E}{RT}} + q\right) \qquad \text{Eqn. 5.4}$$

Where

C_B = Oxygen concentration

n = Reaction order

Waldman & Summerfield (1969) apply this relationship to shock tube autoignition by adapting the temperature rise due to adiabatic compression/ shockwave heating, T_r, (shown equation 5.5) as the Temperature, T. As under shock tube conditions the rise in gas pressure will cause the 'interface temperature' to jump rapidly, basing the shift on classical heat conduction theory.

$$t_{ig} = \frac{\pi}{4}(T_0 - T_r)^2 \left[I_g^{\frac{1}{2}} + I_A^{\frac{1}{2}}\right]^2 (\Delta H_c \, A C_B{}^n e^{-\frac{E}{RT}} + q) \qquad \text{Eqn. 5.5}$$

Data from work by Kashiwagi et al (1973) have been taken here and compared with results from the heterogeneous model proposed by Waldman & Summerfield (1969) at 1800K, for Polyethylene and Polyurethane. The graphs in figure 5.2 and 5.3 show that the model is relatively accurate above 3 MPa for this temperature, and a range of oxygen concentration.

Figure 5-2 Time to ignition data for Polyurethane from Kashiwagi et al (1973) compared to the Waldman & Summerfield (1969) model

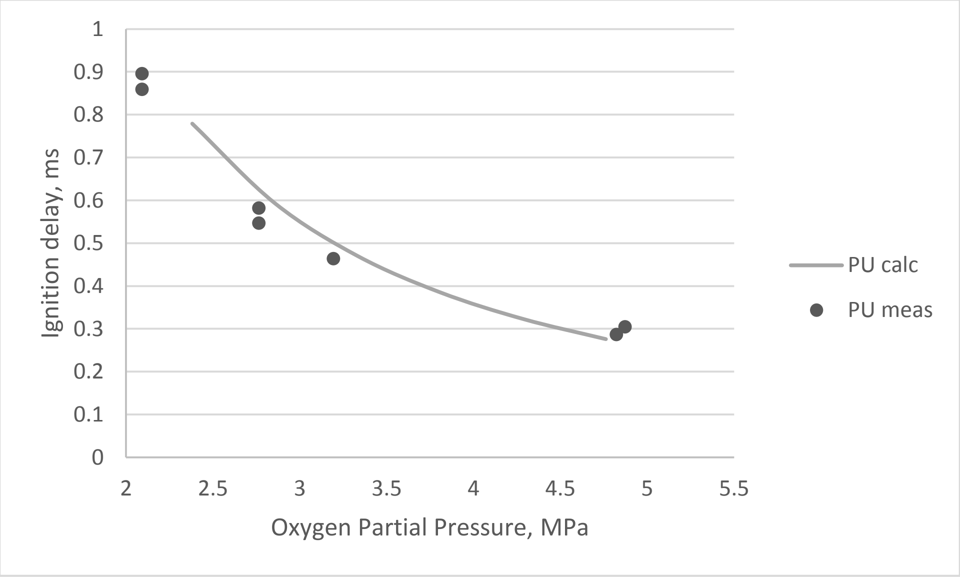
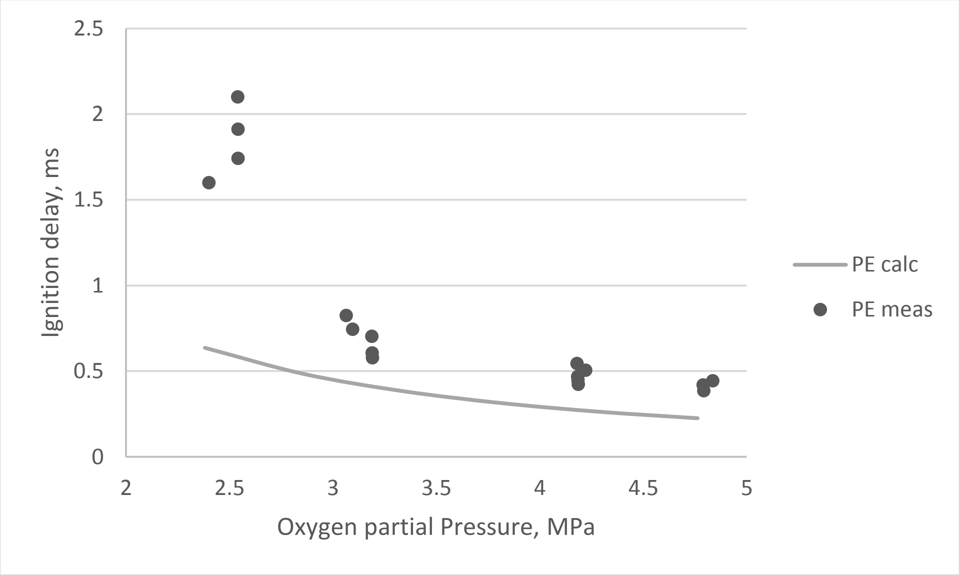


Figure 5-3 Time to ignition data for Polyethylene from Kashiwagi et al (1973) compared to the Waldman & Summerfield (1969) model



It should be noted that these tests were done with Nitrogen as the diluent gas. The effect of changing diluent gases has been explored by Wurmel et al (2007) and Shen et al (2008) who show ignition delay for Iso-Octane are shorter in oxygen/ Argon mixes, than Oxygen/ Nitrogen mixtures, by 20 – 40%). Kashiwagi et al (1973) also explored the difference between dry and wet surface propellants (i.e. those that melt on heating, and those that don’t) and finds that in high pressure enriched oxygen there is no discernible difference in behaviour between these 2 groups.

It might therefore be reasonable to assume we can apply this model across a range of polymers and circumstances, however the model does not seem produce consistent results at other gas temperatures. So while the model at 1800 K might be used as a good guide, it is far from a useful too. Instead a better way to estimate the minimum time to ignition might be to use surface temperature and heat transfer rates.

5.3 Simple heat transfer models for application to oxygen systems

In a system, materials will always tend towards thermal equilibrium. Depending on the media within that system the transfer of heat can occur by three modes; Conduction, convection and radiation. While conduction occurs within a solid, or between a series of adjacent solid materials, convection occurs in fluids (including gases) and radiation to a surface. When analysing heat transfer in any complex system with different states of matter, materials, and geometries, understanding the component interaction and heat transfer between components is extremely important. However, the complexity can result in expensive, time consuming and unworkable methods for real-life application.

When discussing heat transfer, items can be divided into two categories; ‘thermally thick’ and ‘thermally thin’ (Tewarson et al 2000). Thermally thin materials are regarded as being so thin that heat will be absorbed extremely quickly, meaning there is no significant gradient through the material. This classification is generally determined using the Biot number, Bi, a dimensionless constant which is essentially a ratio between convective and conductive properties. It is calculated by,

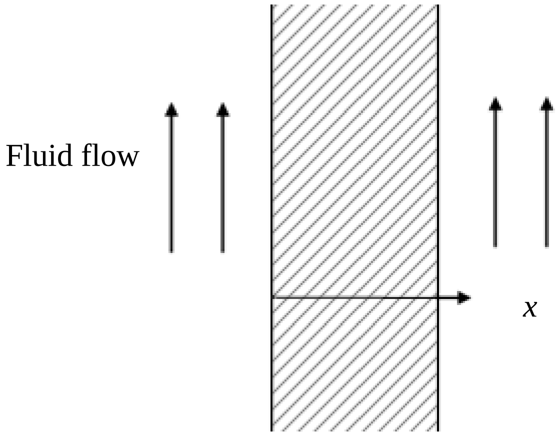
$$Bi = \frac{hL}{k} \qquad \text{Eqn. 5.6}$$

where h is the heat transfer coefficient (W/m^{2}K), L is the characteristic length (generally defined as volume divided by surface area), and k is the thermal conductivity of the body. As a general rule items that have a Biot number above 0.1 are regarded as thermally thick (Janna 1986). Given their thermal conductivity, metal components, particularly smaller items, can be regarded as thermally thin as the temperature gradient will not be significant. Therefore for these materials a simple ‘BOC-style’ steady state approximation (see section 2.3.2) might be made. For polymers Tewarson et al (2000) demonstrated the thermally thick nature of materials with a thickness of at least 4mm or more, and Delichtasios (2000) states that thermally thick behaviour is generally the case for materials with a thickness of 1mm or more. Given their use and hence their thickness, it seems unlikely that many polymeric components will behave as thermally thin materials. Therefore for polymers this work will concentrate on analysis of thermally thick materials. This classification is particularly important when creating a simple model to approximate a system because it enables identification of the heat transfer mode(s) that has/have the most impact. For thermally thick materials it is accepted (Drysdale 2011, Mowrer 2003) that the thermal inertia governs temperature rise in the material.

The following derivation is adapted from Kreyszig (1983).

If we assume for a homogenous material that heat transfer is controlled primarily by conduction, we can model a simple situation where surface resistance can be considered to be negligible. The temperature, T, might then be calculated at a given depth, L, into a material of thickness, x, and at a time, t. If we consider a semi-infinite (thermally thick) solid plate of thickness 2L:

Figure 5-4 Illustration of heated fluid flow across a solid plane



$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha}\frac{\partial T}{\partial t}$$ Eqn. 5.7

With boundary conditions (B.C.):

B.C.1: $x = 0$ $T = T_{1,}$ B.C.2: $x = 2L$ $T = T_1$

Initial Conditions (I.C): $t = 0$ $T = T_i$

and where α is the solid material thermal diffusivity.

In order to make the equation dimensionless we define the variables:

$$\Theta = \frac{T - T_1}{T_i - T_1}$$ Eqn. 5.8

$$\xi = \frac{x}{L}$$ Eqn. 5.9

$$\tau = \frac{t}{t_r}$$ Eqn. 5.10

Thus

$$\frac{\partial^2 \Theta}{\partial \xi^2} = \frac{L^2}{\alpha t_r}\frac{\partial \Theta}{\partial \tau}$$ Eqn. 5.11

With boundary conditions (B.C.):

B.C.1: $\xi = 0$ $\Theta = 0$ B.C.2: $\xi = 2$ $\Theta = 0$

Initial Conditions (I.C): $\tau = 0$ $\Theta = 1$

Using the separation of variables (product method) from Kreyszig (1983) section 11.3, p507-509 we can assume

$$\Theta(\xi, \tau) = F(\xi)G(\tau)$$ Eqn. 5.12

Thus

$$\frac{\partial^2\Theta}{\partial\xi^2} = F''(\xi)G(\tau)$$ Eqn. 5.13

$$\frac{\partial\Theta}{\partial\tau} = F(\xi)G'(\tau)$$ Eqn. 5.14

Hence

$$F''(\xi)G(\tau) = \frac{1}{\mu^2}.F(\xi)G'(\tau)$$ Eqn. 5.15

where the Fourier number is represented for convenience as c^2:

$$\mu^2 = \frac{\alpha t_r}{L^2}$$ Eqn. 5.16

Equation 5.15 can be rearranged, and it can be assumed that both sides are equal to a separation constant $-\lambda^2$

$$\frac{F''(\xi)}{F(\xi)} = \frac{1}{c^2}\frac{G'(\tau)}{G(\tau)} = -\lambda^2$$ Eqn. 5.17

Thus

$$F''(\xi) + F(\xi)\lambda^2 = 0$$ Eqn. 5.18

and

$$G'(\tau) + \mu^2\lambda^2 G(\tau) = 0$$ Eqn. 5.19

Using the general solution for separated variables (Kreyszig 1983 section 11.3, p509) we find;

$$F(\xi) = A\cos\lambda\xi + B\sin\lambda\xi$$ Eqn. 5.20

And using the general solution to homogenous first order differential equation (Kreyszig 1983, section 1.7, p28, equations 1-3):

$$G(\tau) = De^{-\mu^2\lambda^2\tau}$$ Eqn. 5.21

To satisfy BC1

$$F(0) = A\cos\lambda\xi + B\sin\lambda\xi$$ Eqn. 5.22

$$\therefore A = 0$$ Eqn. 5.23

and

$$F(\xi) = B\sin\lambda\xi$$ Eqn. 5.24

To satisfy BC2

$$F(2) = B \sin 2\lambda = 0 \qquad \text{Eqn. 5.25}$$

$$B \neq 0 \qquad \text{Eqn. 5.26}$$

otherwise solution is trivial.

$$\therefore \sin 2\lambda = 0 \qquad \text{Eqn. 5.27}$$

$$2\lambda = 0, \pi, 2\pi, \ldots. \qquad \text{Eqn. 5.28}$$

$$\lambda = \frac{n\pi}{2} \qquad \text{Eqn. 5.29}$$

Recombine separated variable solutions, substituting equations 5.21 and 5.24 into 5.12.

$$\Theta(\xi, \tau) = B \sin \frac{n\pi\xi}{2} \, De^{-\mu^2\lambda^2\tau} \qquad \text{Eqn. 5.30}$$

Combination of the constants *B* and *D* into an overall constant *J* results:

$$\Theta(\xi, \tau) = J \sin \frac{n\pi\xi}{2} \, e^{-\mu^2\lambda^2\tau} \qquad \text{Eqn. 5.31}$$

For linear homogenous Partial Differential Equations (Kreyszig 1983 p58, example 1):

$$\Theta(\xi, \tau) = N_1 \Theta_1 + N_2 \Theta_2 \qquad \text{Eqn. 5.32}$$

So

$$\Theta(\xi, \tau) = \sum_{n=1}^{\infty} J_n \sin \frac{n\pi\xi}{2} e^{-\mu^2\lambda^2\tau} \qquad \text{Eqn. 5.33}$$

At τ=0, $e^{-\mu^2\lambda^2\tau} = 1$. Thus

$$\Theta(\xi, 0) = \sum_{n=1}^{\infty} J_n \sin \frac{n\pi\xi}{2} \qquad \text{Eqn. 5.34}$$

This can be solved using a Fourier sine series half range expansion (Kreyszig 1983 section 10.5, p479-480). Let $\Theta(\xi, 0) = f(\xi)$

$$f(\xi) = \sum_{n=1}^{\infty} J_n \sin\frac{n\pi\xi}{K} \qquad \text{Eqn. 5.35}$$

Where the coefficient is

$$J_n = \frac{2}{K}\int_0^K f(\xi)\sin\frac{n\pi\xi}{K}d\xi \qquad \text{Eqn. 5.36}$$

And where

$$0 \leq \xi \leq 2$$

Where the upper boundary limit *K* is equal to 2.

$$J_n = \int_0^2 f(\xi)\sin\frac{n\pi\xi}{2}d\xi \qquad \text{Eqn. 5.37}$$

At τ = 0 (initial conditions)

$$\mathrm{f(\xi)} = \Theta = \frac{T_i - T_1}{T_i - T_1} = 1 \qquad \text{Eqn. 5.38}$$

Thus

$$J_n = \int_0^2 \sin\frac{n\pi\xi}{2}d\xi \qquad \text{Eqn. 5.39}$$

Let

$$u = \frac{n\pi\xi}{2} \qquad \text{Eqn. 5.40}$$

Thus

$$\frac{du}{d\xi} = \frac{n\pi}{2} \qquad \text{Eqn. 5.41}$$

Where $\xi = 0, u = 0$ and $\xi = 2, u = n\pi$

$$\begin{aligned} J_n &= \int_0^{n\pi} \frac{2}{n\pi}\sin \mathrm{u}\, du = \frac{2}{n\pi}[-\cos u]_0^{n\pi} \qquad \text{Eqn. 5.42} \\ &= \frac{2}{n\pi}[(-\cos n\pi) - (-cos\ 0)] \\ &= \frac{2}{n\pi}[(\cos 0 - \cos n\pi)] \end{aligned}$$

Where $n = 1{,}3{,}5\ldots$

$$J_n = \frac{2}{n\pi}[(1 — 1)] = \frac{4}{n\pi} \qquad \text{Eqn. 5.43}$$

Where $n = 2{,}4{,}6\ldots$

$$J_n = \frac{2}{n\pi}[(1-1)] = 0$$ Eqn. 5.44

Substituting 5.43 into equation 5.34 gives,

$$\Theta(\xi,0) = \sum_{n=1}^{\infty} \frac{4}{n\pi} \sin\frac{n\pi\xi}{2}$$ Eqn. 5.45

$$n = 1,3,5\ldots$$

Inserting 5.45 into equation 5.33

$$\Theta(\xi,\tau) = \sum_{n=1}^{\infty} \frac{4}{n\pi} \sin\frac{n\pi\xi}{2} e^{-\mu^2\lambda^2\tau}$$ Eqn. 5.46

$$n = 1,3,5\ldots$$

From equations 5.16 and 5.29

$$\mu^2\lambda^2 = (\frac{n\pi}{2L})^2 \alpha t_r$$ Eqn. 5.47

Thus

$$\Theta(\xi,\tau) = \sum_{n=1}^{\infty} \frac{4}{n\pi} \sin\frac{n\pi\xi}{2} e^{-(\frac{n\pi}{2L})^2 \alpha t_r \tau}$$ Eqn. 5.48

$$n = 1,3,5\ldots$$

Using equations 5.9 and 5.10,

$$\frac{T - T_1}{T_i - T_1} = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} e^{-(\frac{n\pi}{2L})^2 \alpha t} \sin\frac{n\pi x}{2L}$$ Eqn. 5.49

$$n = 1,3,5\ldots$$

Where x has a value of L (i.e. the mid plane of the plate)

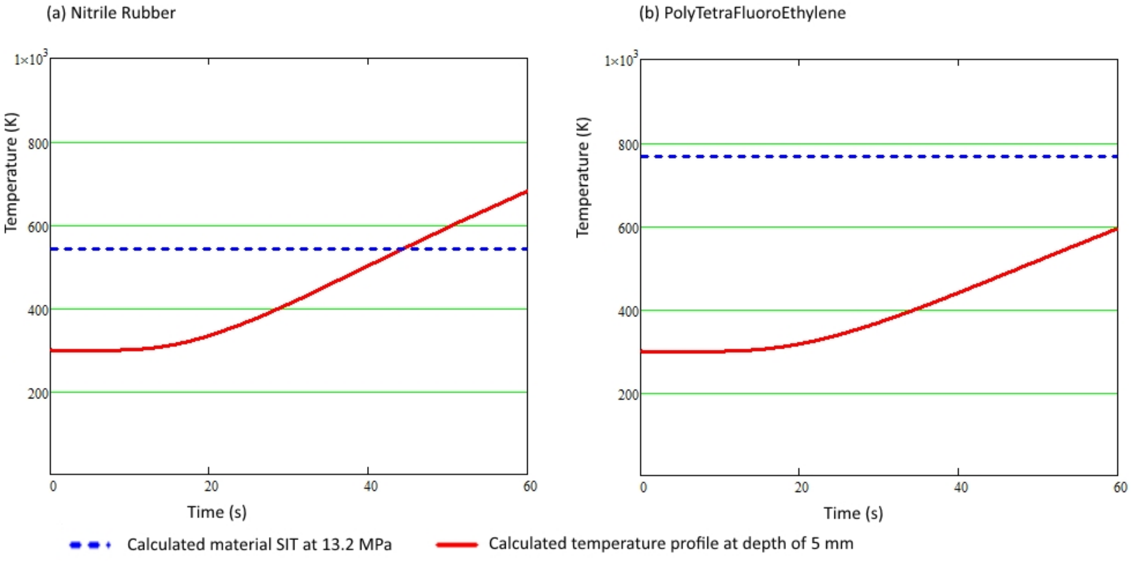
$$\frac{T(L,t) - T_1}{T_i - T_1} = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} e^{-(\frac{n\pi}{2L})^2 \alpha t} \sin\frac{n\pi}{2}$$ Eqn. 5.50

$$n = 1,3,5\ldots$$

The final version of this relationship, equation 5.50, is given in Janna (1986). Although very approximate, with knowledge of the materials involved and their thermal properties, this relationship can be used to model the temperature change within a material over time and distance. The model can be used to look at a constant surface temperature, for example Figure 5-5 shows the temperature profile at a specified time through both a Nitrile rubber plate, and a PTFE plate, with a constant surface temperature of 1500 K. The dotted lines represent the SIT temperature at 13.2 MPa. It would be extremely useful to look at individual components in oxygen systems to understand the effect the heat transfer has on the ignition point, but also how the heat transfer to other surfaces will affect possible ignition of other materials.

The temperature profiles in Figure 5-5 show the temperature at a depth of 5 mm through two polymeric plates. While the temperature rise in Nitrile rubber is faster than in the PTFE the graph shows that a far more significant factor is the much lower SIT of Nitrile rubber. This is so low that the temperature profile crosses the line for the ignition temperature at 44.5 s, while for the PTFE material the autoignition line is not reached across the 60 s period. All of this analysis is thoroughly dependent on being able to identify the polymeric materials used, and also knowing the thermal properties of those materials (as these can vary from batch to batch). Ideally samples of any remaining debris or unused samples of the same type from the scene should be collected so that this can be ascertained as accurately as possible if required.

Figure 5-5 Graphs showing the use of the negligible surface resistance equation to predict the temperature rise at 5mm depth of polymeric oxygen components with a surface temperature of 1500 K.



The other advantage of using the simple heat transfer method over more complex models is that similar relationships for other geometries (e.g. cylinders) have been developed and are shown in Heisler charts, such as those shown by Janna (1986) enabling investigators without access to complex mathematical programs to work out approximate temperature changes in objects.

The model can also be used for a system where there is a rising surface temperature due to an applied heat flux. This could be done either by modelling the surface temperature rise as a simple linear function of time, but can be done more accurately using the external heat flux in the relationship reported by Beaulieu (2005) using Lawson and Simms (1952):

$$T_s = T_0 + \frac{2q}{\sqrt{\pi}}\sqrt{\frac{t}{k\rho c_p}} \qquad \text{Eqn. 5.51}$$

where

T_0 = Initial temperature

q = Heat flux

t = Time

k = Solid material thermal conductivity

ρ = Solid material density

cp = Solid material specific heat

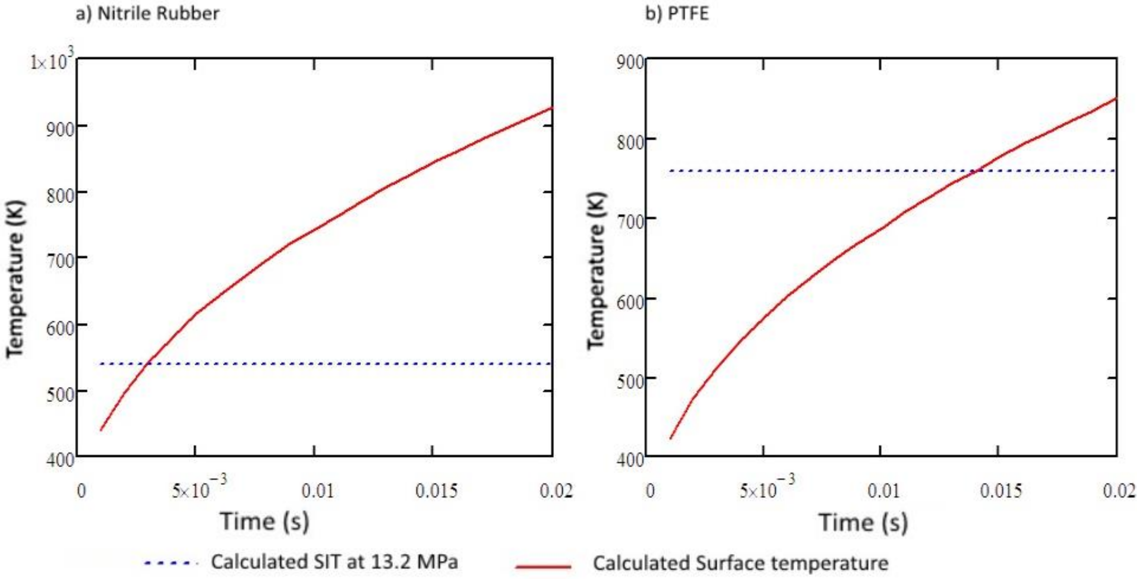
Then T_s, found in equation 5.51, can be inserted into T_1 of equation 5.50. The Lawson and Simms model is recommended for use for a number of reasons (Ashe & Rew 2003) the primary being that while being relatively accurate, it is conservative with respect to the data for both long and short term heat flux exposures. This is very similar to a relationship derived by Mikkola & Wichman (1989), except a net heat flux figure is used for q, taking into account heat loss, as opposed to the applied heat flux used by Lawson and Simms. Section 5.4.3 shows an example of how this might be used to predict onward kindling chain ignition.

The convective heat flux is calculated using the convective heat transfer coefficient, h (a constant relating to the gas medium and nature of the convection, be it free or forced), the surface area, S_A, and the difference in gas and solid temperatures, T_g and T_s respectively:

$$q = hS_A(T_g - T_s) \qquad \text{Eqn. 5.52}$$

For example, in an environment where the gas temperature reached 12000 K (based on the estimations in Newton and Steinberg 2009), if we assume that the heat transfer coefficient is 250 W/m^2 K, the highest possible for a gas undergoing free convection (Zhu et al 1988, Lin 2007) then the surface of a PTFE component sitting at 298 K might be expected to reach the SIT at 13.2 MPa (approximately 760K) after only 14ms (see Figure 5-6 below), while a Nitrile rubber surface is calculated to reach the SIT (approximately 540 K at 13.2 MPa) at 3ms. This difference would vastly affect the likelihood of ignition, especially under adiabatic/ shockwave ignition conditions where, as work by Newton (2011) has demonstrated, high temperatures are expected to remain for only a few milliseconds.

Figure 5-6 Graphs showing the use of the negligible surface resistance equation to predict the surface temperature rise of polymeric oxygen components in a gas temperature of 12000 K.



If greater accuracy is preferential, where the Biot number has been calculated exactly and lies between 0.1 and 40 specific Heisler charts exist for a range of Biot numbers, and geometries. However it is reported (Thirumaleshwar 2006) that the use of these is most useful in situations where the Fourier number is greater than 0.2, where error is reported to be 2% at most.

This method of approximation is pessimistic as it assumes that the conductive forces, not convection or radiation are the primary influence on the heat transfer through a material and may therefore underestimate the possible time to ignition.

5.4 Analysis of the major ignition modes in oxygen system incidents

According to Gallus and Stoltzfus (2006) the most common modes of initial ignition are judged to be adiabatic compression/ shockwave and particle impact, which appears to agree with the causes identified in Bradley and Baxter (2002). This section will show

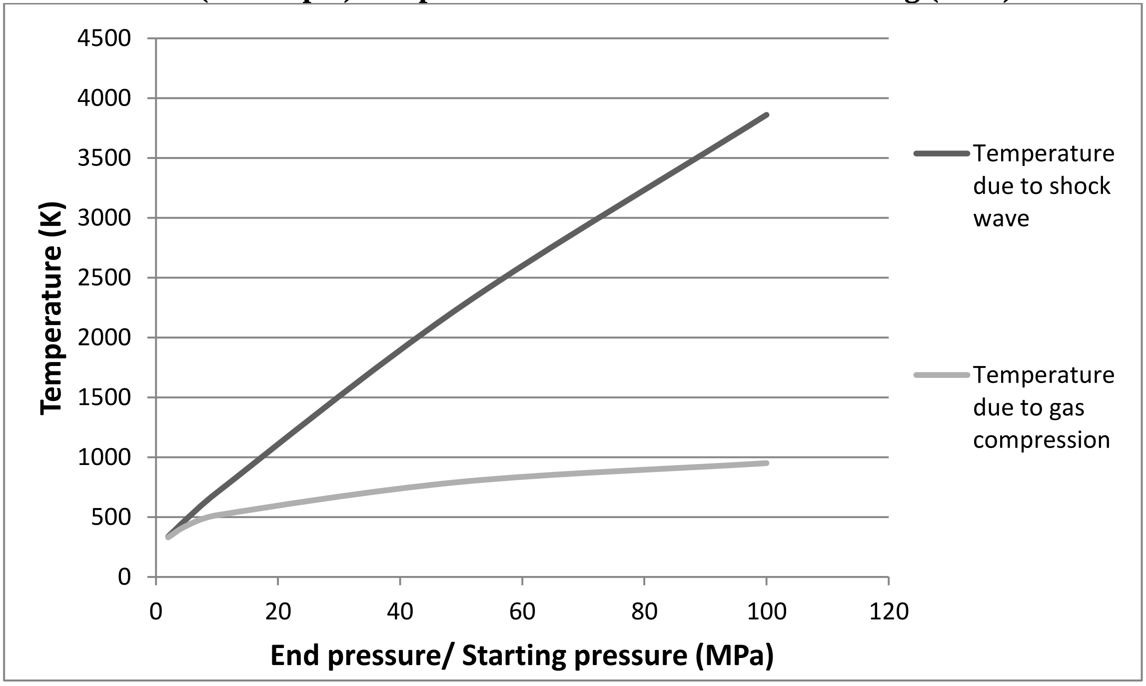
how, where information of system dimensions and chemicals has been collected, the models in chapter 4 and section 5.1 can be applied to illustrate these ignition sources in an investigation setting.

5.4.1 Adiabatic compression and shockwave ignitions

Where a fast opening valve is opened and allows a high velocity stream of oxygen to travel through an oxygen a shockwave may be formed. The valve opening can result in a series of compression waves (Newton and Steinberg 2009). As each rise in pressure raises the temperature of the gas stream the speed of sound for the following wave increases. As these compression waves coalesce a shockwave forms. A shockwave is a very small region of gas where the density and temperature increase dramatically. Where the shockwave is reflected, such as in a system with a dead-ended tube, increased compression of the gas causes a further rapid increase in the temperature. The resulting high gas temperatures may be capable of heating surrounding engineering materials.

Newton and Steinberg (2009) calculate the possible temperature rises due to shockwaves and adiabatic (or to be correct isentropic) compression (shown in Figure 5-7). Some effort has also been made by Newton and Steinberg to calculate these more accurately for specific environmental starting conditions, but are not applicable across multiple systems.

Figure 5-7 A graph showing the calculated system temperatures due to shockwave and adiabatic (isentropic) compression from Newton and Steinberg (2009)

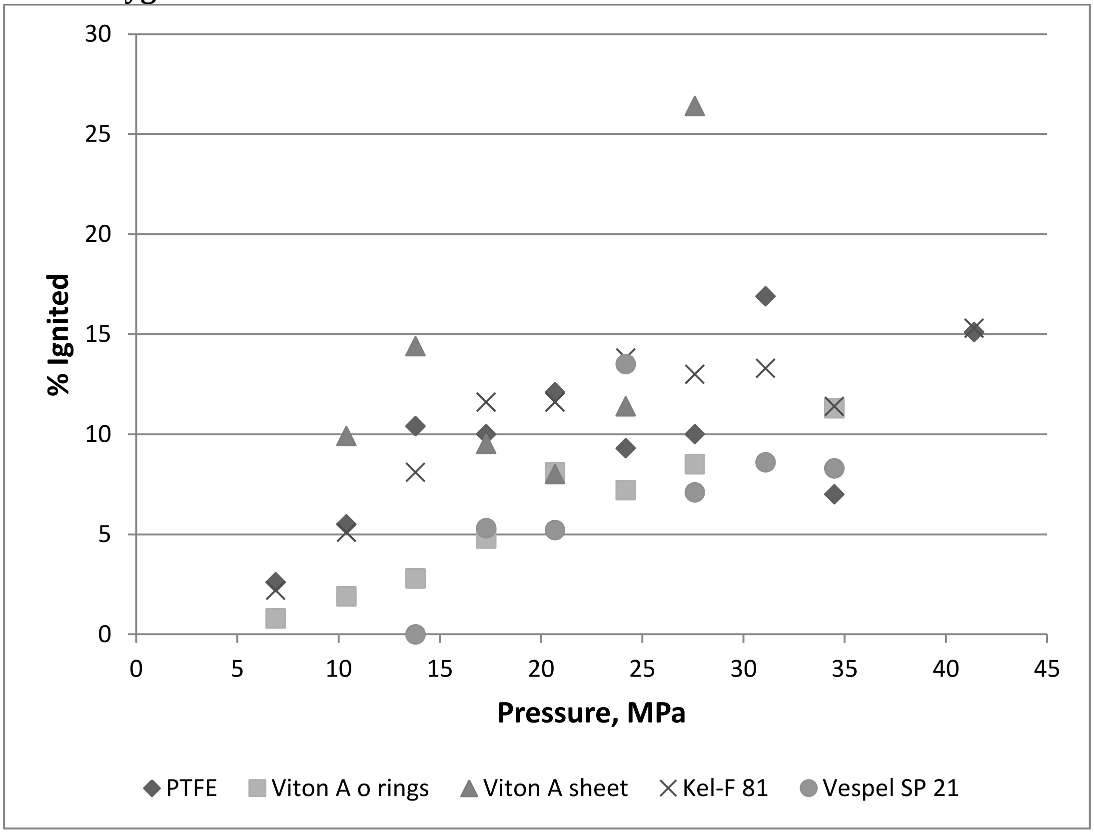


This could be used in 2 ways. Firstly, it can be used to identify if the environment has reached a temperature above the SIT of materials used as part of that system. We can use SITs of non-metals as a bench mark of ignition likelihood. In fact autoignition data represents a worst case scenario in terms of the temperature exposure of the material as SITs are measured at a comparably large volume, with a relatively low mass and high surface area to mass ratio. Also the ramp heating occurs relatively slowly. For this reason the SIT can be taken as a lower safety bound for this section of the analysis. In industry the SIT has been used as a lower safety boundary (BS 4N 100 – 6 1999) and a measure of whether ignition will occur (Stoltzfus et al 2012). This therefore this seems an ideal application for the calculated SITs obtained using equation 4.14, enabling fast calculation of a lower safety limit for a specific set of environmental conditions.

Secondly, it can be used to calculate the effective heat flux, which can be inserted into the negligible surface resistance heat transfer model described in section 5.3. It seems reasonable to assume a constant surface temperature i.e. negligible surface resistance may be applied. This is generally defined by a Biot number of greater than 40 (Janna 1986) however shockwave heating may well negate this requirement due to the extreme turbulent disruption of the boundary layer. As the gas environment can be extremely hot this may be an example of forced ignition meaning higher possible heat transfer coefficients (Glassman and Yetter 2008b), but with no pilot flame present (no chain branching and lack of radicals)

Another method that could be explored, particularly for the use of fault tree analysis (see section 6.1.2), is a probabilistic method. However the difficulty of this is that to predict or describe this fully a very large number of tests need to be carried out which would be expensive and time consuming. Hirsch et al (2003) compiled pneumatic impact test data for a range of engineering polymers, calculating the percentage of ignitions at different test pressures. Figure 5-8 shows the 5 most complete of their datasets. Although the number of different batches tested at each pressure does vary (from 4 to 51) there are no fewer than 54 separate tests conducted for each result, with the average number of samples tested at each pressure being 213. Due to the variation it is not possible from this data to discern any useful pattern in relation to probabilistic prediction of ignition.

Figure 5-8 A graph showing data from Hirsch et al (2003) depicting the percentage of polymeric test samples ignited by pneumatic impact at different pressures in 100% oxygen.



5.4.2 Particle impact ignitions

Although systems are generally designed to reduce any particulate contamination, particle impact still represents a significant cause of oxygen incidents. Metal filters, and non-return valves (particularly from cylinders), are used to reduce the chance of particle impingement. Nevertheless contamination from external areas, and particles created internally from part wear or shearing can still occur. The danger is greater in faster gas streams. According to Forsyth (2012) 45 m/s is required for particles to ignite, however Stoltzfus and Rosales (2010) state that a particle impact situation is regarded to be possible at gas speeds of over 30m/s where an impact point ranges from 45° to perpendicular to the gas stream path. Additionally Williams et al (1988) demonstrate that particles themselves can ignite at far lower velocities, and these might then move through a system to ignite other materials in a promoted ignition combustion event.

There are a number of factors that contribute to this mode as a source of ignition. Firstly as a particle impacts on a site kinetic energy can be transferred to heat via vibration. In a simplistic way where a small particle is impacting on a far larger body the maximum possible energy transferred can be calculated using equation 1.2,

$$E = \frac{1}{2}mv^2$$ Eqn. 1.2

However it is also possible, particularly for organic materials, the particle itself will ignite. Thus the calculation of heat release by the particle must be considered, calculated by:

$$\Delta H = m\Delta H_c$$ Eqn. 2.5

Added to this friction from the side walls on the particle as it is propelled through the system may cause the particle to be heated when it impacts, and the fast gas stream may cause adiabatic or shockwave heating of the surfaces, again increasing the energy at the point of impact and thus the likelihood of ignition. Crofton and Petersen (2010) also identified substantial fragmentation of particles on impact. This reduction of the materials to finer powder might make it more likely to ignite due to the increase in surface area to volume ratio.

Benz et al (1986) compares the possible kinetic energy of particle to the total heat of combustion for aluminium and 304 stainless steel particles and shows that the maximum possible kinetic energy is dramatically lower than the maximum possible heat of combustion (for example for a 1600 µm aluminium particle the possible kinetic energy on impact was calculated to be 0.49 J [at approximately 409 m/s], while the heat of combustion is calculated to be 176 J). Benz et al (1986) do go on to state that there was no evidence the stainless steel particles had actually ignited. Thus knowing the possible particle material is key to fully understanding the mode of ignition.

The approximate maximum downstream velocity, v_d, that can be produced by a pressure differential between an upstream pressure, P_u, and a downstream pressure, P_d, with a downstream temperature of T_d (Kelvin) can be estimated using the equation ASTM G88-05 (2005) (see equation 5.53 below). However, this is only accurate below Mach 0.7 (Perry and Chilton 1973) due to shockwave interference (under choke flow conditions) and is therefore primarily used to demonstrate that at relatively small pressure differentials the minimum gas velocity required for ignition by particle impact, 30-45m/s (Stoltzfus and Rosales 2010, Forsyth 2012), can be attained.

$$v_d = \sqrt{\left[2g_c\gamma_{cp}RT_d\left(\left(\frac{P_u}{P_d}\right)^{\frac{1}{\gamma_{cp}}} - 1\right)\right]}$$ Eqn. 5.53

where

g_c = Constant 1 kg m/N s^2

R = Specific gas constant 260 N m kg^{-1} K^{-1}

γ_{cp} is a constant related to the ratio of specific heats and has a value of 3.5.

Polymers are generally more flammable than the majority of metals and alloys and tend to have a far lower density. Dees et al (1995) conducted tests using a number of engineering polymers (Teflon, Kel-F, Vespel SP-21, and Viton A) as projectile particles (0.25-2 mm), fired towards a stainless steel target. A system pressure of approximately 27.6 MPa was used, but the target temperatures were only increased to 93°C (366 K). Dees et al (1995) show that under these conditions none of the particles cause the ignition of the stainless steel surface, however given the relatively low flammability of stainless steel at this temperature (Stoltzfus et al 1988) and the relatively low density and heat of combustion of polymers this is not surprising. Unfortunately without data at higher target temperatures it impossible to quantify the risk of ignition from polymeric contamination.

Forsyth et al (2000) explored polymers as the target for metal particles. Teflon, PEEK, Kel-F and Vespel SP-1 are exposed to pressures up to 27.5 MPa, with 2mm Aluminium 2017 particles being projected at them, the results of which can be seen in table 5.1. Forsyth et al (2000) also refer to work by Williams and Linley (1985) using particles made from AR-7, which Calle et al (2002) describe as an aluminium filled nitrile rubber matrix. The target temperatures at ignition for the polymer/ metal blend are clearly lower than for the aluminium particle (although it is unclear what mass particles were used in this study). The information in table 5.1 demonstrates how much changing a particle material can change the ease with which a target can be ignited.

Table 5-1 A table showing the temperature at which polymer target ignited when impacted with particles from Forsyth et al (2000)

Target material	2mm aluminium 2017 particle, K	AR-7 Aluminium filled Nitrile rubber, K
Teflon	478	384
PEEK	268	N/A
Kel-F	423	325
Vespel SP-1	393	N/A

As the size and chemical make-up of the particle, and the material at the impact site will influence these to a great degree the identification of these materials is extremely useful, or perhaps even crucial for full evaluation of a catastrophic failure situation.

Obviously identification of the particle material may be difficult however a full system examination may identify areas of damage/ shearing the particle could have originated from, or identify other particles that may give an indication of the particle involved in the impact of the material.

While it is possible to calculate, or at least approximate the energy transfer, or heat release involved in these ignition processes, understanding how that then translates into the ignition of a material is a more complex subject. The same can be said for understanding subsequent kindling chain ignitions. To follow these processes it is necessary to understand the heat transfer to, through and from the material involved, and the point at which this translates into material ignition.

5.4.3 Kindling chain ignitions

Following initial ignitions there may be further materials ignited, referred to as kindling chain ignition. Two things must be considered when gauging the possibility of a kindling chain ignition. Firstly the energy release (perhaps as adiabatic flame temperature, or heat flux) from the initial ignition and secondly the ignition likelihood of the other system components related to their flammability under those conditions and their position in the system. The overall energy release, ΔH, of the material first ignited can be simply calculated using the material mass, m in grams, and the heat of combustion, ΔH_c, in kJ/g, as shown in equation 2.5,

$$\Delta H = m\Delta H_c \qquad \text{Eqn. 2.5}$$

Under high pressure enriched oxygen conditions the rate of reaction will increase, causing faster energy release, thus when smaller components burn it may be simplest to consider the overall energy release from the combustion as being instantaneous, with an infinite heat flux and immediate transfer to other components. For situations where larger material combust, as the energy release will not occur as quickly, the adiabatic flame temperature might be used to estimate the heat flux other materials are exposed to. However there are problems associated with the adiabatic flame temperature, which is a maximum possible temperature, rather than a probable flame temperature (Babrauskas 2015). Beaulieu (2005) reports that for a number of materials, such as PMMA, the adiabatic flame temperature for enriched oxygen will be approximately 100K higher than that in 20.9% oxygen, but was shown to be as high as 500K for a variety of polyoxymethylene. Some materials have been burned in pure oxygen and where data is available it would be best to know the exact adiabatic flame temperature, however, in the absence of data in oxygen it may be necessary to assume a flame temperature of 100K greater than that in air where the exact value is not known.

Work relating to piloted ignition and promoted ignition combustion testing shows how materials might behave if exposed to burning materials in an oxygen system. Hshieh and Beeson (1995) reported that the critical heat flux (minimum heat flux received at a material surface required for ignition) is relatively unchanged from 15% to 30% oxygen at 1 atmosphere, however, as with time-to-ignition calculations discussed in section 5.2, studies have not explored high-pressure enriched-oxygen systems in enough detail to provide the information to calculate time-to-ignition under piloted ignition conditions. However, in terms of assessing onward kindling chain this might be a useful measure in the absence of more information, particularly where the melting of metals is concerned.

McIlroy et al (1988) use a system of promoted ignition that provides approximately 42 kJ. The result for these tests, and similar can be seen in Table 2-6. The test reveals the exemption pressure of the metal tested, i.e. the pressure at which the ignition system failed to ignite test samples. Although this test does give a good indication of safe working pressures, they are specific to the ignition energy, and sample configuration (generally a 0.32 cm diameter rod) used. It is possible that a higher energy source could cause the ignition of materials at a lower pressure (or equally a lower energy source at a higher pressure). Also a higher surface area to mass ratio can affect the exemption pressure (see section 5.4.4).

However, by estimating the heat flux produced by the first material in a kindling chain and using equations 5.50 and 5.51 it would be possible to estimate the time that the surface would take to reach the SIT of that material under those circumstances, and thus give an indication of time to ignition. Thus the simple heat transfer method in section 5.3 can be used to give greater detail about the possible kindling chain.

5.4.4 Other factors involved in the ignition of materials in oxygen systems

There are a number of factors that seriously affect the likelihood of ignition that must be kept in mind while trying to assess the initial cause of ignition in an oxygen system.

Firstly the presence of any foreign material lining or caught in parts of the system may increase the chance of an ignition. This is particularly true if the system is contaminated with even very small amounts of non-oxygen use greases. Under investigation circumstances greases might be detected in other, undamaged, areas of the system. Additionally the burn residue may indicate a foreign substance, however, this relies on swab or other samples being collected.

Secondly the presence of filters, particularly the sintered variety, although present to reduce ignition problems by preventing particles from entering a system, may cause an increased probability of ignition. By their very nature they lie directly in the gas stream, and are designed to catch flammable material. They are therefore vulnerable to particle impact ignition. Added to this it has been shown by Schadler and Stoltzfus (1993) that sintered materials can have a far lower extinguishing pressure than the bulk metals variety, e.g. a sintered Monel 400 filter has an extinguishing pressure of 0.69 MPa, compared with over 68.9 MPa for the bulk metal. Metal powder is well known to have far lower ignition temperatures than bulk metals, due to the increased surface area to mass ratio (Gordon et al 1968, Schadler and Stoltzfus 1993). Sintered filters are made by melting powders together in an inert atmosphere to form a solid matrix. However it is not known how this phenomena affects all sintered metals. Little work has been done to assess the flammability of these materials beyond identifying material affected the least by the change in configuration (tin-bronze according to work by Schadler and Stoltzfus (1993) comparing it to Monel and stainless steel 316). Thus ignition at a sintered filter, as the first system material to be ignited, should not be automatically ruled out just because the component is made of metal.

Thirdly there may be a combination of factors involved, for example the temperature caused by a shockwave may not be great enough to cause ignition of a polymeric or metallic component, but by raising the surface temperature the probability of ignition by other causes, such as impacting particles is increased (see section 5.4.2).

5.4.5 Use of road maps for the investigation of oxygen incidents

The use of a structure, such as road maps or checklists can significantly improve task success. Van Klei et al (2012) reported the introduction of checklists for use in surgical operating theatres has resulted in a significant drop in mortality. A road map is a structured process to achieve a prescribed goal, or decide on a course. Road maps have been used for a number of years to detail strategies or paths to achieve goals in technical areas such as nuclear safety engineering (Kempsell et al 2001). Stephenson (2003) reports road maps have also been employed to combine computer technology with traditional investigative methods to investigate digital incidents/ crimes and Mansi (2012) proposed their use to guide general fire investigators at scenes. Mansi (2012) produced over 200 Fire Investigation Road Maps (FIRMs) to enable a structured way to assess each scene, and to make sure that no possible fire cause could be missed. They take the form of flow diagrams containing boxes that represent actions, decisions to be made, and conclusions that can be drawn.

While excellent for training purposes it seems unrealistic that every fire investigator attending a scene very soon after the fire, generally with extremely little information on the nature of the fire, would be carrying a 150 page volume (although the use of technology in future e.g. an app on a tablet computer makes this more feasible). However, in insurance or Health & Safety Executive investigations it is far more likely that more specific information on the fire/ explosion would have been given, e.g. an oxygen cylinder has exploded during charging. Under these circumstances having a few road maps to analyse the likelihood of each possible ignition source is a far more realistic strategy. They provide a series of logical steps, each assessing the factors that might contribute to ignition. These are ideal for ignition assessment of oxygen incidents to quickly focus investigation to relevant areas, and therefore reduce time and resource use.

Having established a series of tools that can be used to analyse an oxygen incident the following chapter will demonstrate the use of this ‘tool kit’ to gain the maximum information following such an event.

Chapter 6
Application of data and models to 'real world' situations and the development of an oxygen incident investigation 'toolkit'

This section will be looking at 'real life' incidents, i.e. actual configurations of materials in oxygen systems that have ignited in the past and how relationships, data and knowledge discussed in this thesis on SITs, heat transfer, and collection of information can be effectively incorporated into oxygen system incident investigation.

Although some level of assumption or educated guesswork might still be necessary in the absence of all necessary information, these processes should aid in turning the incident investigation into one based more in scientific reasoning, and to make certain that relevant information is collected should even greater depth investigation be required at a later date. It should also provide greater insight into possible incidents of the future, the importance of material selection, and why knowledge of the physical and thermal properties of the materials involved is also so important.

6.1.1 Investigation aims and objectives

Internationally these are subjective. Occupational health and safety organisations around the world define their aims in different ways (UK HSE hsg245 2004, US department Occupational Health and Safety Administration accident/ incident investigation 1989, Canadian centre for occupational health and safety accident investigation 2006), however, they do share the primary aims. The main aims of any incident investigation will be to:

1) Identify the reasons for an incident, both immediate and underlying
2) Identify the remedies

While blame, cost (or compensation) or compliance with regulations and the law may also be involved, these are the 2 main purposes of an investigation. By looking at a number of investigations into oxygen incidents from public and private organisations, a number of objectives have been formulated in this work to enable effective information collection and analysis.

The objectives identified in this work to aid the scientific analysis of oxygen system incidents:

1) Examination and documentation of the system. This should include system schematic and detailed descriptions of individual components including as much information as possible, such as dimensions, masses, and materials, as well as the

environmental conditions like oxygen concentration and pressure. Ideally photos or diagrams with scale should also be present.

2) Determination of the SIT of component parts. The SIT of each of the non-metal components can be calculated based upon material, oxygen concentration, and environmental pressure (see Chapter 4). For metal components the melting temperature may be used, as described in section 4.5, excepting Aluminium materials where the melting temperature of aluminium oxide is used.
3) Identification of possible ignition modes using information on the system layout and components, the damage, and the flow direction (appreciating back flow may have occurred in some circumstances). A road map approach may aid in this (see section 5.4.5)
4) Identification of the possible or most likely seat(s) of ignition, i.e. First item in kindling chain by understanding the possible ignition modes and examination of the damage from the incident.
5) Calculate energy release of first material in chain, and determine subsequent possible ignition points.
6) Construct a likely kindling chain order, and determine the events leading to the fire or catastrophic failure incident.
7) Determine the immediate and underlying causes for the event, such as use of inappropriate materials or components, poor instructions of use, poor cleaning or maintenance, etc. A fault tree is one method to identify events that lead to a catastrophic failure event (see section 6.1.2)
8) Make recommendations to prevent the incident happening again.

6.1.2 Use of fault trees for the investigation of oxygen incidents

The use of fault tree analysis and similar techniques has been a staple of the incident investigation in the process industry for a number of decades (Mannan 2005) and are recommended for use by and by the NFPA 921 (2014) for investigation of fire incidents. They show events (including decisions made) that must occur for a top incident (generally in investigative terms an undesirable incident) to result using a series of ‘And’ and ‘Or’ gates (BS EN 61025 2007). It is qualitative, but can also be quantitative if the probability of an event occurring is known or can be identified. The advantage with oxygen incidents, as in most cases, is to represent all the stages of an incident, and to break down each stage into the contributory factors. NFPA 921 (2014) states that knowledge of the system components, their relationship to each other and understanding the validity of any data is necessary to carry out this form of analysis. This is therefore an ideal way to check that all possibilities are being considered, and that information is fully recorded should the incident, however minor, need to be revisited. For example, if on identification that a particular component was the first to ignite, identifying all the factors that contributed to its ignition would be a useful way to fully assess all of the issues or errors that might have been taken into account or might in future be improved upon, e.g. was the material being used in an area that was too hot (i.e. above its SIT), or was it in a position in the system that contributed to the ignition source. While Fault Tree Analysis has been applied to oxygen systems (Santay 1989), the focus has been mechanical, while detailing of the thermal and chemical processes, as well as the human decision making, and the recording of all this information in a fault tree (especially in combination with a checklist) allows a full analysis resulting in a better understanding of the event, and a firm record of all the necessary information for future review or analysis.

6.1.3 Examples of an application to a real world situation

The following section will demonstrate the use of the relationships established in Chapter 4 and sections 5.1and 5.4 and investigation tools for the purposes of deeper understanding of an incident, and recording of all necessary information. The following information on an incident has been obtained from an in-depth incident component examination report carried out by the Health and Safety Laboratory (Geary 2007a). The in-depth investigation was requested as this was the fourth in a series of similar incidents to occur. Where information has not been provided a likely value has been assigned, and is labelled as such.

Incident Introduction

In February 2007 a PTFE lined oxygen supply hose attached to a cylinder ignited and failed during recharging at Mansfield Mines Rescue Service. There was extensive damage to the hose, as well as evidence of heat damage and fusion to the internal components of an attached bleed valve.

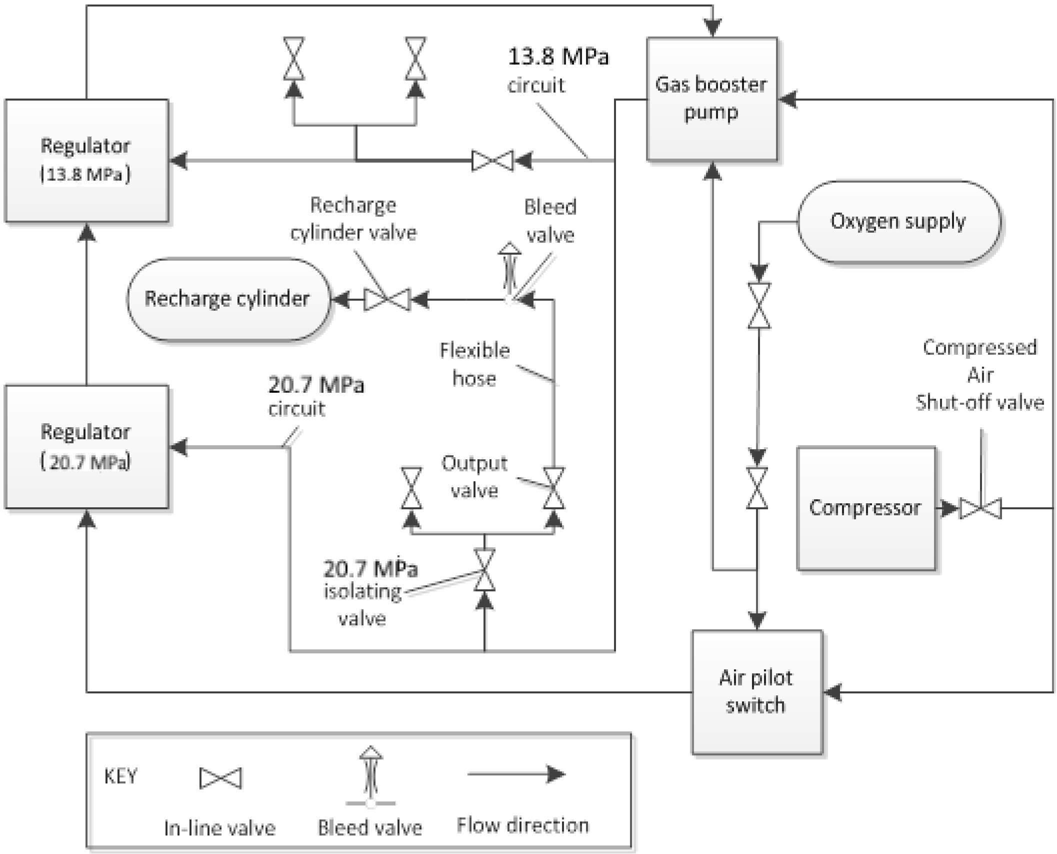
Several cylinders needed recharging. Following the successful filling of three cylinders, the process of filling a fourth cylinder, a 2 litre BG4 cylinder, was begun. Following the opening of the output stop valve, but prior to the opening of the recharge cylinder valve the operator noticed that the flexible hose between the two was glowing. This was very quickly followed by the hose rupturing. The oxygen supply was isolated, and the fire extinguished.

Although a series of pressure step rises are written into the charging procedure the step rises were only implemented for the first cylinder being charged. Thus the hose and other components supplying oxygen to any subsequent cylinders were exposed to the full charging pressure, 20.7 MPa.

System

The system was located in Mansfield Mines Rescue Service, and is for recharging high oxygen cylinders at high pressure. The system is capable of recharging using a 2000 psi loop (13.8 MPa) and a 3000 psi loop (20.7 MPa). The layout of the full system is shown in Figure 6-1. Although the whole system was examined, the region of most interest, where the catastrophic failure occurred, is the area between the 3000 psi circuit isolating valve and the recharge cylinder.

Figure 6-1 System schematic showing the components and oxygen flow during recharging of a cylinder which resulted in catastrophic failure



Filling procedure

- Open oxygen supply cylinder valve
- Switch on compressor
- Open 3000 psi isolating valve

- Connect recharging cylinder
- Open output stop valve
- Open recharge cylinder valve
- Allow booster to operate and maximum pressure to be generated (by opening compressed air shut off)
- Allow recharge cylinder to fill
- Close cylinder valve
- Close output valve
- Close air supply shutoff valve
- Bleed off hose at bleed valve
- Disconnect recharge cylinder

(If further cylinders require refilling return to “connect recharging cylinder” step and repeat steps from there. If no further cylinders require filling, continue with points below.)

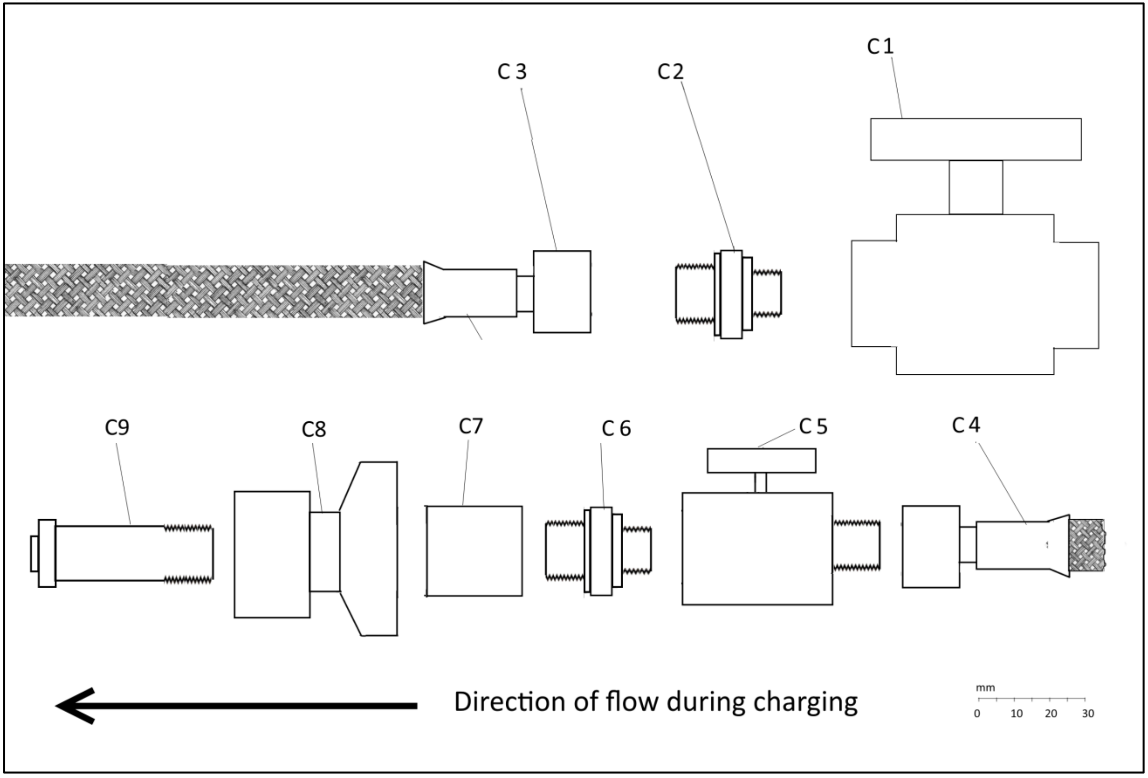
- Attach cylinder hose to docking point
- Switch off compressor and open drain valve
- Close oxygen supply valves
- Close compressor drain valves, bleed valves and isolating valves.

This filling procedure had previously been identified by Geary (2006) as good practice due to the gradual rise in pressure in the system, however, investigators ascertained that in reality the full three-stage pressurisation process (with the full 3000 psi (20.7 MPa) booster pressure being applied after the cylinder pressures) was only followed by operators for the first cylinder being filled. For subsequent cylinders the hose could go from ambient pressure (having been bled) to being subjected to the full booster pressure of 20.7 MPa.

System components

All of the system components were examined by investigators, however, most did not display anything unusual or any indications they may have contributed to the incident, other than by providing the high pressure oxygen. This report section will therefore primarily concentrate on the components between the system output valve and the cylinder valve, as these display damage or soot depositions (see Figure 6-2) and are judged to have been directly involved in the incident.

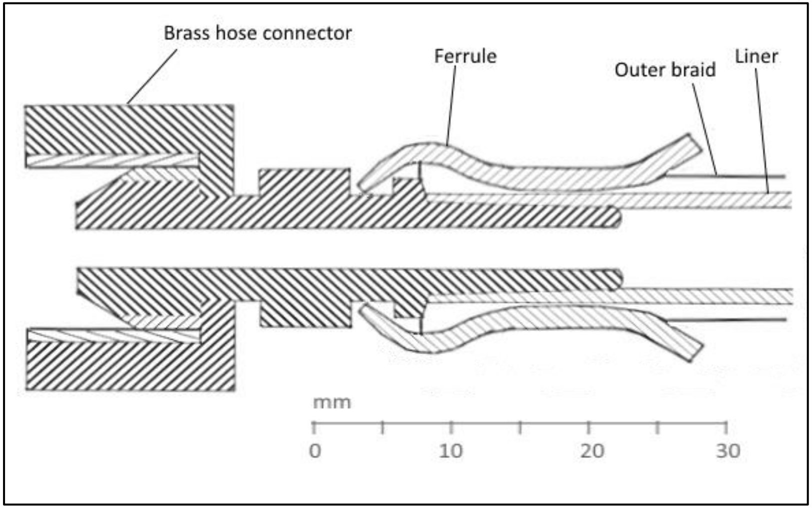
Figure 6-2 3000 psi cylinder charging bleed valve and connector arrangement



Component C1 represents the output stop valve in Figure 6-2. This valve is capable of fast opening and allows the 20.7 MPa filling. It consists of a cube shaped chamber with 2 ports made from a copper alloy. C2 is a connector piece. These were in good condition following the incident with no damage or soot.

Components C3 and C4 (see Figure 6-3) are the metallic ends of the flexible PTFE lined hose which burst in the incident, each with some of the hose still attached (180mm and 10mm respectively).

Figure 6-3 The hose connection and crimped end that failed in the oxygen incident

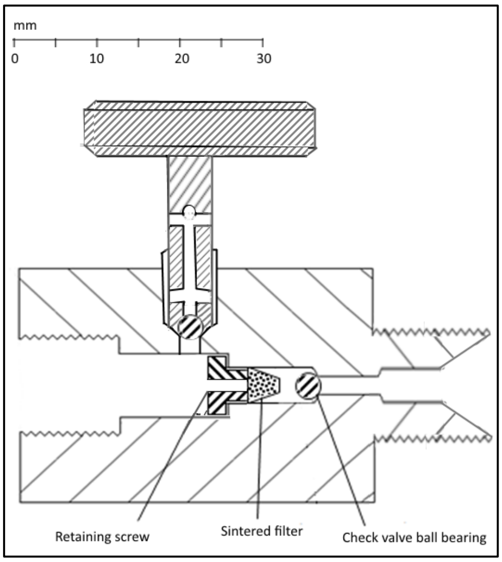


The hose ends were made of leaded 60/40 brass, while the outer braid sheathing (external diameter, 11 mm) and ferrules connecting the hose to the end piece were made from 314 stainless steel. The inner lining of the hose was made of PTFE (external diameter, 8.42-8.51 mm, thickness, 0.957-0.999 mm). At the system pressure of 20.7 MPa the SIT of PTFE has been calculated to be approximately 760 K, while the stainless steel and brass materials have melting points (used as a likely SIT value) of 1783K and 1173K respectively, but extinguishing pressures of 6.9 and 68.9MPa respectively. The original hose was approximately 630mm including the fittings.

The hose showed evidence of 2 failure events. Firstly the hose tube liner and braiding had split and broken off approximately 10 mm from the hose connector piece at the bleed valve end. The lack of combustion evidence suggests this was an overpressure issue. Further along the tube there were a number of areas that showed evidence of melting and incomplete combustion of the stainless steel braiding. A significant amount of the PTFE had burned away. Where the tube liner was still in place, the liner showed evidence of internal thinning to an average thickness of 0.43 mm.

C5 is the oxygen supply hose bleed valve unit. A diagram of this component, including the internal parts, can be seen in Figure 6-4. There is a central bore running through the main valve body, in which there is a small ball bearing (which acts a check valve, preventing gas from the cylinder moving past this point), a sintered filter to prevent particles from travelling into the system, and a retaining screw with a hollow bore through the centre.

Figure 6-4 Aluminium bronze bleed valve diagram (perpendicular to bleed valve shaft)



The main valve body is made of aluminium bronze. Although the likely ignition temperature of the bulk material is over 2000K (over the melting temperature of Aluminium Oxide) this is not regarded as being suitable for high pressure enriched oxygen service as ignition occurs at pressure as low as 3.5 MPa. The internal component parts in the direct gas stream are made of bronze (most likely tin bronze from debris analysis). Tin Bronze has a melting temperature of approximately 1127 K and an extinguishing pressure of at least 68.9 MPa, although small components have a higher surface area to mass ratio making the materials more prone to ignition (Tin bronze sintered filters have been shown in limited test runs by Schadler and Stoltzfus (1993) to ignite at 37.9 MPa).

There is also a bore at right angles with the main central bore. This contains a metal shaft which can be screwed in and out using the wheel at the top. At the base of the shaft is another ball bearing. This section of the component acts as the bleed valve for the charging hose.

Table 6-1 The component parts of a bleed valve involved in a catastrophic failure event in 2007

Component part	Dimensions	Mass	Approx. SIT
Valve body (Al Bronze)	5.7mm long (4.3mm body)	Approx. 200-250g	2072
Retaining screw (314 Stainless steel)	7mm diameter Approx. 5mm length	Approx. 5g	1783
Sintered filter (Tin bronze)	Approx. 4.4 mm	Approx. 1g	1127 (powdered bronze SIT = 655K)
Check valve ball bearing (Tin bronze)	3.2 mm diameter	Approx. 1g	1127
Bleed valve shaft (314 Stainless steel)	Approx. 5mm diameter	Approx. 4g	1783
Bleed valve ball bearing (Tin bronze)	3.2 mm	Approx. 1g	1127

The damage in the bleed valve was contained in the main central bore. The retaining screw was undamaged however the sintered filter had broken into pieces and showed signs of oxidation. There was some of the check valve ball bearing left behind, although the mass of debris has not been defined. The shaft and ball bearing in the bleed valve mechanism had not been damaged, but were covered in soot.

Components C6 to C9 are various detachable connector pieces which allow the valve to be connected to the cylinder valve. It is not clear why so many connector pieces were required. Reports by Geary (2006) and Geary (2007b) suggest the same arrangement was not being used in systems in similar facilities. It is possible they were used to convert different threads. They are undamaged by the fire, however soot deposits in the tubes reveal that gas flowed in the direction of the cylinder from the bleed valve.

Ignition modes

The lack of electrical, fast moving parts or rubbing parts next to the areas of damage means that electrical, mechanical impact and frictional heating can be dismissed as probable cause of ignition. For cavity resonance to occur the main requirement is an area of stagnation (such as a dead ended off shoot from the system) where contaminants might accumulate. Although the system does contain a T junction with such a stagnation point, this is beyond the region that was pressurised (i.e. the wrong side of the cylinder valve) and does not show any evidence of heat damage or soot. Thus cavity resonance can also be dismissed as a likely possible cause of ignition. This leaves the most common cause of oxygen incidents, adiabatic heating and shockwave ignition, and particle impact ignition.

Particle Impact

Based on information throughout this thesis Figure 6-5 has been developed to show the steps that need to be confirmed for particle impact to be considered as a possible cause of ignition. Using Figure 6-5 the following facts have been compiled:

- The pressure the system was exposed to has been identified by investigators as 20.7 MPa pure oxygen which is well in excess of the 23.5% and 3 MPa requirements for the system to be regarded as high pressure enriched oxygen.

- The output stop valve has been identified as being fast opening (hence the immediate exposure to the gas pressurised to 20.7 MPa). Assuming the pressure in the hose was 0.101 MPa the possible gas velocity can be estimated, using equation 5.53 from ASTM G88-05 (2005), as being over 1300 m/s (assuming isentropic flow). Although this is speed is well above the maximum speed of

Mach 0.7, the criteria for applicability of this equation (Perry and Chilton 1973), it is a good indication that the flow speed would be very fast, and well above the 45m/s required for particle impact ignition. Both of these points show that fast fluid flow was possible.

- Some hydrocarbon contamination on the outside of the hose was identified by investigators but there was no organic contamination inside the pipe. Only a very small amount of inorganic dirt was identified using swabs in the output valve. The presence of a check valve and sintered filter to prevent contamination by larger particles from recharging cylinders suggests that this type of contamination, though not impossible, would be unlikely.
- The hose used for recharging was flexible meaning it is possible for the hose to have presented a face to the onward flow for a particle impact situation to be possible. Also the check valve ball bearing was directly in the main gas stream with the sintered filter immediately behind it. All three of these items showed a significant level of damage.

Although it is not possible to completely rule it out the lack of serious particulate contamination identified in the system makes particle impact unlikely.

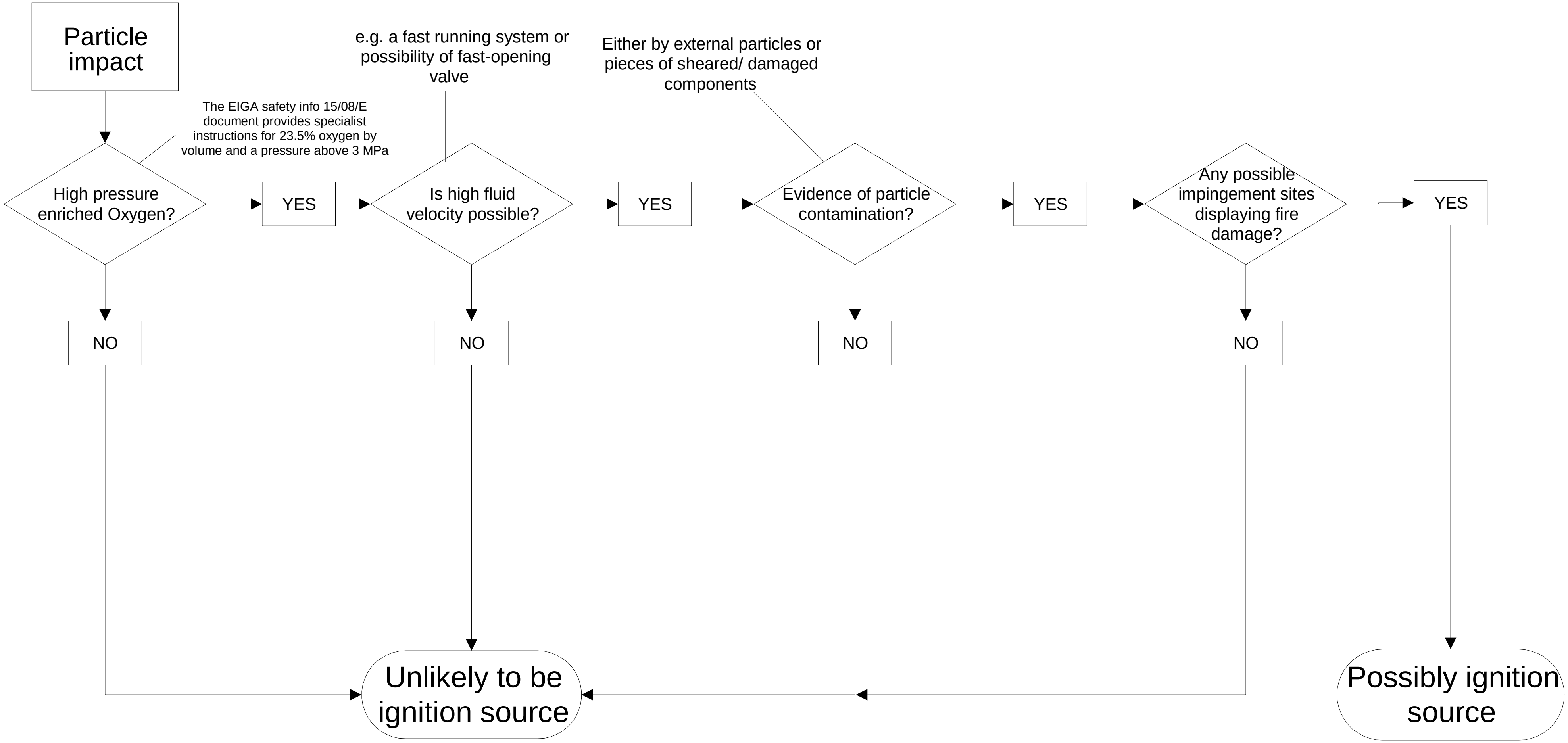
Adiabatic heating/ pressure shock

Based on information throughout this thesis Figure 6-6 has been developed. This road map itemises, in a step-by-step way, the necessary conditions for shock/ adiabatic compression to be considered as a possible cause of ignition.

By following Figure 6-6 the following points have been identified:

- A system pressure of 20.7 MPa pure oxygen has been identified by investigators, which is well in excess of the 23.5% and 3 MPa requirements for the system to be regarded as high pressure enriched oxygen.
- The ‘output stop valve’ had been opened while the recharge cylinder valve at the end of the supply hose had not been opened making the tube dead-ended.

Figure 6-5 Road map to assess the likelihood of particle impact as a possible ignition source



- As mentioned previously in this chapter the fast opening valve (hence the immediate exposure to a pressure of 20.7 MPa) and possible rapid pressure rise from 0.101 MPa to 20.7 MPa. The possible gas velocity can be estimated, using equation 5.53 as being well over the 30-45 m/s threshold for possible particle impact ignition. Fast fluid flow was, therefore, possible.

- Some hydrocarbon contamination on the outside of the hose was identified by investigators but did not identify any particulate beyond that produced by the fire in the incident. The presence of a check valve and sintered filter to prevent contamination from recharging cylinders suggests that this type of contamination, though not impossible, would be unlikely.

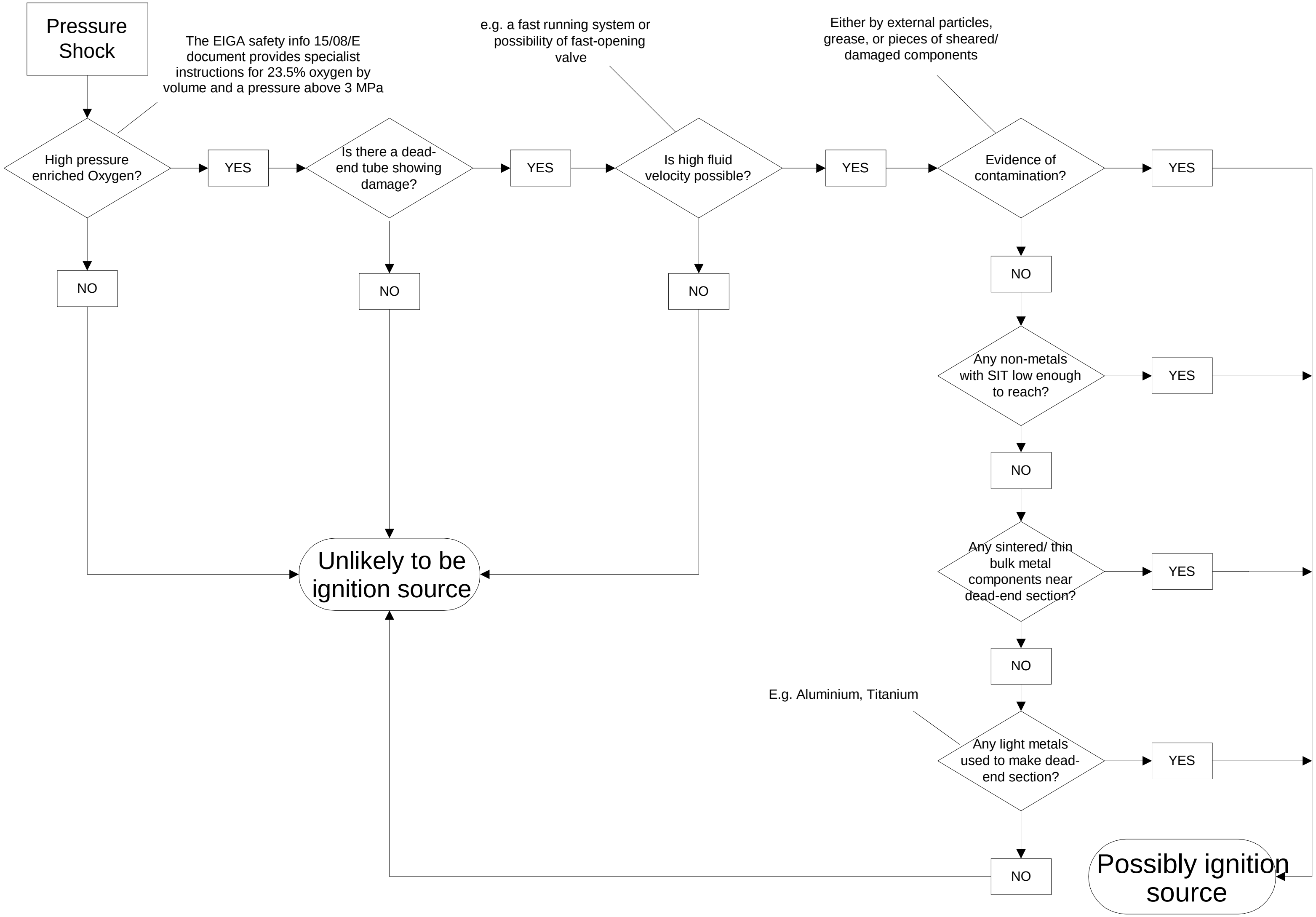
- In the area of ignition the only polymeric material is the PTFE liner of the filling hose. Using equation 4.14 the SIT of PTFE can be estimated to be approximately 763 K. gain assuming atmospheric pressure in the system before pressurisation, and using information in Newton and Steinberg (2009), the temperature of an ideal gas can be estimated as being between 1339 K (due to isentropic compression) and 11568 K (due to shock factors). Although these temperatures would be momentary they are well above the SIT of the PTFE component.

- There is a bronze filter directly in the gas stream. Although bronze generally has good oxygen service properties (e.g. Melting point of 1127 and EP of 68.9 MPa for tin bronze) the high surface area to mass ratio may lessen the resistance to ignition. Powdered tin bronze will ignite at 655 K.

- The bleed valve body has been identified as being made from Aluminium bronze. Any components made of aluminium or similar light metals are more susceptible to ignition than heavier iron or copper based materials.

All of the requirements for an adiabatic compression/ shockwave ignition are present making this the most likely source of ignition. Road maps for other causes of ignition in oxygen systems can be found in Appendix E.

Figure 6-6 Road map to assess the likelihood of pressure shock as a possible ignition source



Possible seats of ignition

Using the process in Figure 6-6 three areas have been identified as a possible seat of ignition, i.e. the region the initial ignition took place.

- Aluminium bronze bleed valve body. This did not show any specific damage as a result of combustion. It is unlikely that this was the site of ignition.

- Sintered bronze filter. This lies directly in the dead–end valve section and appeared to have completely burned away. There were signs of combustion (discolouration). The location of un-combusted the check valve ball bearing, and direction of the soot suggests smoke (and therefore heat) travel would have been predominantly towards the cylinder valve making the ignition of the PTFE from this section of the valve unlikely.

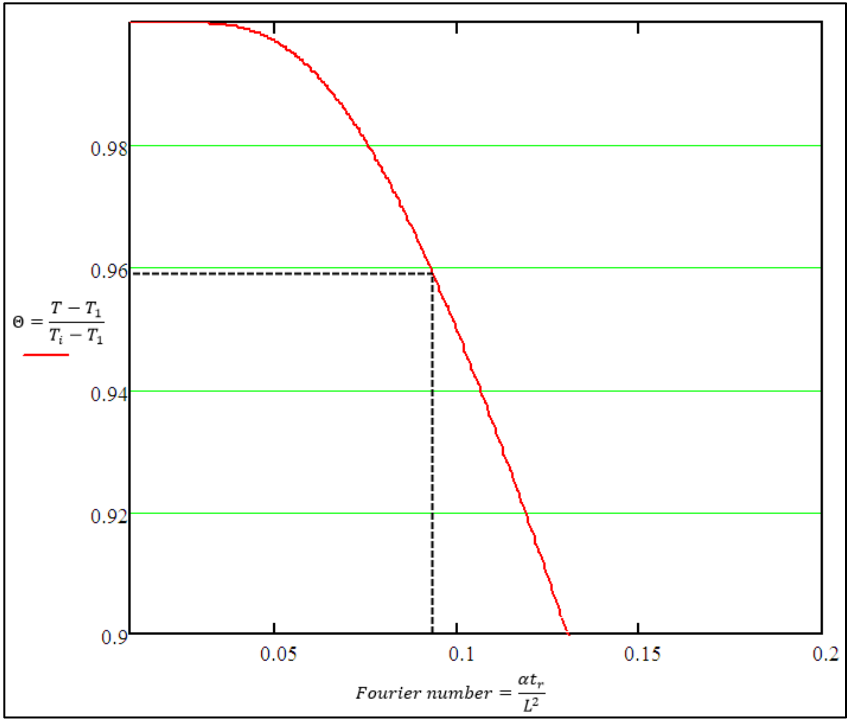
- PTFE hose liner. This material has an SIT of approximately 760 K in these conditions which is far lower than the metallic items. The end of this tube would very likely have been exposed to extremely high temperatures being directly next to the dead-end formed by the closed bleed valve. The inner 0.5 mm of the tube in some places had burned away, and the tube had burned and burst in some areas. It seems most likely the fire began at the bleed valve end of this hose.

Using the Heisler chart method we can calculate the time for different depths of PTFE to reach the SIT temperature assuming a surface temperature of 11568K (due to pressure shock) and negligible surface resistance. Using equation 4.14 and data from section 3.13 the SIT of PTFE has been calculated as 763 K. We know,

$$\Theta = \frac{T - T_1}{T_i - T_1} = \frac{763K - 11568K}{298K - 11568K} = 0.959 \qquad \text{Eqn. 5.8}$$

Where Θ is a function of the Fourier number. This can be used on a Heisler chart (see figure 6-7) and gives a corresponding Fourier number of 0.094.

Figure 6-7 A Heisler chart showing the relationship between the Fourier number and the system temperature ratio for a plate



The time that the SIT can now be calculated using equation 5.16:

$$Fourier\ number = \frac{\alpha t_r}{L^2} \qquad \text{Eqn. 5.16}$$

Thus where L is 0.5mm, t can be calculated

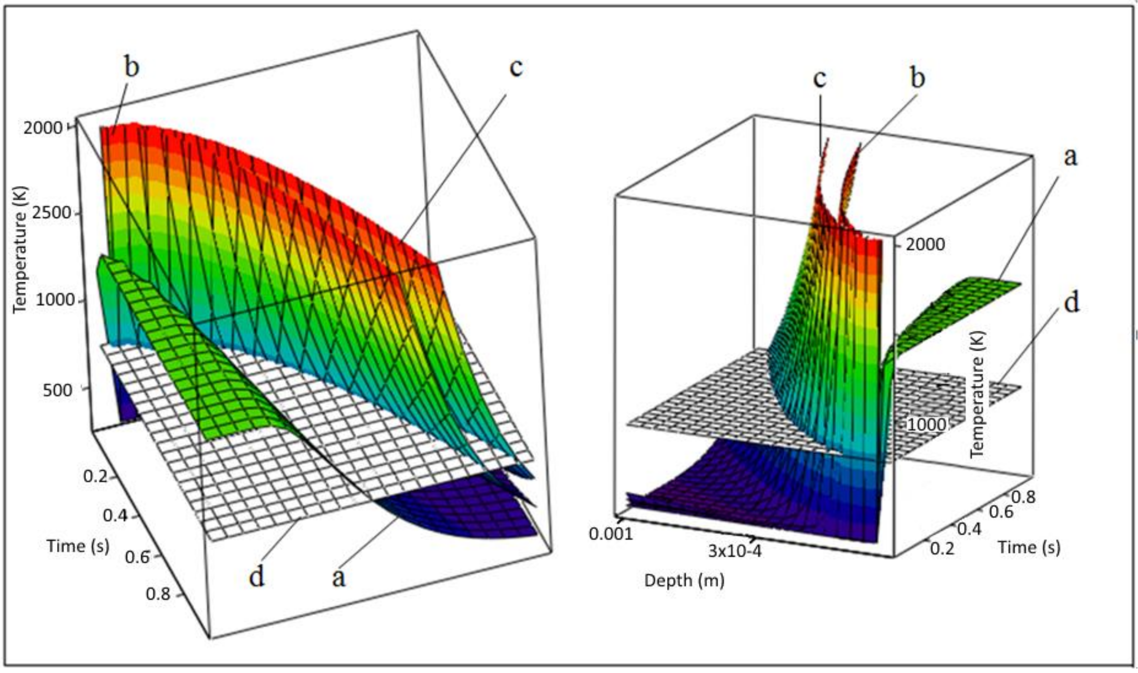
$$t_r = \frac{0.094(0.0005^2)}{8.74 * 10^{-8}} = 0.27s$$

The thickness of an undamaged hose liner involved in the incident is on average 0.92 mm, while burning inside the hose reduced this by approximately of 0.5 mm. This gives an indication that a high temperature environment could raise the temperature of the burned section of the tube thickness to the SIT in just over a quarter of a second.

Equation 5.50 can be used to provide a range of answers across time and space (within the material). For example Figure 6-8 below, showing 2 views of the same 3-dimensional graph, demonstrates the effect that different external surface temperatures would have on the heat flow through a slab of PTFE. These have been calculated assuming a constant surface temperature and negligible surface resistance under the shockwave conditions. Arrays a, b and c show heat transfer for external surface temperatures of 1339K, 6454K, and 11568K respectively, over 1 second and 1 mm.

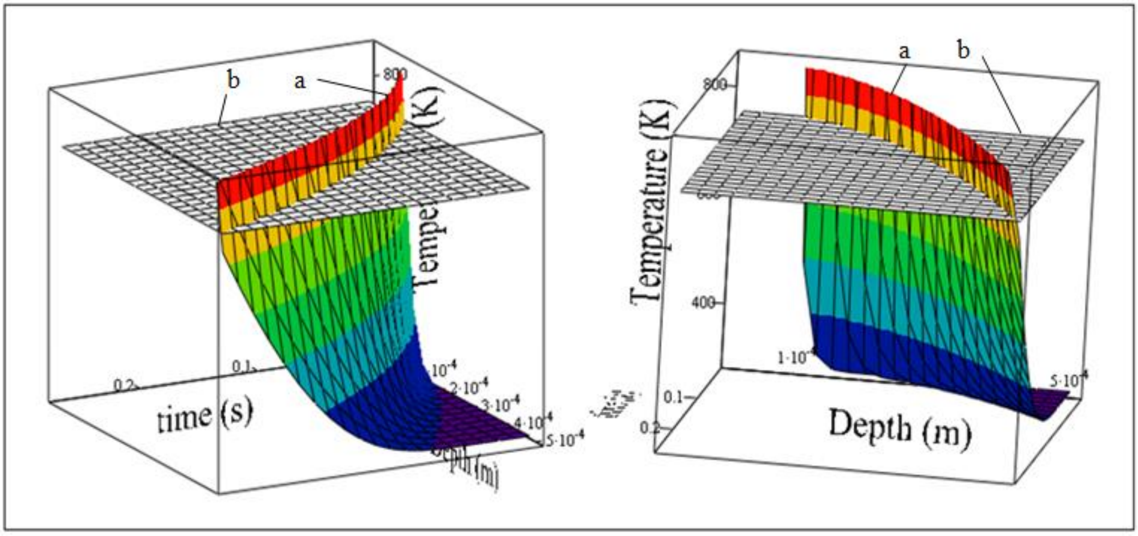
Figure 6-9, showing the same graph from 2 different angles, shows the speed at which a 0.5mm layer might be heated to the ignition temperature of PTFE in 20.7 MPa oxygen if exposed to the maximum temperature of 11568 K at the surface. PTFE is one of the most ignition resistant polymers. Figure 6-10 demonstrates a Nitrile rubber layer under the same conditions. The SIT is clearly reached sooner. Very few polymeric materials would have resisted ignition better.

Figure 6-8 A comparison of the heat flow through a layer of PTFE when exposed to different external temperatures, assuming negligible surface resistance



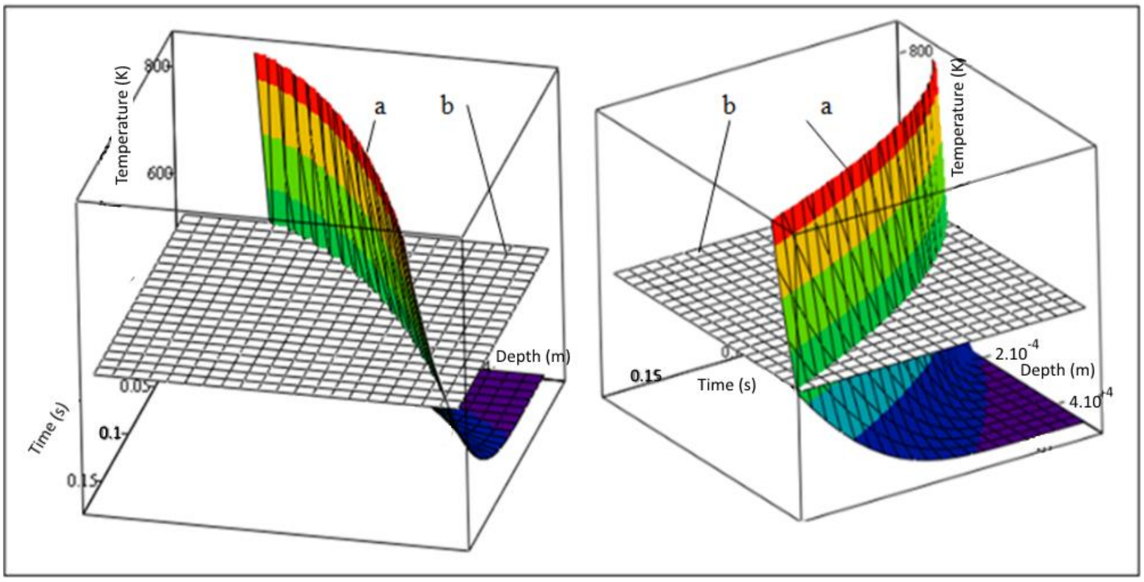
Curves for constant external surface temperatures of a) 1339K; b) 6454K; c) 11568K. Layer d) is at 760 K, the SIT of PTFE. Initial temperature of 298 K.

Figure 6-9 Heat flow through a layer of PTFE when exposed to an external temperature of 11568 K, assuming negligible surface resistance



a) Curve for constant external surface temperatures of 11568K. b) 760 K, the SIT of PTFE. Initial temperature of 298 K.

Figure 6-10 Estimation of the heat flow through a Nitrile rubber layer when exposed to an external temperature of 11568 K, assuming negligible surface resistance



a) Curve for constant external surface temperatures of 11568K. b) 545 K, the SIT of Nitrile rubber. Initial temperature of 298 K.

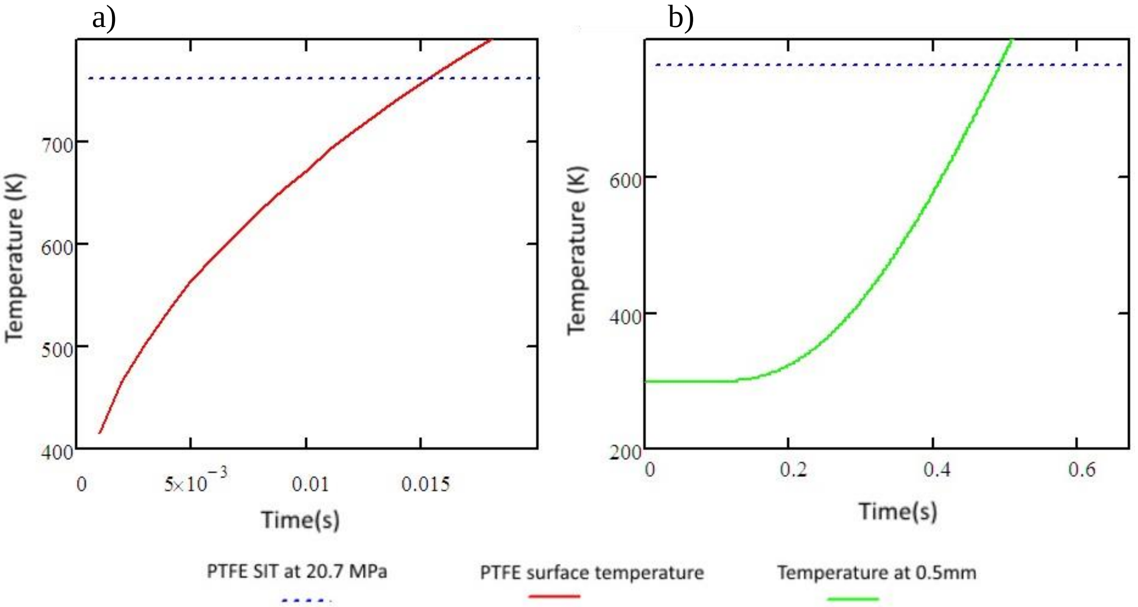
Alternatively we can calculate the surface temperature rise by calculating the convective heat flux from a fluid at 11568K, and applying that mathematically to the PTFE surface.

Using,

$$q/S_A = h(T_g - T_s) \qquad \text{Eqn. 5.52}$$

and assuming the highest natural convection heat transfer coefficient of 250 W/m^2 K and a surface area of 1m^2, we can calculate the convective heat flux per unit area to be 2.8 MW/m^2. Incorporated into the relationship from Lawson and Simms (1952) in equations 5.51 and 5.50 the graphs in Figure 6-11 have been produced. The first, a), shows the rise in surface temperature under these conditions. It shows under the high heat flux the surface could reach the SIT in a small fraction of a second. Graph b) of Figure 6-11 shows the length of time taken for the PTFE to reach the required 763K at a depth of 0.5mm under the same conditions.

Figure 6-11 Graphs showing the rise in surface temperature and internal temperature at a depth of 0.5mm in a PTFE component exposed to a gas temperature of 11568K in 20.7 MPa.



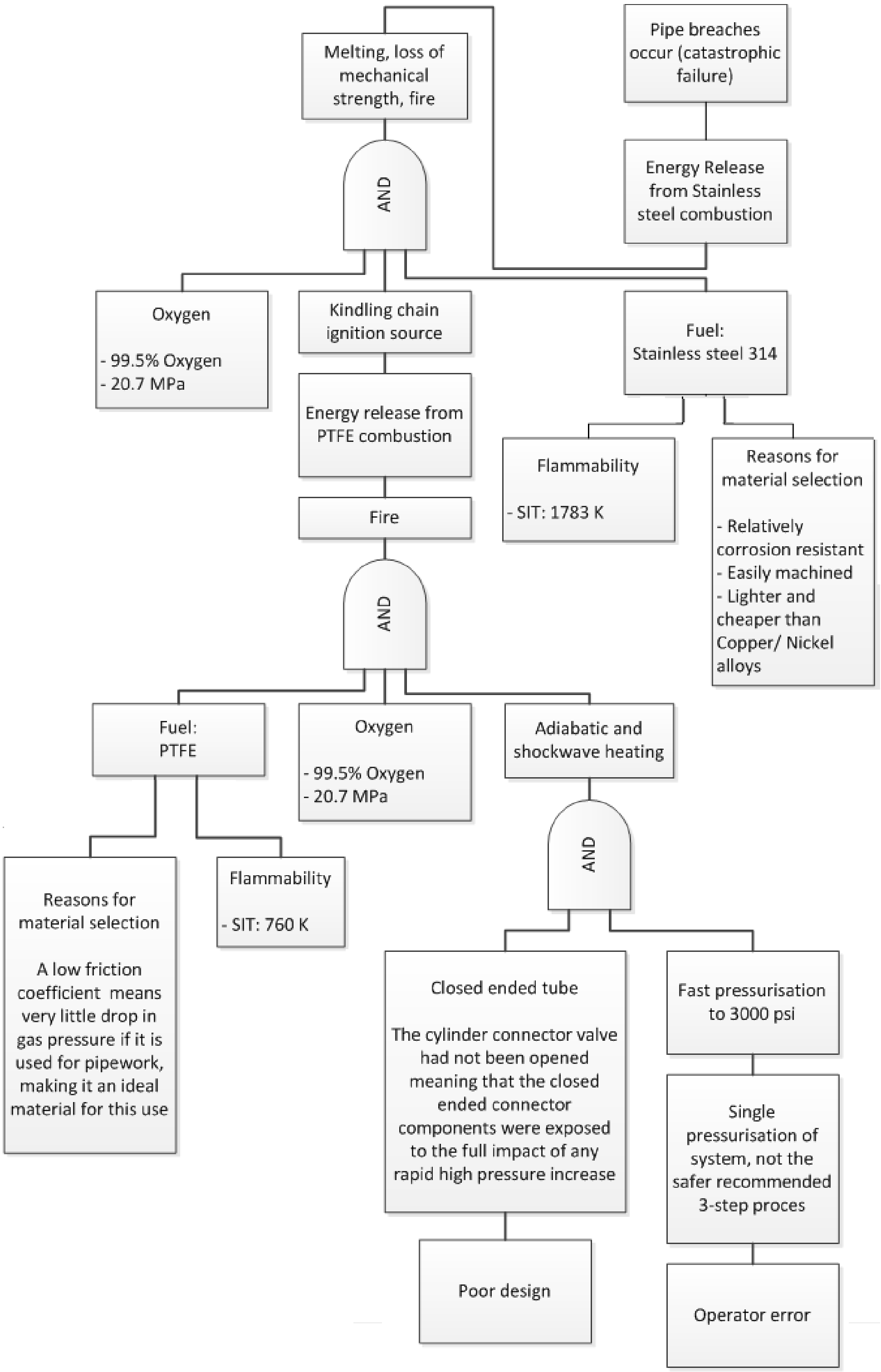
Kindling chain ignition following polymer ignition

The evidence suggests the ignition started with the PTFE tube liner, which in turn ignited other components including the surrounding stainless steel braid, which would also have had reduced mechanical strength due to increases in temperatures..

Based on the description of the system after the failure it is clear most of the PTFE tubing was burned away. Given the dimensions of the missing and damaged tube an estimate of the volume of PTFE that burned away has been calculated as 10.5 cm^3, equating to a mass of approximately 26g and a total heat of combustion of 154 kJ. As the PTFE burned directly next to the stainless steel braid this can be compared to promoted ignition tests where an igniter burns against a rod shaped sample. The total energy release from the burned PTFE is well above the energy used by McIlroy et al (1988) (42 kJ) to ignite similar materials in the promoted combustion test.

The combustion of the stainless steel was limited to small regions, and the mechanical failure was the major cause of the pipe failure. Although the bronze sintered filter was ignited, the damage surrounding it, and soot deposition, suggest it was damaged after the filling tube. The event can be shown using a fault tree, demonstrating the main path of the fire, and reasons for the catastrophic failure.

Figure 6-12 A fault tree showing the paths of a fire in an incident in Mansfield, in 2007



Engineering solution and recommendations

The fault tree demonstrates the 2 main causes of the incident. One is operator error, where the full charging process is not followed by those using the system. Thus, where the charging panel should be completely discharged to atmospheric pressure, the system remains at a high pressure of 20.7 MPa. Clear instructions, training and regular checks should be made to make sure the correct filling procedure is always followed.

Secondly, the poor system design allows this incident to occur. The output valve is capable of fast opening, and the end section of the tube to the bleed valve is made of a polymer. Adding a slow opening valve would prevent possibility of a shockwave from developing. Putting in a section of metallic tube immediately before the cylinder valve would reduce the chance of ignition due to adiabatic compression/ shockwave heating.

6.2 Analysis of existing oxygen components

BS 5N 100 – 5: (2006) reported an incident involving a valve (described as valve MK10A by Scanlan 2008). The operator "cracked open" the outlet valve momentarily to check its contents and function. The valve burst into flames causing severe injuries to the operator. Examination afterwards showed considerable damage to the components.

The first item ignited was judged to be the valve, and the cause was believed to be adiabatic compression/ shockwave heating. The main faults with the valve, identified by investigators were:

- The body was manufactured from aluminium, one of the more flammable metals when fresh metal exposure occurs.
- The PTFE seat was directly in the oxygen stream, making it prone to impact and heating.
- The PTFE seat had sharp edges allowing shearing to occur as it was re-inserted into the body.

The report therefore advised that a more suitable material, such as brass, be used for the body, and that the PTFE seal should be attached to a floating spindle to prevent shearing. The valve was replaced by a GA 3030.

The same system that has been developed to examine past incidents can be used to predict the behaviour of components currently used in oxygen systems. In section 6.2.1 this process is applied to the replacement valve GA3030.

6.2.1 GA3030 Oxygen valve

The design for GA 3030 employed some of the recommended changes. It had a brass connector added on the high pressure side of the valve, and the new rounded PTFE seal was moved to be contained in a stainless steel surround. A brass disc was placed at the top of the spindle (protecting the adjusting knob). However the main body of the valve, and some internal components were still made of aluminium.

Examination of the valve has led to the most likely causes being identified, and some being dismissed. An incident caused by mechanical impact is extremely unlikely due to the limited movement of parts. A cause of frictional heating would also be unlikely for the same reason, and due to the low friction coefficient of the PTFE seal. The component does not appear to contain any dead-end tubes that might result in the energy from resonance. This leaves electric arc/spark, adiabatic compression and particle impact as the most likely possible causes of an incident in this part.

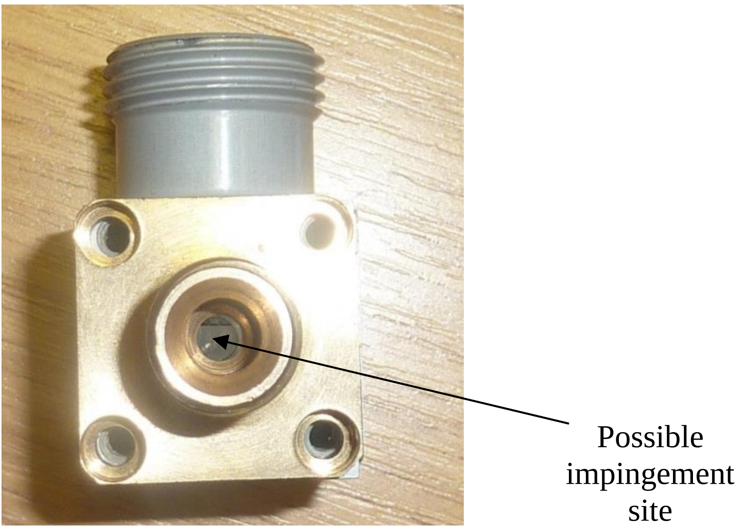
Electric arc/spark – The possible energy levels could be massive if there was an unexpected arcing from an adjacent system. In this case any materials might be expected to ignite. This would depend upon a number of external design factors, not upon the design of the valve, or the materials used.

Adiabatic compression – It might be possible for the small internal components to be heated by the adiabatic compression within the system, but that would mean that other components in the system enabled this to occur. The position of the PTFE 'O' ring makes it unlikely that it could be combusted easily in this situation due to the fact that it is covered by aluminium or stainless steel on all sides when the valve is closed. The stainless steel has a melting point (and therefore SIT) of 1783 K. Under these circumstances ignition by adiabatic compression is extremely unlikely.

Particle impact – Visual inspection of the valve shows that there is an obvious possible impingement site directly in the path of the gas stream. In the event of the fast opening of a valve (should particles be in the system) a particle might travel through the brass connector, and impact directly on to the surface of the valve body. In the case of aluminium this is a problem. The relatively high IT of aluminium is attributed to the thick layer of aluminium oxide that covers its surface. However, should this layer be breached, and fresh pure metal be exposed to both heat and high pressure oxygen, the IT might be reduced to as little as 933 K (the melting point of aluminium). The heat of combustion of aluminium is so high (30 kJ/g) that any aluminium oxidation would result in a further self-sustaining oxidation reaction.

Figure 6-13 Valve GA3030 anodised aluminium body and brass inlet

Figure 6-14 Side view of GA3030 aluminium body and brass inlet showing the flat impingement site directly ahead of the inlet tube



Based on equation 2.6 the maximum possible temperature of the valve body can be calculated:

$$\Delta H = mc_p\Delta T \qquad \text{Eqn. 2.6}$$

It would take from between 25.8 kJ – 37.7 kJ to raise the temperature of all 44g of aluminium to 955 K (depending on any heat loss to the surrounding environment). If the same component were made of brass it would be approximately 137g and would require between 45.7 kJ – 46.5 kJ to raise the temperature to the SIT of the brass. Brass would clearly be a safer option, as it would take more energy to ignite it than the same component made of aluminium, and has a far higher threshold pressure.

6.2.2 Use of 'tool kit' for prediction and system analysis

Some of the tools used to analyse existing systems and catastrophic oxygen incidents could be used to aid in the selection of correct materials, and to predict possible configurational issues.

The use of the SIT relationship, in equation 4.9, would enable prediction of polymer behaviour at different pressures. This would mean that a designer could use existing data for material they have used at one pressure, and extrapolate the flammability of the same materials at different pressures and oxygen concentrations, without the need for large scale, complex, and expensive extra testing. Alternatively if no data is available the use of smaller scale apparatus like PDSCs would be extremely useful in place of the far less accessible bomb-test.

The road maps, developed to identify possible system weaknesses, and probable causes of ignition following an event could also be used as a predictive analysis tool. They would allow a designer, or end user of system components, a quick and easy way to assess the safety of their components or system set up, in order to minimize the risk of an incident, or catastrophic failure event.

Chapter 7
Conclusions and Future work

This work has collected a large amount of information, and formed methodologies to model and apply that information to real-life oxygen system components and configurations. While the aims have been met, there have been some obstacles, and areas of difficulty highlighted by this work, where further scientific investigation is required. This section will relate conclusions directly back to the original aims and objectives stated at the start of this work. It will also offer a critique of this work, identifying the successes and limitations.

The primary aims of this work have been to develop a model predict the spontaneous ignition temperature (SIT) of materials used in oxygen systems using known data, to enable the use of alternative, cheaper, smaller scale and more accessible test apparatus to assess the flammability of materials for use in those systems, and to develop a scientific methodology in order to record, and understand oxygen incidents with particular reference to kindling chain events. A number of objectives were identified to achieve these aims, and these are discussed in the following sections.

7.1 Initial literature survey

The initial aims of this work were to review the literature on the oxidation of materials in high pressure enhanced/ pure oxygen atmospheres, to review the results of current ignition and flammability tests and to combine data bases relating to both metals and non-metals.

Chapter 2 includes a lot of detailed information identifying the current state of knowledge in relation to oxygen incidents, and the flammability of both metals and non-metals, including test methods used to assess their flammability. Having carried out this research it is clear that there is a lack of information on the fundamentals associated with combustion in high-pressure enriched-oxygen, and this may be hampering advances in this field. Although initially a great deal of work on the flammability of metals and polymers in high pressure oxygen was identified, the effect of configuration change, and behaviour in different positions, was far less well explored. A body of work has been built up on materials and their fire behaviour, but upon approaching analysis of systems, it became clear that fundamental information on the behaviour of the materials in this specialised environment is missing. The lack of fire engineering fundamentals like time to ignition, critical heat flux, and chemistry fundamentals like knowledge of kinetics makes reliable analysis problematic. Unfortunately the ability to measure this information depends on a range of different, often purpose built apparatus, often made of expensive materials, and requiring a high level of safety consideration. With unlimited time and resources the development of a high pressure oxygen cone calorimeter, or similar controlled-environment and heat flux ignition system, would be extremely useful, although by no means easy to make (where material selection, ignition-source type, and a number of other engineering problems would require significant thought). However, such an apparatus could provide extremely useful information for this challenging atmosphere.

7.2 Experimental work and modelling

This work has shown a number of relationships which allow test data, measured at a range of pressures and under different conditions to be compared, and to be applied to other circumstances. The model derived in chapter 4 enables the calculation of the SIT of a non-metal at any pressure, and oxygen concentration. This calculation cannot be done without some data on that material, so some form of SIT test must be done, but it does allow test results measured in 2 or 3 MPa to be extrapolated to, for example, 15 or 20 MPa with reasonable accuracy for a number of materials. Some form of safety buffer should be incorporated for its use, as with any calculation method, to allow safe use. This has been shown to work for most materials tested, and means that more accessible options can be used to determine materials suitability for high pressure oxygen. With more time and access to the PDSC apparatus, and hind sight, more materials might have been tested, and a series of measurements at 5 MPa could have been taken for direct comparison with the lower temperature measurements taken in the bomb test.

Further work is needed to increase this data base to establish ignition test data and thermodynamic constants to allow for the direct comparison. More data, particularly for other materials, should be acquired for a range of flammability and calorific test procedures. As well as including the PDSC and Bomb apparatuses used in this study, other methods such as Accelerating Rate Calorimetry should also be explored to identify the relationships or variation between data produced. A range of apparatus and conditions should also be investigated to expand the knowledge on the use of materials in flowing oxygen atmospheres, and to establish the relationship between SITs in static and flowing environments.

The investigation of polymer use in oxygen systems has highlighted two areas of interest. Firstly the number of types of polymers employed, and secondly the variation of properties that can occur within each polymer type. A large number of materials can, and are, used in oxygen service. This is not inherently a bad thing, but polymers with the same base molecule can have vastly different properties depending on the chemicals added to the base mix, such as plasticisers or retardant materials. Polymer manufacturers provide materials with particular mechanical properties (guaranteed to lie within a stated range). The ignition or flammability characteristics of materials are not generally specified. This means that manufacturers can vary the chemistry of a material from batch to batch, keeping to their specified characteristics, while varying ignition and other properties substantially. This work suggests that materials like polychloroprene and Nylon 6,6, can vary significantly between batches. There are also indications that the flammability properties can change over time. The use of materials with such variation in oxygen systems should be examined to identify if there is any risk. It might be useful if the ignition properties of polymers used in oxygen systems were specified by manufacturers, or for the types of additives to be kept to a tighter recipe. This would reduce the amount of testing required by engineers, and the cost of using oxygen systems.

Another area requiring further research is the unusual behaviour of materials containing chlorine. Polymers with a molecular structure which contains chlorine atoms are well known to display an increased level of fire-retardancy compared with similar, non-chlorinated materials. The data in this work seems to suggest that the flammability behaviour of these materials does not adhere to the relationships described in chapter 4, relating to pressure and SIT. Work should be carried out to explain and define this effect, and to explore the role of other halogens and halogen-containing materials in high-pressure oxygen-enriched atmospheres.

The attempt to identify a simple method of SIT estimation based on thermal desorption and pyrolysis products was largely unsuccessful. The complexity of the polymer degradation products made this process difficult. Added to this, access to the apparatus used in this process, and resources, were extremely limited. The Thermal desorber maximum temperature of 250°C made proper analysis of the higher specification engineering polymers, like PTFE, impossible. Had there been access, use of a much higher temperature Pyrolysis system would have been more suitable for this work, or possibly even evolved gas analysis mass spectrometry. Also, although identification of many peaks was possible with the GC 1701 column, the more complex larger molecules might have been easier to identify with a less polar column, with a more extensive library, like an Equity-1. The use and behaviour of metals has been explored extensively by others. The majority of metals and many alloys have been tested to assess ignition behaviour and Highest No-Burn Pressures to identify the most suitable for different applications (See ASTM G94-05). However work by Schadler and Stoltzfus (1993) and Zabrenski et al (1989), and incident reports from real-life incidents have exposed an area where there is a hole in our knowledge. The configuration of metals (i.e. the shape, surface area etc.) appears to alter the 'rank order' of these materials. Further research should examine the effect of the change on trends, and identify why altering the geometry of a mass of metal can also alter how it burns in relation to other metals. Modelling such changes should also be explored for prediction purposes.

One particular area that should be explored is the use of sintered filters. It is well known that powders burn more easily and ferociously than bulk metals, and Schadler and Stoltzfus (1993) show that changing materials to sintered configuration can have a huge impact on the flammability of a metal. However the full impact of this has not been explored. Studies to identify the trend or shift in flammability and ignition characteristics as surface area increases would enable engineers to identify where the use of components with a high surface area to mass ratio, such as sintered items, is safe, and to find the reasons for this change in properties. It may be that incidents involving sintered filters are caused by the ignition of materials accumulated in their matrix. Testing could identify this, explore what materials accumulate, and result in recommendations as to how often they should be changed. Again the further exploration of materials in high pressure oxygen consists of significant challenges, and the limitations of time, equipment, and budget involved in this work prevented further exploration of this subject.

7.3 Oxygen incident investigation 'tool kit' and methodology

A number of tools have been developed to improve the quality of data recording, ease of investigation, and more fully analyse oxygen incidents. The aim in this has been to form more structured and robust methodology for the investigation of oxygen incidents. Information collection and analysis follow a systematic procedure, ensuring full data capture, and better understanding and prediction of sequential ignitions and kindling chain path.

As well as general observations on lack of consistent and thorough recording in incident investigation reports this section of the work concentrated on four areas;

- converting knowledge of ignition modes into investigation road maps,
- the use of SITs in material selection and incident investigation,
- the use of negligible surface resistance heat transfer models to understand heat transfer in oxygen components and predict ignition,
- and using fault trees to record the kindling chain and details on items involved.

The 'tool kit' has been applied in chapter 5 to enable a clear, scientific methodology. The road maps are an excellent way to ensure no ignition source is missed, and that all the factors involved in the chance of ignition are taken into account. The ability to check probably SITs of materials without having to test those materials under different, possible hazardous, conditions is extremely valuable from an investigative perspective. It not only saves time and money, but allows a greater array of conditions to be modelled than might be tested given the resources available to some investigations, particularly small scale events. The use of heat transfer calculations to analyse possible ignition sources, and to indicate time to ignition is another way to gain further insight to these events. While it is difficult to validate this work without information on critical heat flux, and time to ignition data it does provide a conservative method to predict the time to ignition under external heat flux, and adiabatic compression/ shockwave ignition situations. Finally the use of fault tree analysis is not a new investigative technique, but the use of such a device to record a kindling chain event proves a very useful and unique way of tying together investigation, analysis and component properties to ensure full and proper collection of data and recording of information. It is hard to know the full implication of this work but better analysis and recording of information must enable better understanding of oxygen incidents, and inform designers of the future in helping to identify hereto unknown problems.

As stated in section 6.2.2 it is possible that the new SIT information and ignition source road maps could be used to aid material selection, giving an indication of likely ignition sources, and the materials most prone to these issues. It would enable a faster, and less expensive way to check a system is safe and fit for purpose.

7.4 Incorporation of new knowledge into BS 5N100

The knowledge gathered in this work, and the further work noted in this chapter should be incorporated into new sections of BS 5N 100. This should include the updated combustion model, the use of a range of ignition tests, and the ability to convert/ compare the results, as well as ignition source road maps for easy identification of the causes of oxygen incidents. The relationship, and any further information, on materials behaviour in flowing oxygen environment should also be included. There should also be further recommendations on the use of polymers with unspecified, or a range of, flammability properties.

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For details on standards and standard guides see the “Standards and Guides” reference list further on in this work.

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Appendices

Appendix A. Bomb test full operating procedure

- Solid sample preparation

A 100 ±2 mg sample is taken, and split into 20 equally sized blocks, and the samples are then cleaned. A diagram of the system layout is in figure A-1 (including all the components described in the following procedure).

- Purging and filling

The sample is inserted into the combustion boat, and the head and combustion boat are lowered into the containment vessel.
All valves must be checked before proceeding.
Open both oxygen and nitrogen bottles.
Open valves V1N, V2N and V3N inlet.
Open V4 outlet and containment vessel vent valve. Close V3N and V1N.
Open N bottom vent (venting Nitrogen from lines). Close N bottom vent and V2N.
Open valves V1Ox, V2Ox, and V3Ox inlet.
Close V3Ox inlet and open Ox bleed valve. Then close Ox bleed valve and open V3Ox inlet.
Repeat this cycle four times clear the air from the combustion vessel.
Close V3Ox inlet and V1Ox.
Open Ox bottom vent (venting oxygen from the lines).
Close Ox bottom vent and V2Ox.

- Pressurizing gas booster

Check all valves are closed
Open valves on the Oxygen and Nitrogen bottles (if extra Nitrogen is required open V1N and V2N).
Initiate the gas booster and open V3N when the pressure is the same as that already in the containment vessel.
Close valve V3N, turn off gas booster, and close V1N.
Open N bottom vent to discharge residual nitrogen from the lines.
Close N bottom vent and V2N. (If extra oxygen is required, open valves V1Ox and V2Ox, then open V1 to purge residual nitrogen from the gas booster using oxygen. Close V1
Initiate gas booster and Open V3Ox inlet when the pressure is the same as that already in the combustion vessel.
Close valves V1Ox and V3Ox inlet.
Open Ox bottom vent (discharging residual oxygen pressure from the lines)
Close Ox bottom vent and V2Ox (If elevated pressures are required repeat the above procedure)
Achieve pressure equalisation.
Once test pressure and equalisation is reached, close all valves after the lines have vented. Vent Nitrogen last so there is no oxygen in the lines.

- Conducting the test

The test should be controlled by providing the heating rate required by the test protocol. For standard test conditions use a heating rate of 10K/min at a constant pressure of 13.2MPa.

- Venting

After testing is complete vent the oxygen at the same time as the nitrogen depending on the pressures involved.

Open Ox bleed valve (to vent oxygen).
Open V4 outlet and containment vent valve (venting Nitrogen).
Vent lines by opening V2Ox and Ox bottom vent and/or V2N and N bottom respectively.
Alternatively open V1 along with V3Ox and V3N to vent the system from the rig directly, for safety, should anything go wrong.

After the test is complete and all gases are removed the containment vessel should be opened and allowed to cool (a fan may be used to assist). The apparatus can be dismantled when it goes below 313K (40°C). Finally close bottle bank valves and vent all lines.

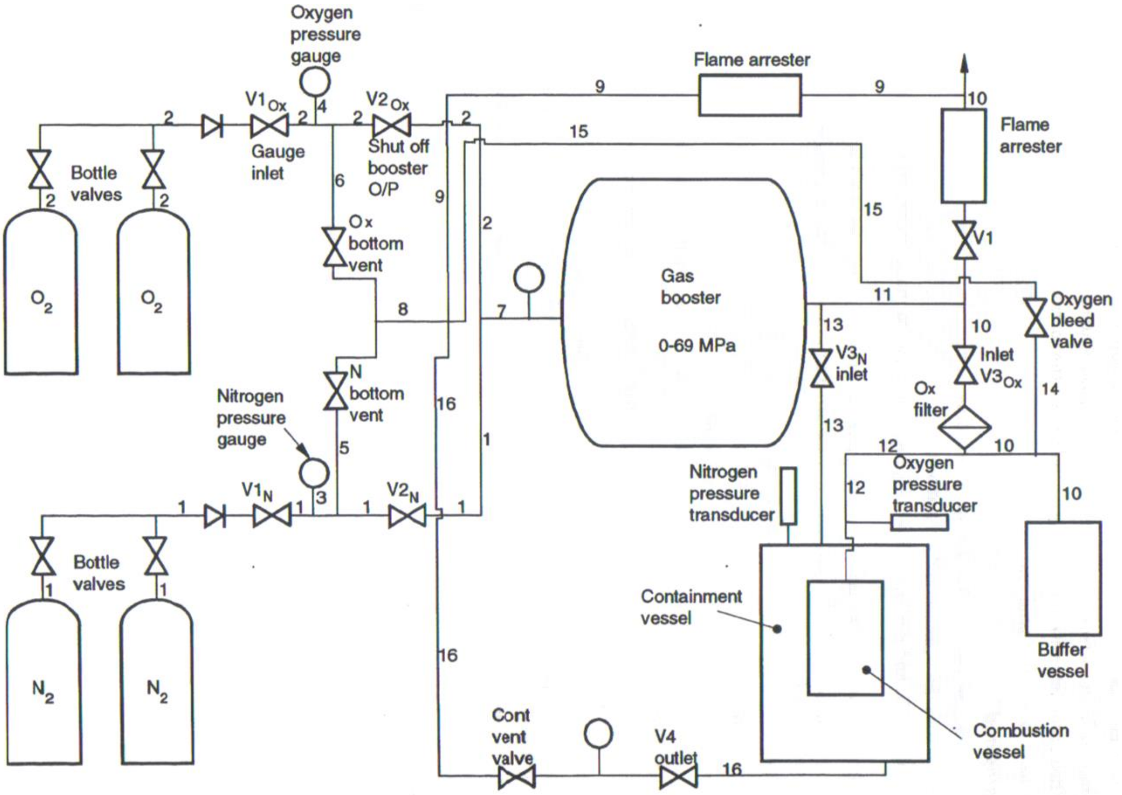
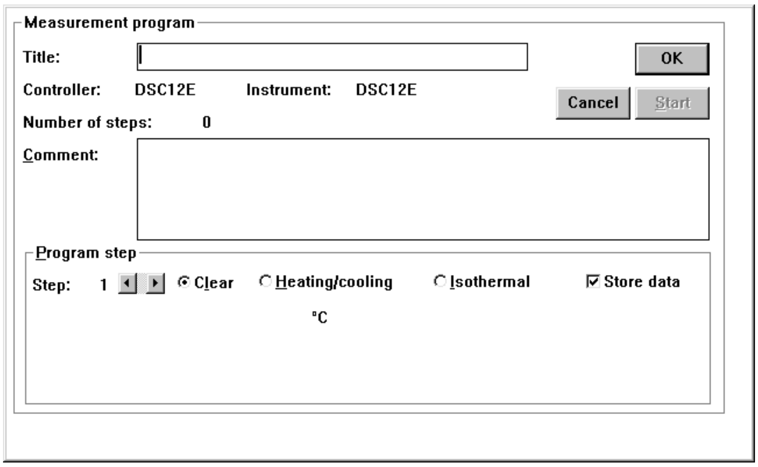


Figure A-1. High Pressure bomb system design

Appendix B. Differential Scanning Calorimetry full operating procedure

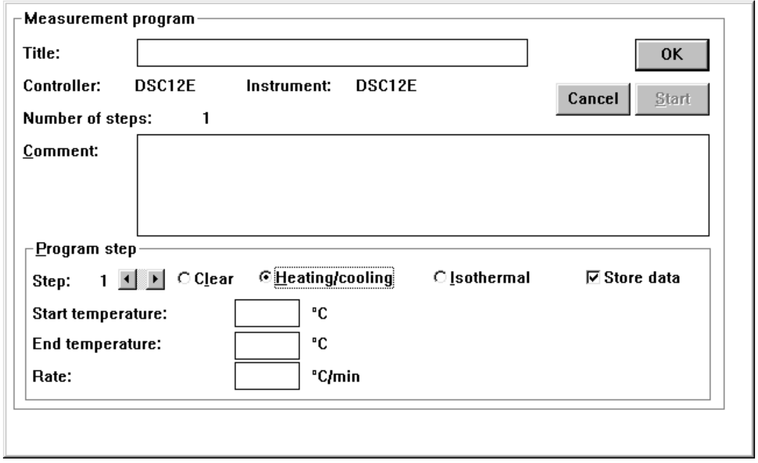
Open Mettler TA89E software.

Setting up a program
On the program menu select “New”.



Controller: DSC12E
Instrument: DSC12E
Number of steps: 0
Step: 1
● Clear ○ Heating/cooling ○ Isothermal ☑ Store data

Title program e.g. polymer 2
Select the Heating/ cooling choice

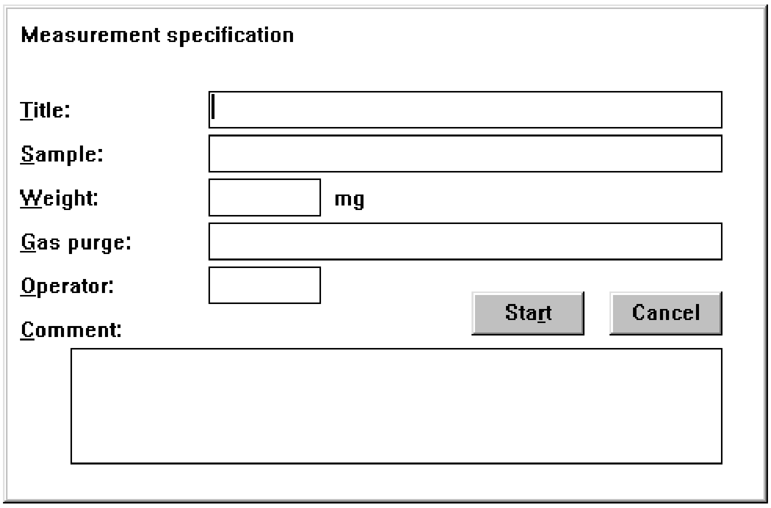


Controller: DSC12E
Instrument: DSC12E
Number of steps: 1
Step: 1
○ Clear ● Heating/cooling ○ Isothermal ☑ Store data
Start temperature:
End temperature:
Rate:

Enter 323K (50°C) for the start temperature and 673K (400°C) for the End temperature.
The rate should be 2°C /min
There should be just 1 step selected, and the Store data box should be ticked
Click OK and save the program as Polymer 2
Once a program has been set up in the Mettler software the same program can be used for a number of different samples

Starting a test run

Cut one small sample of the polymer (between 5 and 10 mg)
Place it in a sample holder with the small plate, and lid on top and seal closed using a press.
Open the correct saved program (e.g. Polymer 2).
On the Control menu select “Start”

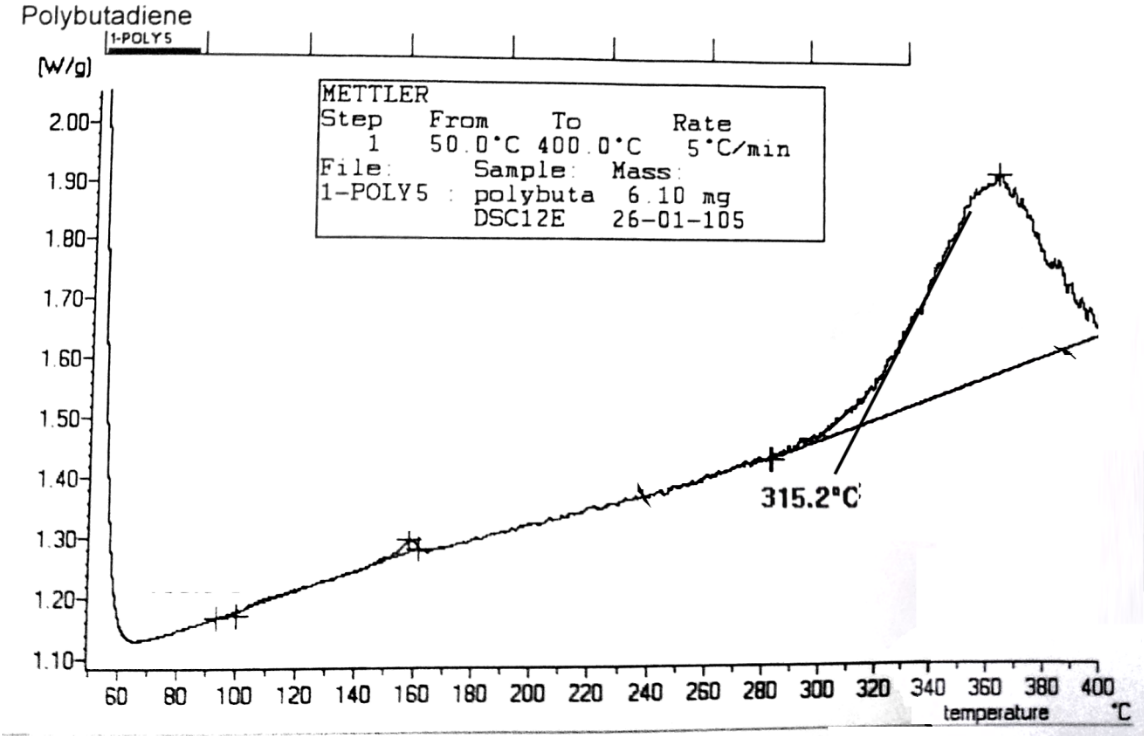


Enter the run title (e.g. NBR2), the sample name, and weight. The other two are optional

The software then asks if sample is inserted. Insert the sample, and the empty sample holder for comparison and click “Yes”.

To view graph of the data as the test is being run open the “View” menu and select “Running”.

- Example thermogram from Mettler DSC 12E



Appendix C. Pressurised Differential Scanning Calorimetry full operating procedure

Loading a sample

- Close IN control valve
- Open pressure release valve and leave open
- Unscrew the three thumb screws. If difficult then possibility of some pressure in cell, Check the valves and repeat.
- Remove top plate, cell cover and silver lid. Caution of heat if cell has been used.
- Load sample and reference as normal.
- Replace silver lid, cell cover and top plate
- Uniformly finger tighten the three thumb screws.

Replacing Gas in PDSC Cell

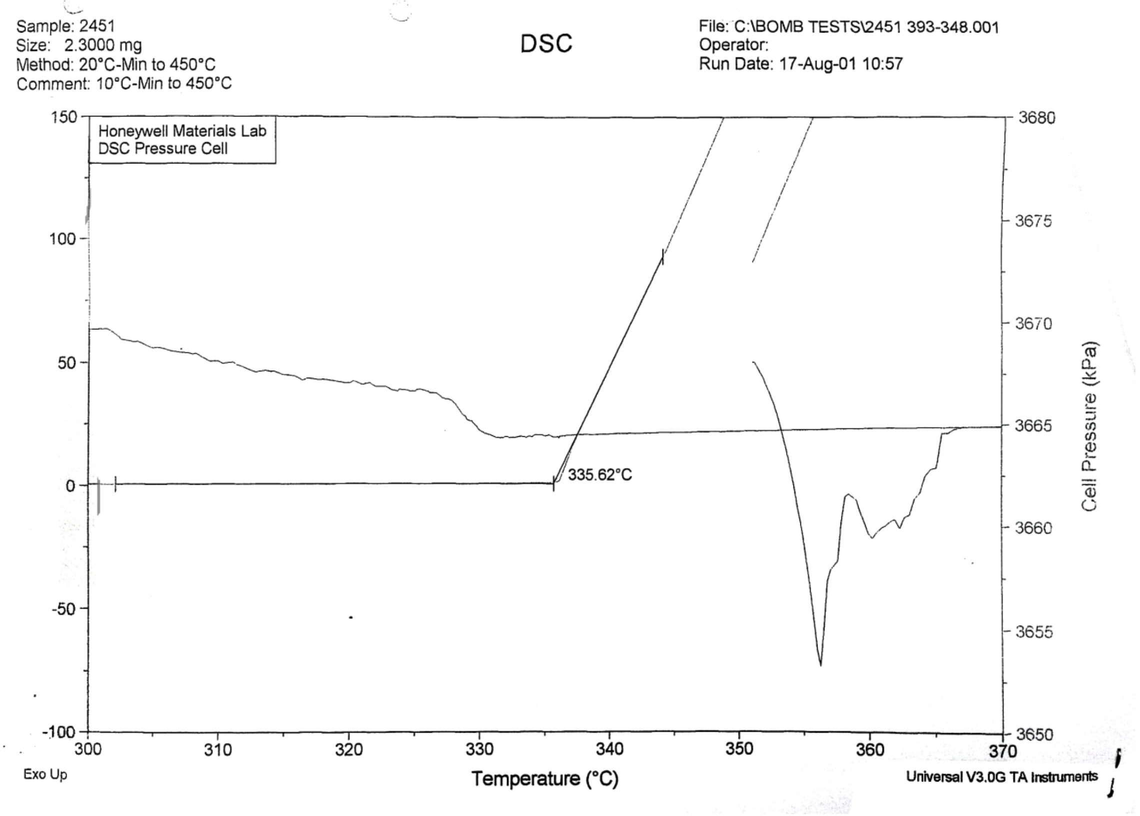
- By Evacuation

1. Close the IN control valve.
2. Close the OUT control valve.
3. Set the PURGE/FILL valve to fill.
4. Set the output regulator on the source gas cylinder to the maximum initial pressure of the experiment. If the cell is to be operated at constant volume, do not exceed 7 MPa (1000 psi).
5. Slowly open the IN control valve, and allow gas to fill the cell to about 2 MPa (300 psi).
6. Close the IN control valve, then open the pressure-release valve and allow the pressure to return to ambient.
7. Close the pressure-release valve.
8. Repeat steps 5 through 7 two times.
9. Open the IN valve, and allow the pressure to build to the desired level.

PDSC pressure by Constant volume

- Cell is sealed – pressure will increase with temperature
- After replacing the gas, check that all three cell valves are closed, that the cell is at some positive pressure, and the PURGE/FILL valve is set to purge. Use the cell pressure shown on the instrument display to determine the internal pressure of the cell. If the cell pressure is lower than the desired starting pressure, use the IN valve to raise it.
- If the cell pressure is too high, use the OUT valve to lower it. However, use the IN and OUT valves conservatively; there is a lag in the reading of any pressure gauge, and if the valves are opened too rapidly or too far, the final pressure will overshoot or undershoot the desired starting pressure.
- The maximum permissible starting pressure for constant volume operation is 7 MPa (1000psi) at room temperature. DO NOT exceed this value.

Example Thermogram produced of results from TA 2910 PDSC



Appendix D. TD/ GC full operating procedure

Sample preparation

a) Cut a small section of the polymer chosen for analysis (30 – 40 mg)
b) Cut a small amount of glass wool (≈ 5cm)
c) Wrap the polymer sample in the glass wool and place it inside the thermal desorption sample tube.

Two-stage thermal desorption

In two-stage desorption, the personal monitoring tube is first thermally desorbed into a cold trap. The trap is then heated rapidly at more than 1200 K/min to introduce the sample as a narrow band into the chromatograph column.

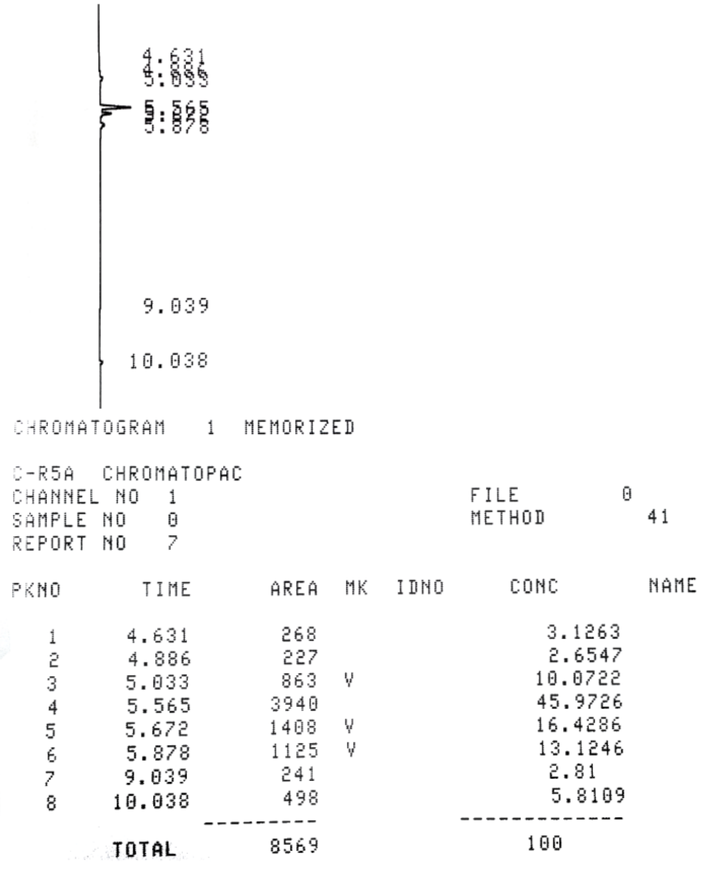
a) Press the GEN key; the GEN key, the METHOD key and the METHOD legend will all light.
b) Select the method number (e.g. 1) by pressing the numeric key 2 then the ENTER key; the MODE key will light.
c) Select mode 2 to obtain two-stage desorption by pressing the numeric key 2 and then the ENTER key; the OVEN key will light,
d) Similarly enter the required temperature for primary desorption (e.g. 353K, 80°C); the DESORB key will light.
e) Enter the primary desorption time (e.g. 10 minutes); the BOX key will light.
f) Enter the valve BOX temperature (e.g. 353K, 80°C); the CTL key will light.
g) Enter the cold trap minimum temperature (e.g. 300K, 30°C); the CTH key will light.
h) Enter the maximum temperature for secondary desorption (e.g. 573K, 300°C); the ANAL key will light.
j) Enter the time required for G.C. analysis (e.g. 30 minutes.); the FIRST key will light.
k) Enter the first tube position (e.g. 1); the LAST key will light.
i) Enter the last tube position number (e.g. 1); the PRESS key will light.
m) Enter the minimum carrier pressure value e.g. 0.28 MPa (approximately 90% of the column pressure.) The last operation of the ENTER key enters the total method into memory and extinguishes all keys and displays.

Gas Chromatography

Single ramp program 323K (50°C) for one minute followed by 15°C/minute program to 523K (250°C), which is then held for 30 minutes.

a) Set the oven temperature to the required initial temperature (323K, 50°C).
b) Set d 1 to zero
c) Set rl to any value.
d) Set l1 to 50°C
e) Set d2 to 1 minute
f) Set r2 to 15°C/minute.
g) Set l2 to 250°C.
h) Set d3 to 30 minutes.

Example chromatogram from AMS Model 93 Gas chromatograph



```
CHROMATOGRAM   1  MEMORIZED

C-R5A  CHROMATOPAC
CHANNEL NO  1                          FILE        0
SAMPLE NO   0                          METHOD       41
REPORT NO   7

PKNO      TIME      AREA  MK  IDNO     CONC       NAME

   1     4.631       268                  3.1263
   2     4.886       227                  2.6547
   3     5.033       863  V              10.0722
   4     5.565      3940                 45.9726
   5     5.672      1408  V              16.4286
   6     5.878      1125  V              13.1246
   7     9.039       241                  2.81
   8    10.038       498                  5.8109
               ---------           -------------
        TOTAL       8569                 100
```

Appendix E. Road map approach to oxygen incident ignition causes.

Figure E-1. Road map to assess the likelihood of pressure shock as a possible ignition source

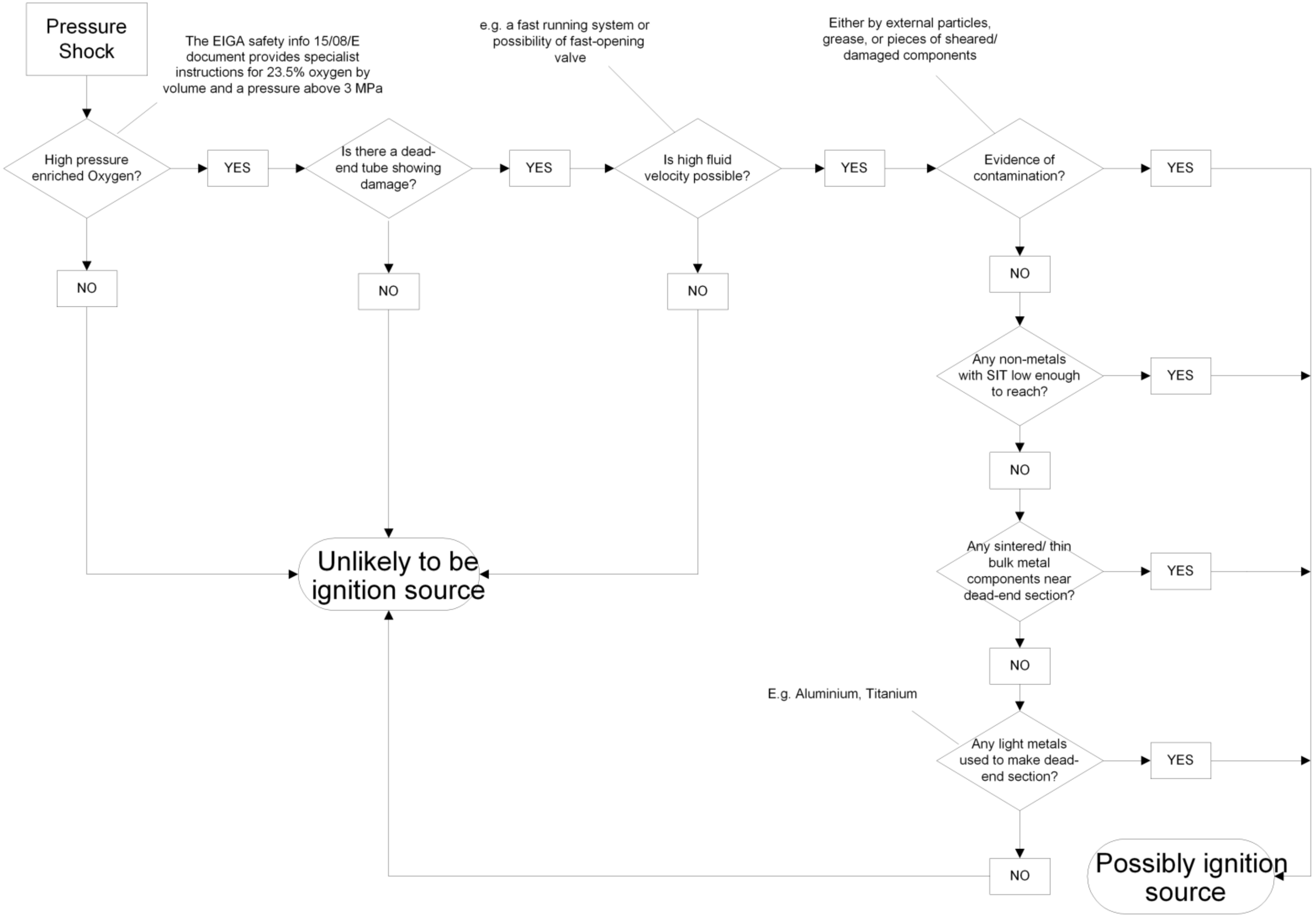


Figure E-2. Road map to assess the likelihood of mechanical impact as a possible ignition source

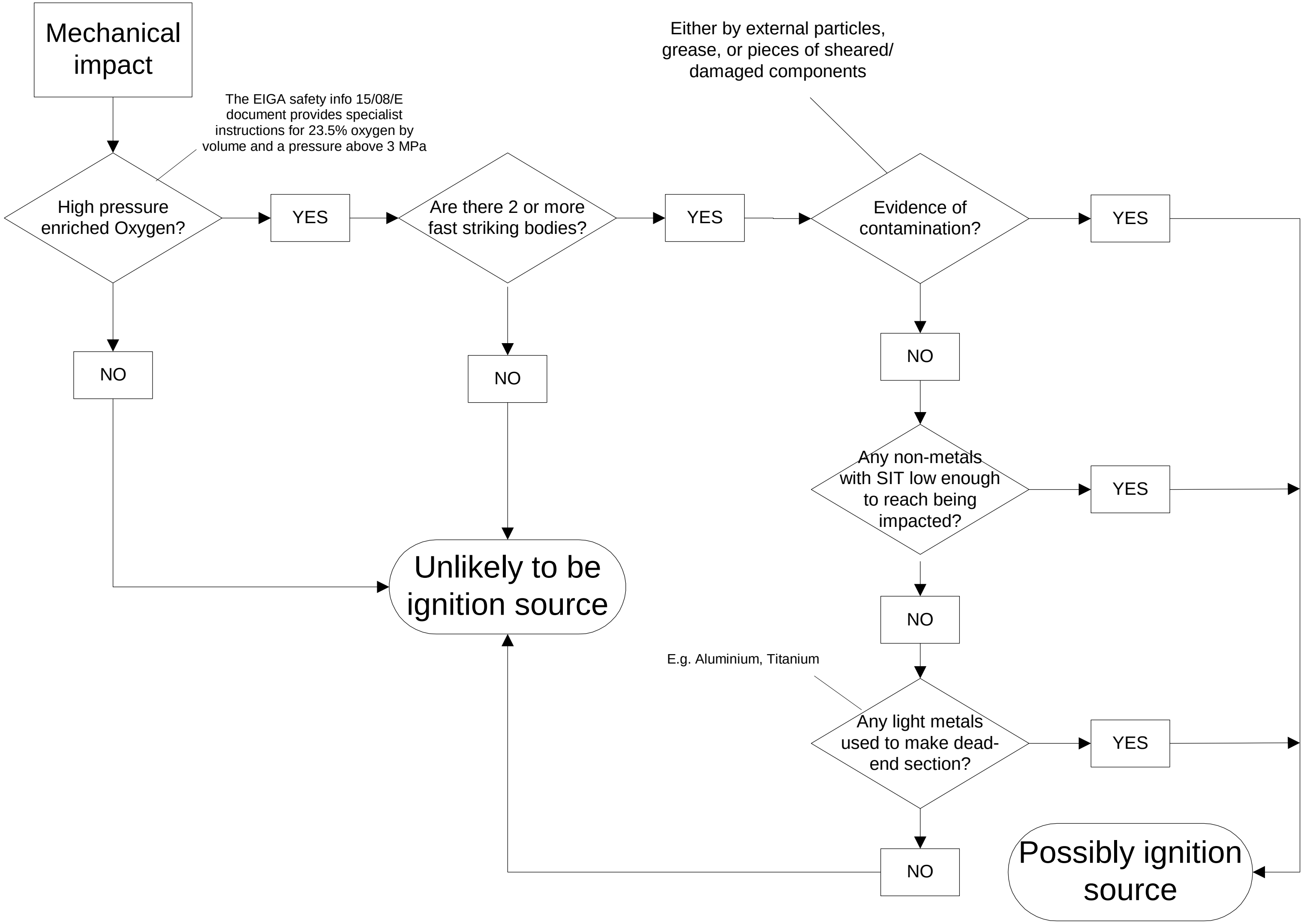


Figure E-3. Road map to assess the likelihood of frictional heating as a possible ignition source

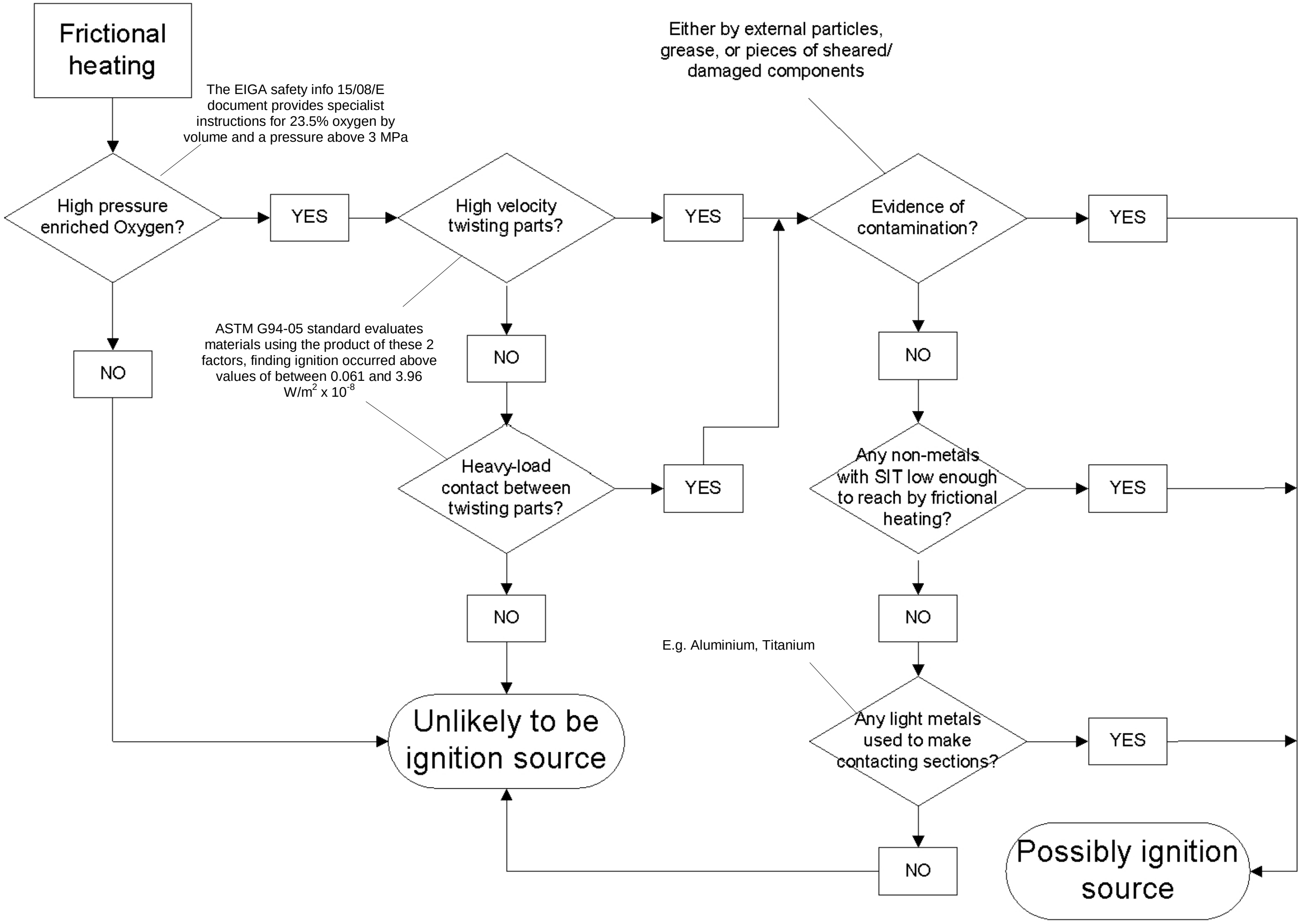


Figure E-4. Road map to assess the likelihood of particle impact as a possible ignition source

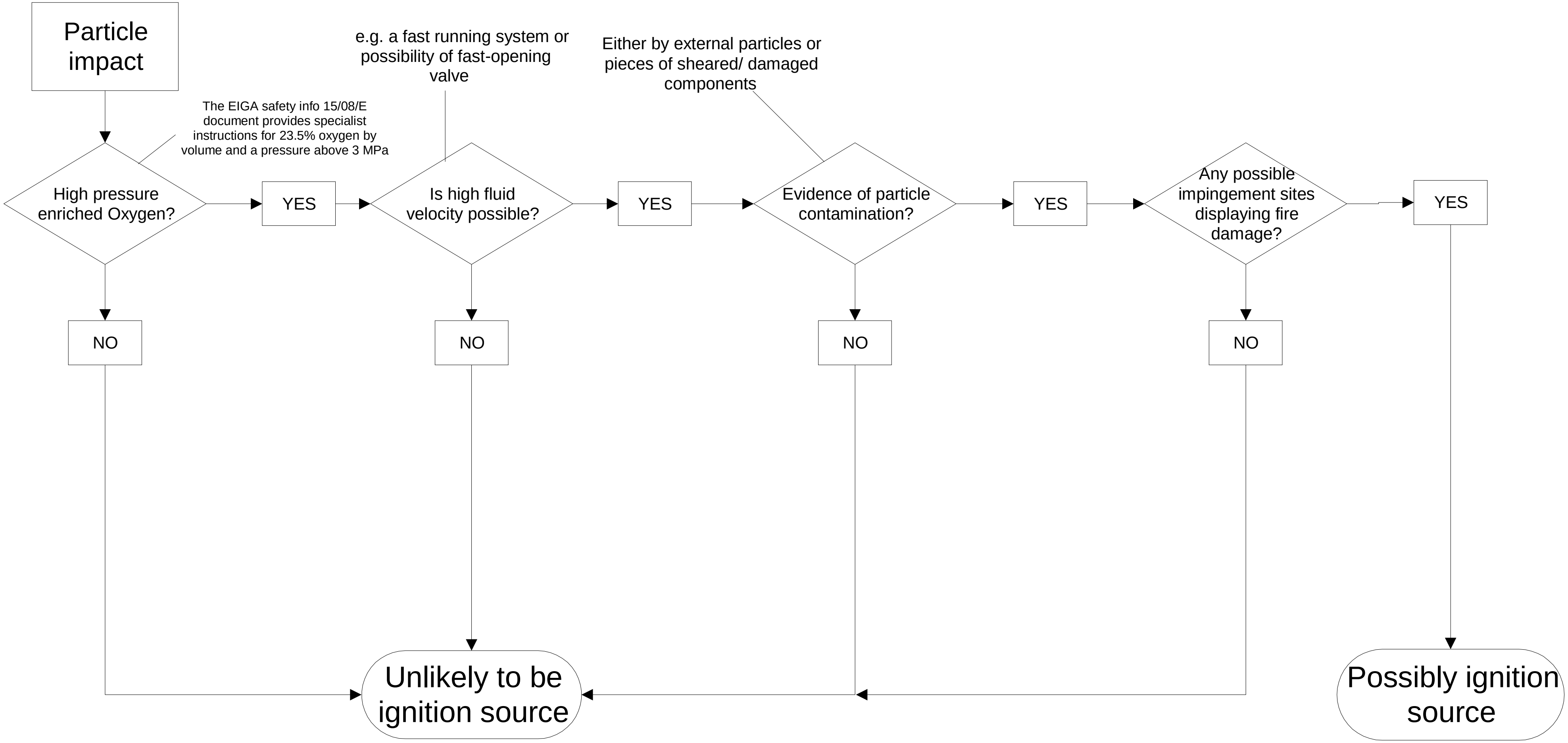


Figure E-5. Road map to assess the likelihood of cavity resonance as a possible ignition source

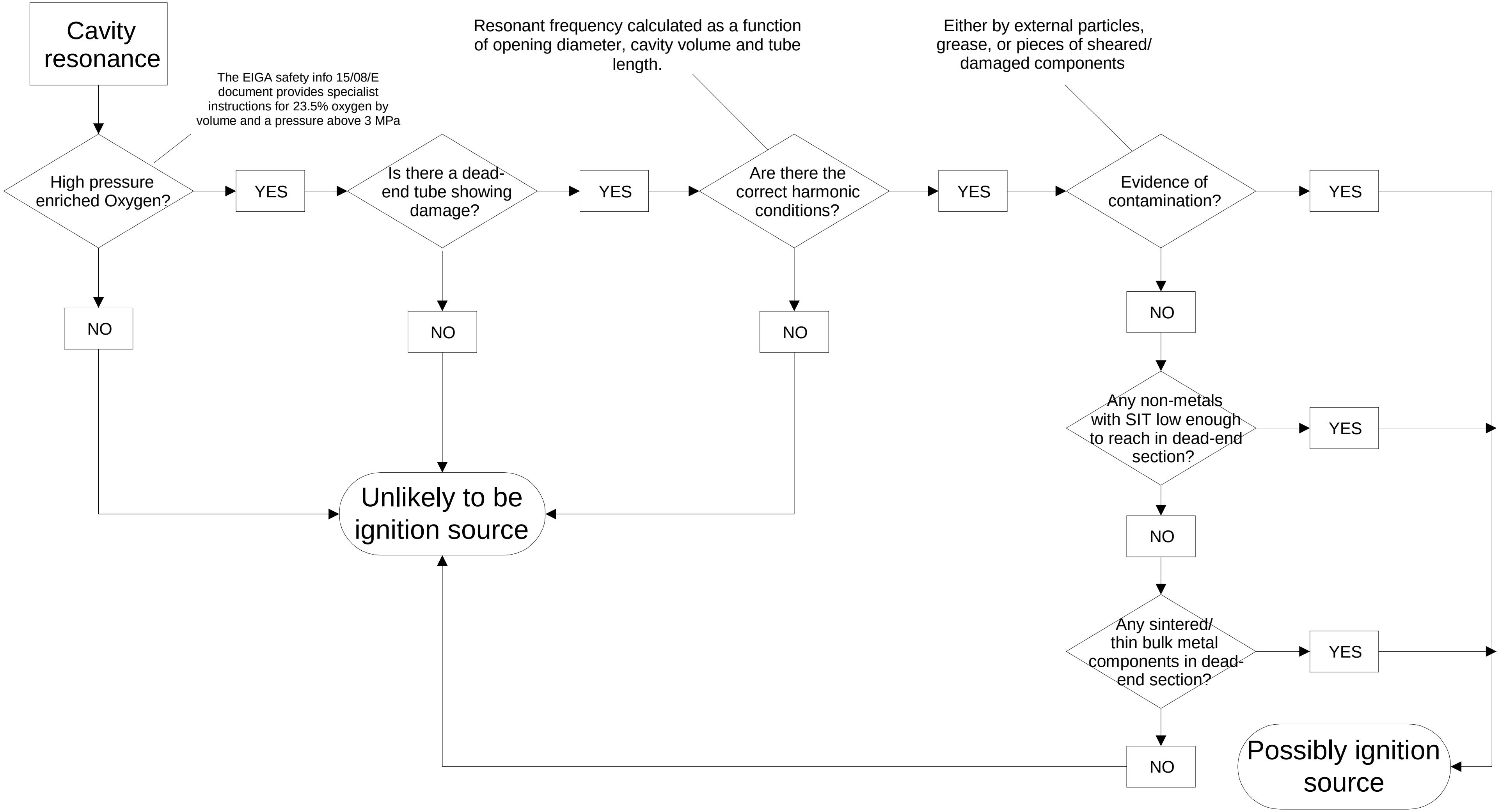


Figure E-6. Road map to assess the likelihood of electric arcing/ sparking as a possible ignition source