



The development of a model for the prediction of polymer spontaneous ignition temperatures in high pressure enriched oxygen across a range of pressures and concentrations



C.M. Benson ^{a,*}, A.M. Bishop ^b, J.M. Ingram ^a, R. Phillips ^b, P.F. Nolan ^{a,1}

^a London South Bank University Explosion & Fire Research Group, 103 Borough Rd, SE1 0AA, UK

^b Honeywell Aerospace, Bunford Ln, Yeovil, BA20, UK

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ABSTRACT

High pressure enriched oxygen is used in a wide number of areas, including aircraft, medical breathing apparatus, diving, mining and mountaineering operations. It is also used for a number of industrial processes, but is most commonly used for combustion. 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. Thus the criteria used for polymer selection is key to preventing, or at least limiting, the possibility of a catastrophic oxygen incident which endangers both property and human life. In this work spontaneous ignition temperature (SIT) data obtained in high pressure enriched oxygen from both differential scanning calorimetry and oxygen bomb testing are compared. A model is derived to enable the calculation of a SIT of a non-metal at any pressure and oxygen concentration using existing test data from other pressures. This has been shown to work with reasonable success for most materials tested, being validated using the comparison of test data from the oxygen bomb test and Pressurised Differential Scanning Calorimetry (PDSC) testing. These results may indicate the suitability of a PDSC for safety testing in the future. Further work is needed to increase the data base of ignition test data from PDSCs, and thermodynamic constants to allow for the direct comparison, and to assess the suitability of this apparatus for safety testing of more materials.

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1. Introduction

Oxygen is vital to sustain life and for this reason life support systems or breathing apparatus are used in a wide number of areas, including civil and military aircraft, medical breathing apparatus and hyperbaric chambers, and diving, mining and mountaineering operations. It is also used in a number of industrial processes, but is most commonly 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 resultant energy released is enough to bring about further oxidation of any fuel, and 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 complete failure of the system. These catastrophic failure events in oxygen systems, known as oxygen incidents, can result in the destruction of property, injury or endangerment of life.

There are relatively few recognised causes of ignition in oxygen incident scenarios (BS 5N 100-5, 2006). The majority of these often involve the ignition of non-metals. Non-metals feature in almost all oxygen system components. Although they are far more prone to ignition than metal components non-metals are selected due to their necessary physical properties, e.g. elasticity. The criteria used for polymer selection is key to preventing, or at least limiting, the possibility of an oxygen incident. This is particularly true in high

* Corresponding author.

E-mail address: bensoncb@lsbu.ac.uk (C.M. Benson).

¹ Deceased, August 2014.

pressure enriched oxygen systems as increasing the oxygen pressure or concentration causes the Spontaneous Ignition Temperature (SIT) of the polymer, the temperature at which it will auto-ignite with no other required external energy input, to be dramatically reduced.

Crude guidance for polymer selection is available from 'league tables' and from experimental data obtained from various methods and equipment (Benson, 2015), but these only apply to particular environmental conditions. They do not take into account changes in oxygen concentration, or pressure. They also do not allow engineers to 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. Thus there is a need for predicting the performance of materials under a variety of conditions.

This work will continue to develop and apply a mathematical relationship to predict a non-metal's SIT, validated with experimental data (both Bomb and Differential scanning calorimetry tests), and show that it can be applied to any conditions employed in new designs, or involved in an incident. This universal model will also enable the use of more accessible measurement apparatus.

1.1. Illustrative oxygen incidents and the scale of the problem

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). This section will demonstrate both how serious oxygen incidents can be, and the scale of the problem showing the number of serious incidents that have occurred over the course of a relatively short period of time, both nationally in the UK, and internationally. A large number of oxygen incidents have been described in the literature.

Fowler and Baxter (2000) detailed the occurrence of several incidents in the UK involving pressurised oxygen in the period 1996–1998. One involved an oxy-acetylene cutting equipment incident. 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 £1M worth of damage, but fortunately no one was injured. Seven of the incidents reported by Fowler and Baxter (2000) involve 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.

Other hazards of high-pressure oxygen can be demonstrated using two other incident case-studies. 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 contamination, e.g. by 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 contaminant particle impact.

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 23 MPa. 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.

Dicker and Wharton (1988) reported 28 high pressure oxygen incidents between 1982 and 1985. Gregson (2008) recorded 158 oxygen incidents had been reported to the HSE between 1996 and 2002, including 59 minor injuries, 25 major injuries and 5 fatalities. Of course these are just the reported cases. It is possible that a number of more minor cases may have gone unreported.

One recent example, described by Kelly et al. (2013), details a regulator failure in an Intensive care unit in. This incident resulted in one patient having severe burns, 2 staff member having breathing difficulties and a great deal of disruption to other patients and staff on the medical ward.

This is not just a problem in the UK, but also internationally. The NASA Oxygen-Enriched Fire Incidents reporting site (2013) records 119 documents on oxygen incidents between 1984 and 2009, primarily in the US armed forces, hospitals or similar commercial establishments in the USA. 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. Of the incidents listed 12% mention incorrect material use (all but 3 are incorrect polymers), 5% are attributed to contamination (usually of oil), 4% to adiabatic compression/pressure shock and 3% to particle ignition. However 54% do not state a cause, or identify, either, contamination, particle impact or adiabatic compression/pressure shock as possible ignition sources due to burn damage and insufficient evidence. 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

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