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.

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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.

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.

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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 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 pressurized 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 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.

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 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). Huang et al (2009) discuss 38 incidents in hyperbaric chambers in China resulting in 77 deaths.

These incidents not only show how oxygen systems and their use can cause serious incidents, they show how big an issue this is for a range of industries. One way of limiting the problem is the selection of the correct materials. Some compatibility criteria have been developed to aid in the material choices to prevent or reduce the chances of ignition, and are described in the following section.

1.2. Historical polymer selection

Historically there are a number of criteria that have been used for assessing the flammability of materials in high pressure enriched gaseous oxygen. They include criteria created by industry bodies, engineering companies and from academia. A summary of the major methods can be seen in Table 1.

One of the best methods for polymer flammability assessment is the Lapin (1973) "Acceptability Index" and "Equivalence Concept". This was used by Air Products Ltd to assess every polymer for use with oxygen service (Ikeda 1983). Lapin determined that the Oxygen Index of a material would be the most important since it was desirable that a material should not burn at all, however 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.

He devised a scale of minimum Acceptability Indices (i) for specific end use materials, using:

$$i = \frac{O^2 T_{AI}}{\Delta H_c}$$
Eqn. 1

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 and is still used today to assess materials flammability (McCord et al 2008), but is complex, requiring the use of 3 different test procedures which makes it far less repeatable than other methods. The oxygen index test was originally not done at elevated pressures although this was facilitated later (Benning 1983).

In the UK the main standard is BS 4N 100-6 (1999). In the USA, the ASTM G88-05 (2005) incorporates a number of other standards to give an overall picture of oxygen system risk assessment and materials' selection. They both primarily rely on the following tests. They also contain some existing ignition test rank tables for assessing the suitability of material use in high pressure enriched oxygen systems, which industry may use instead of doing expensive and time consuming testing of materials at high temperatures in pure oxygen.

One of the main methods of flammability assessment is the oxygen bomb test. Results from McGuire (1993) using this test are used in this work for comparison with the derived model. This method covers the determination of the temperature at which liquids and solids will spontaneously ignite. The current UK standard is the BS 4N 100-2 (1999) bomb test (discussed later in section 4.1) although a number of others also exist (ASTM G72/ G72M – 09 2009, Wegner et al 1988, Vagnard et al 1991). The data from these tests would be collated in a league table, enabling comparison of the materials, for example Court (2001) uses the Maximum

Working Pressure (MSP), defining it 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 a figure of 100 °C below the SIT for a working temperature (Wegner et al 1988). These enable comparisons in very specific circumstances. A Differential Scanning Calorimeter (DSC) measures change of enthalpy with time versus temperature (see experimental section for a more detailed description). It compares an empty reference pan to a test sample being heated at a constant rate. Some DSC instruments can be pressurized (PDSC), and operated in oxygen atmospheres to determine the onset temperature of an exothermic event, which can be equated to the SIT.

Pot tests are designed to replicate the conditions in low pressure flowing systems (BS4N100- 2, Keeping 1971, Wegner et al 1988) e.g. conditions found in oxygen hoses or masks, with pressures below 0.69 MPa, and a maximum temperature of 673 K (400 °C). 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.

A standard Critical oxygen index 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 it can be performed at higher pressures depending upon the application of the material under test. High Pressure COI 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 (Benning and Werley 1986). This apparatus increased the previous maximum pressure limit of 2 MPa to 20 MPa. Primarily 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.

One of the simplest criteria that can be used to look at flammability is the heat of combustion (Lowrie 1983). Described by Benning (1983) as the third line of defence, the heat of combustion and mass can be used to work out the maximum possible energy produced by an oxidation reaction in the system. The heat release from combustion allows the reaction to self-perpetuate in the absence of external energy input. 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,

$$\Delta H = m \Delta H_c$$

Eqn. 2

Where
ΔH = Total energy release
m = Material mass

ΔH_c = Heat of combustion of material

Yuen et al (1988) concurs, stating that the heat of combustion has a great influence on whether the combustion reaction will start at all. This is a simple and fast method of assessing a material's flammability, and to compare materials, but is overly simplistic to be relied upon for oxygen system safety, and does not take into account the changes made to polymer makeup beyond the base chemical, or overall ignition probability.

A far more configurational test, although useful, is the pneumatic impact/ adiabatic compression test. This simulates conditions similar to the fast opening of valves, exposing a sample to a series of pressure shocks (BS EN ISO 2503:2009, ASTM G74-08 2008). Adiabatic compression/ shock wave ignition is regarded as one of the most common causes of fires in oxygen systems, (Gallus and Stoltzfus 2006) making the results of this test very useful.   Another test geared towards a particular configuration is the mechanical impact test, which generally

involves a sample being placed in liquid oxygen (BS4N100-2 1999, ASTM G86-98a 2011) and subjected to an impact from a plummet however some work has been done in gaseous environment, but primarily on metals like aluminium (Chiffoleau et al 2006).

Some attempts have been made to model the flammability of materials based on their chemical structure and degradation products gases they give off on thermal degradation (Albahri & George 2003, Gharagheizi 2011, Benson 2015) however these have been mixed in their success. The use of some form of real test data is still regarded as a far better method of material flammability grading.

Of these methods the bomb test is the most common standard method for thermal autoignition assessment however a PDSC may perform a very similar role. In the following sections these two apparatuses are used to find the SIT of a range of polymers and a relationship is developed to compare the 2 sets of data.

Table 1. Summary of major methods to assess polymer suitability for high pressure enriched oxygen

Test/ method	Conditions
Heat of combustion	Simple measure of flammability giving indication of likelihood of onward combustion based on energy release upon initial oxidation. Limited usefulness as pure materials are tested with no batch to batch, configuration, or pressure change, variation consideration.
Differential Scanning Calorimetry	Apparatus commonly used to show polymer properties, such as glass transition temperature. Can demonstrate exotherm onset that can be equated with equated with SIT.
Pot tests	Flowing oxygen environment test for polymer components such as tubes and gas masks. Generally give higher SIT values than the Bomb Test.
Critical Oxygen Index	Flowing oxygen environment test measuring the oxygen concentration capable of supporting combustion. Tests for non-metals generally performed at 1MPa although 20 MPa has been tested. Does not give an indication of temperature and is therefore not useful for high pressure enriched oxygen systems where oxygen concentration are close to 100%.
BS 4N 100 Bomb test	Used to conduct SIT measurement across a range of pressures and oxygen concentrations. Accurate and useful but expensive, time consuming, and ignition temperatures do not take into account variation in rank order across different pressures.
Lapin (1973) "Acceptability Index" and "Equivalence Concept".	Index involving oxygen index, SIT and enthalpy of combustion.

2. Prior oxygen bomb testing - Measurement of Polymer SIT using the BS 4N 100 high pressure bomb test

The high pressure bomb apparatus was used by McGuire (1993) as part of the programme to identify the SIT of non-metals. Tests were conducted on a large number of polymer samples and a description is included here for discussion but fully described in McGuire (1993), and BS 4N100-2 (1999). The London South Bank University bomb is an example of the BS 4N 100-2 (1999) bomb test. It allows test pressures up to 45 MPa and a maximum temperature of 550°C (823 K).

A 100 ±2 mg sample was split into 20 equally sized blocks (i.e. approx. 5mg), and then cleaned (in accordance with BS 5N 100 – 7). The samples were then inserted into the combustion boat, in the combustion vessel, which in turn was lowered into the containment vessel (see figure 1).

The test environment consisted of 99.5% oxygen.   A heating rate of 10°C/min was used. The combustion vessel was purged, and filled with oxygen to the required pressure, while the containment vessel was filled with nitrogen (maintaining the equilibrium. Tests were conducted at a fixed pressure, from 5 to 40 MPa (See Table 2 for pressures McGuire (1993) tested at).

The temperature of the system is raised until ignition is detected by thermocouples places immediately above the sample.   As the temperature of the system is raised, so is the pressure (as it is a constant volume), so gas is vented manually to maintain a constant pressure.

After completion the oxygen was vented at the same time as the nitrogen.

Table 2 shows Spontaneous Ignition Temperature (SIT) test results acquired by McGuire (1993) using the BS 4N100 bomb test, testing in 99.5% oxygen for a number of polymers, in a range of test pressures. McGuire reports standard deviations of 2 materials assessed in the apparatus, Neoprene and Fomblin oil, as 0.43 K and 5.7 K respectively, stating that all materials showed similar levels of repeatability.

Insert Figure 1. A diagram of the Bomb test apparatus

Table 2. High Pressure bomb test results

Material	Pressure, MPa	SIT, K	Material	Pressure, MPa	SIT, K	Material	Pressure, MPa	SIT, K
Aflas	9	609	Polybutadiene	8	473	Silicone Rubber	5	587
	13.2	591		12	461		9	588
	15	585		13.2	460		13.2	583
	25	575		16	452		30	553
	29	573		29	441		36	557
	33	568	Polychloroprene	10	473		40	548
Fluorel	8	623		13.2	466	Vespel SP21	8	691
	13.2	609		25	450		13.2	673
	16	605		39	443		17	673
	31	601	Polyurethane	5	495		25	663
	35	600		6	503		29	660
	40	600		13.2	494		35	660
Nylon 6,6	6	498		15	491		39	660
	13.2	478		27	482	Viton	6	628
	15	475		38	478		12	602
	27	468	PTFE	5	773		13.2	598
	35	463		9	768		16	596
	40	463		13.2	763		33	584
PCTFE	6	728		22	763		35	573
	13.2	708		35	763		37	573
	19	708						
	27	698						
	35	695						

Data from McGuire (1993)

3.   Experimental section - Measurement of the effective polymer SIT using the PDSC – TA Instruments 2910

A Differential Scanning Calorimeter (DSC) calculates the energy released or absorbed by a material by comparing it to an empty reference sample holder.   The instrument heats both at the same rate and measures the temperature difference between them, or the energy required to keep them the same temperature. The TA 2910 is a pressurized DSC. The exothermic onset temperature, or Oxygen Induction Temperature (OIT), can be approximated with a material ignition temperature, and thus the results can be compared with results obtained using the Bomb test apparatus (See section 4-1).

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 apparatus compares the sample in the crucible with an empty reference crucible as they are heated (see figure 2). As the samples must be exposed to the enriched oxygen environment they are tested in an open aluminium crucible. The crucibles are placed on a constantan disc inside the high pressure cell. The PDSC pressure cell is then enclosed inside a steel pressure vessel, capped with a pressure cover, to allow pressurisation.

The apparatus has two pressure control valves (inlet and outlet), a pressure gauge to monitor the internal pressure, and a pressure relief valve at the rear. The chamber was sealed, and purged using Nitrogen, and then filled with oxygen and pressurised to 3.4 MPa.

The chamber was then heated from ambient to 873 K (600°C) at a ramp rate of 10 K/ min (matching the bomb test ramp rate). As the temperature increases 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.

Similar testing was also carried out using a Mettler DSC under atmospheric condition but the majority of materials (as expected) did not ignite making this unsuitable for oxygen service assessments, and thus the results are not reported here.

Insert Figure 2. A representative diagram of the PDSC apparatus

4.   Results and discussion

Table 3 shows results for a number of polymers, acquired at 2.1 MPa and 3.4 MPa, using the PDSC to identify the onset temperature, or effective SIT. It should be possible to develop a relationship between these data for each material i.e. devise an equation, incorporating all of the pressure and temperature variations 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. Similar to the bomb test the majority of test schedule results showed a standard deviation of less than 10K (Nylon less than 15 K).   Only Vespel at 3.4 MPa showed an unusually high standard deviation of 25K.

Table 3. Pressurised Differential Scanning Calorimetry TA Instruments 2910 results

Material	SIT at 2.1 MPa, K	SIT at 3.4 MPa, K
Aflas 100S	628	607
Polychloroprene	688	626
Nylon 6,6	636	628
Polybutadiene	436	431
Silicone rubber 2451	611	605
Silicone rubber S87	585	578
Vespel SP21	782	761

There may be a problem comparing some polymers. 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. 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. The development of a model for the prediction of SITs of non-metals in high pressure enriched oxygen atmospheres

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.

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. The fire triangle demonstrates the three major factors in combustion; fuel, oxygen, and ignition energy. Assuming that ignition energy is supplied 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 and material configuration (e.g. size, shape, thickness etc.).

A relatively simple model is derived here, and data obtained 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 discussed.

Glassman and Yetter (2008) 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:

$$-r = \vartheta C_A C_B \qquad \text{Eqn. 3}$$

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 $_{A \, (polymer)}$ (mol L^{-1})
C_{B0}	=	Initial concentration $_{B \, (oxygen)}$ (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;

$$-r = \vartheta C_{A0}(1 - \omega_A)C_{B0}(1 - \omega_B) \qquad \text{Eqn. 4}$$

The Arrhenius equation is:

$$\vartheta = Ae^{-\frac{E}{RT}} \qquad \text{Eqn. 5}$$

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:

$$C_B = \frac{n}{V} = \frac{P}{RT}$$

<div style="text-align:right">Eqn. 6</div>

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, 5 and 6;

$$-r = Ae^{-\frac{E}{RT_{ig}}} C_A \frac{P}{RT_{ig}}$$

<div style="text-align:right">Eqn. 7</div>

$$\ln - r = \ln A - \frac{E}{RT_{ig}} + \ln C_A + \ln P - \ln RT_{ig}$$

<div style="text-align:right">Eqn. 8</div>

$$\ln P = \frac{E}{RT_{ig}} + \ln RT_{ig} - \ln A + \ln(-r) - \ln C_A$$

<div style="text-align:right">Eqn. 9</div>

$$\ln P = \frac{E}{RT_{ig}} + \ln \frac{RT_{ig}(-r)}{A C_A}$$

<div style="text-align:right">Eqn. 10</div>

This can be written as

$$\ln P \approx \frac{a}{T_{ig}} + b$$

<div style="text-align:right">Eqn. 11</div>

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

$$\log P = \frac{a}{T_{ig}} + b$$

<div style="text-align:right">Eqn. 12</div>

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

$$a = \frac{E}{R}$$

<div style="text-align:right">Eqn. 13</div>

$$b = \ln \frac{RT_{ig}(-r)}{AC_A}$$

<div style="text-align:right">Eqn. 14</div>

The relationship derived in equation 11 might enable smaller scale test data to be used to predict the SIT of non-metals at far higher pressures.

4.2. Hydrocarbon activation energy

Equations 10 and 11 show a constant a defined as the combustion reaction activation energy, E, divided by the universal gas constant, R. Some thermal decomposition products of polymers are smaller constituent molecules. The activation energies for the combustion of some hydrocarbons in a range of conditions are shown below in table 4. They have a spread from 158 to 253 kJ/mol. It might be expected therefore to see values for E/R of between approximately 14500, and 30400 K (2.s.f) (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.

Table 4. Selected hydrocarbon oxidation activation energy

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	O_2 (5- 50%) & air. 503-573K. Up to 0.027 MPa.	217
Egerton et al (1957)	Methane	723-773K 0.013-0.053 MPa.	163
Griffin and Pfefferle (1990)	Methane	800-1100 K	188
Murty Kanury (1975)	Propane	O_2 & air	130
	n-Octane	O_2 & air	167.36
Melvin (1966)	Methane	Air & 60-90% CH_4. 623K. Up to 5.8 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	Diluted CH_4: O_2 mixtures. 1175-1880 K	196
Slack and Grillo (1981)	Methane	Oxygen and air. 1640-2150 K	218.8
Trimm and Lam (1980)	Methane	Stoichiometric CH_4: air mixture. <800K	172
Vandenabeele et al (1960)	Methane	CH_4 (10-25%), O_2 (10%-40%) and N_2; 300-700 K	158

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.

4.3. Prediction and comparison of SIT results at different pressures, oxygen concentrations, and in different apparatus.

Figure 3 below shows the combined data from the LSBU polymer bomb tests (obtained from 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 relatively similar, supporting the hypothesis that one relationship might be used for the calculation of a SIT of any polymer, at any pressure.

Insert Figure 3. The relationship between the reciprocal of the SIT, and the natural logarithm of the environmental pressure

This data and some additional bomb data was analysed and an average gradient of all the trend lines was calculated to be 20934 K (Benson 2015). This is within the bounds predicted in section 5.3 based on the activation energy for the combustion of simple hydrocarbons. It may be possible to use this gradient where no real value of E/R has been obtained to give an approximation, although a material specific value would give far greater accuracy. Using this relationship, it should now be possible to predict the SIT of polymers at any pressure.

4.4. Calculation of SIT at a variety of pressures

The relationship derived from the rate equations and bomb data (equation 11) 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:

$$\ln P_1 - \ln P_2 = \frac{a}{T_{ig1}} - \frac{a}{T_{ig2}}$$

Eqn. 15

Therefore:

$$\frac{1}{T_{ig2}} = \frac{1}{T_{ig1}} - \frac{\ln(P_1 / P_2)}{a}$$

Eqn. 16

This equation should allow the use of one 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 individual polymer should be measured and used.

NASA employees have 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 5.

Table 5. The NASA Bryan and Lowrie (1986) results of the G72/ G72M – 09 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 the relationship in equation 11 is applied 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 16. 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 6.

The calculated SIT values for all materials are similar to those measured using the NASA G72/ G72M – 09 (2009) 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 6. Comparison of Bryan and Lowrie (1986) results with calculated SIT values for 6.8 MPa in 99.5% oxygen

	E/R, *a*	Measured SIT, K	Calculated SIT, K
Polychloroprene	9263	457	448
Vespel SP-21	8415	610	594
Fluorel E-2160	25001	596	589
Nylon 6,6	9958	475	501

Below in tables 7 and 8 equation 16 has been used on the measured PDSC data to calculate predicted results for 13.2 MPa. The model calculated using results in table 8 are also compared Bomb test results in Figure 4.

At 2.1 MPa the calculated SIT for Vespel SP21 is 1% below the measured valued, while at 3.4 MPa the calculated value is 1% above the measured. For both pressures, the predicted results for Aflas 100S, Polybutadiene and the 2 varieties of Silicone rubber are all between 1 and 15 % below the measured ignition temperatures. The results for Polychloroprene, and Nylon 6,6 are well above. This may be due to a number of reasons.

Table 7. A Comparison of SIT values predicted for 13.2 MPa from 2.1 MPa PDSC test data, and Bomb test results for 13.2 MPa

Material	Predicted SIT, K	Measured SIT, K	% variation
Aflas 100S	571	591	-3
Polychloroprene	616	466	32
Nylon 6,6	569	478	19
Polybutadiene	397	460	-14
Silicone rubber 2451	562	583	-4
Silicone rubber S87	539	583	-8
Vespel SP21	668	673	-1

Table 8. A Comparison of SIT values predicted for 13.2 MPa from 3.4 MPa PDSC test data, Bomb test results for 13.2 MPa

Material	Predicted SIT, K	Measured SIT, K	% variation
Aflas 100S	566	591	-4
Polychloroprene	580	466	24
Nylon 6,6	578	478	21
Polybutadiene	403	460	-12
Silicone rubber 2451	545	583	-7
Silicone rubber S87	568	583	-3
Vespel SP21	678	673	1

Insert Figure 4 (a, b and c). Graphs showing a comparison of predicted and measured SIT results (including one standard deviation measure) for selected polymers across a range of pressures in 100% oxygen

*P denotes the line represents the predicted model results calculated using the PDSC result for 3.4MPa.

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. One polymer particularly prone to SIT variation (more than other engineering polymers), although widely used in oxygen systems, is polychloroprene. 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/ G72M – 09 (2009) test at 10.8 MPa auto-ignited at temperatures ranging from 423K to 593K (150°C to 320°C). There is no information whether these tests are performed with the same variety of chloroprene. Future work should examine the variation within this material. Nylon is known to be capable of absorbing water. How it is stored, and how long for, can dramatically affect the SIT and thus SIT results can be extremely variable (Swindells et al 1988). Additionally measured SIT values for Polybutadiene are far lower than expected, and to a similar degree for both test pressures. It is possible that the material was not cured or aged to the same degree as the material used for bomb testing. It is also possible given the unstable nature of materials in the high pressure oxygen environment that this lower temperature ignition might have been due contamination of the sample by oils

either prior to delivery to the laboratory, that were not removed by the cleaning schedule, or following cleaning (although all care was taken for this to not occur).

Variations in this data may also be explained by another factor affecting material's flammability. Swindells et al 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.

It should also be possible to consider oxygen concentration in a similar way. 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 9. 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 9. 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 relationship in equation 16, demonstrating this can be applied to the data from the bomb tests and other oxygen auto-ignition test results.

Table 9. Comparison of SITs at different oxygen and nitrogen levels (Court 2001) with SIT values calculated for different oxygen partial pressures using data for 100% oxygen.

Material	Oxygen %	SIT, K	Calculated SIT, K
Bromo-butyl rubber	100%	464	-
	60%	472	469
	40%	474	474
Nitrile rubber	100%	542	-
	60%	558	549
	40%	555	555
Viton A	100%	591	-
	60%	601	600
	40%	607	607
Makrolon	100%	593	-
	60%	602	602
	40%	609	609

4.5. Other considerations

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.

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.

5. Conclusion

A model derived in this work enables the calculation of the SIT of a non-metal at any pressure, and oxygen concentration for a number of materials with reasonable success. This calculation cannot be done without existing data, 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 testing apparatus can be used to determine materials suitability for high pressure oxygen.

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.

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Figure 1
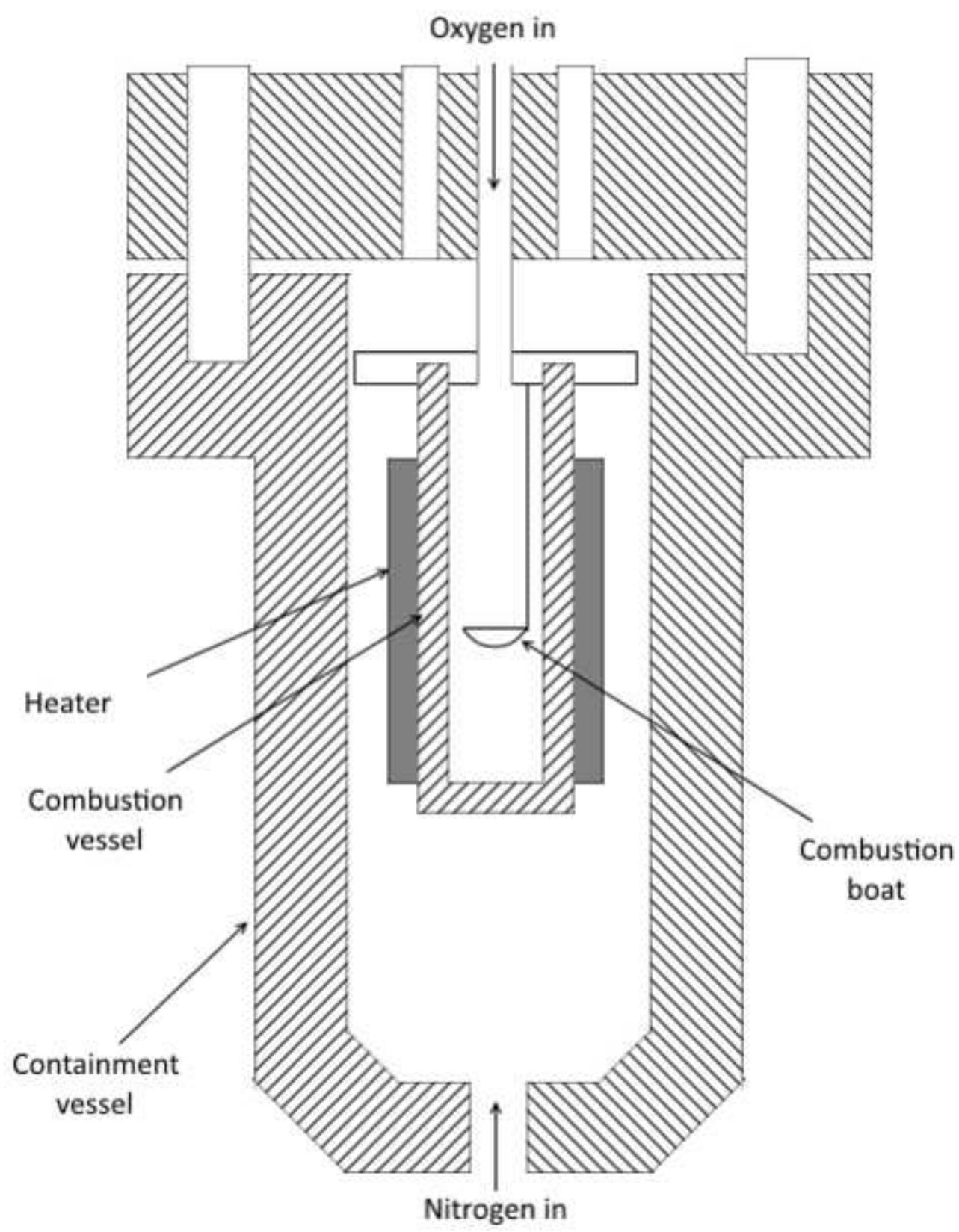**Click here to download high resolution image**

Oxygen in

Heater

Combustion
vessel

Containment
vessel

Combustion
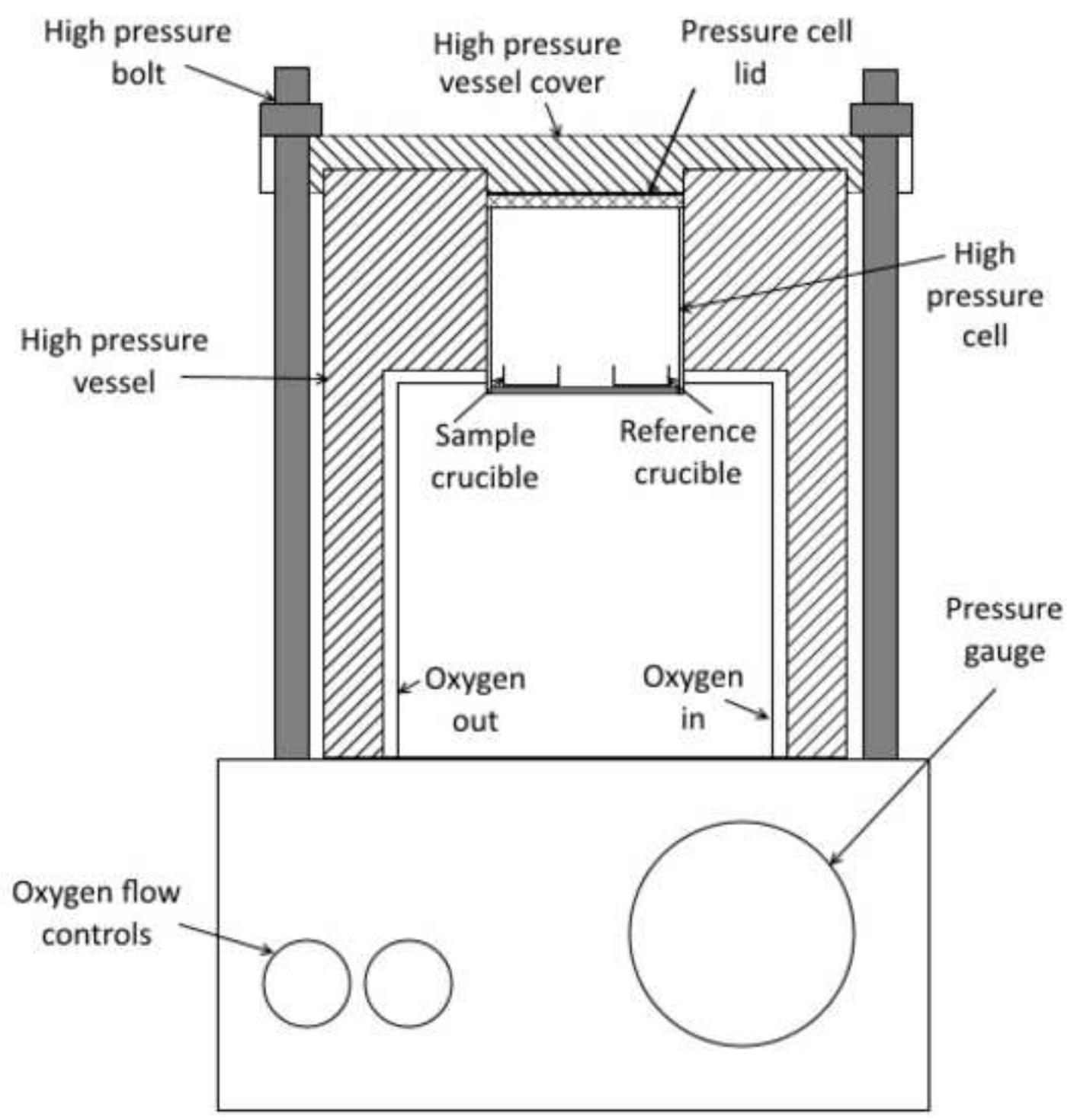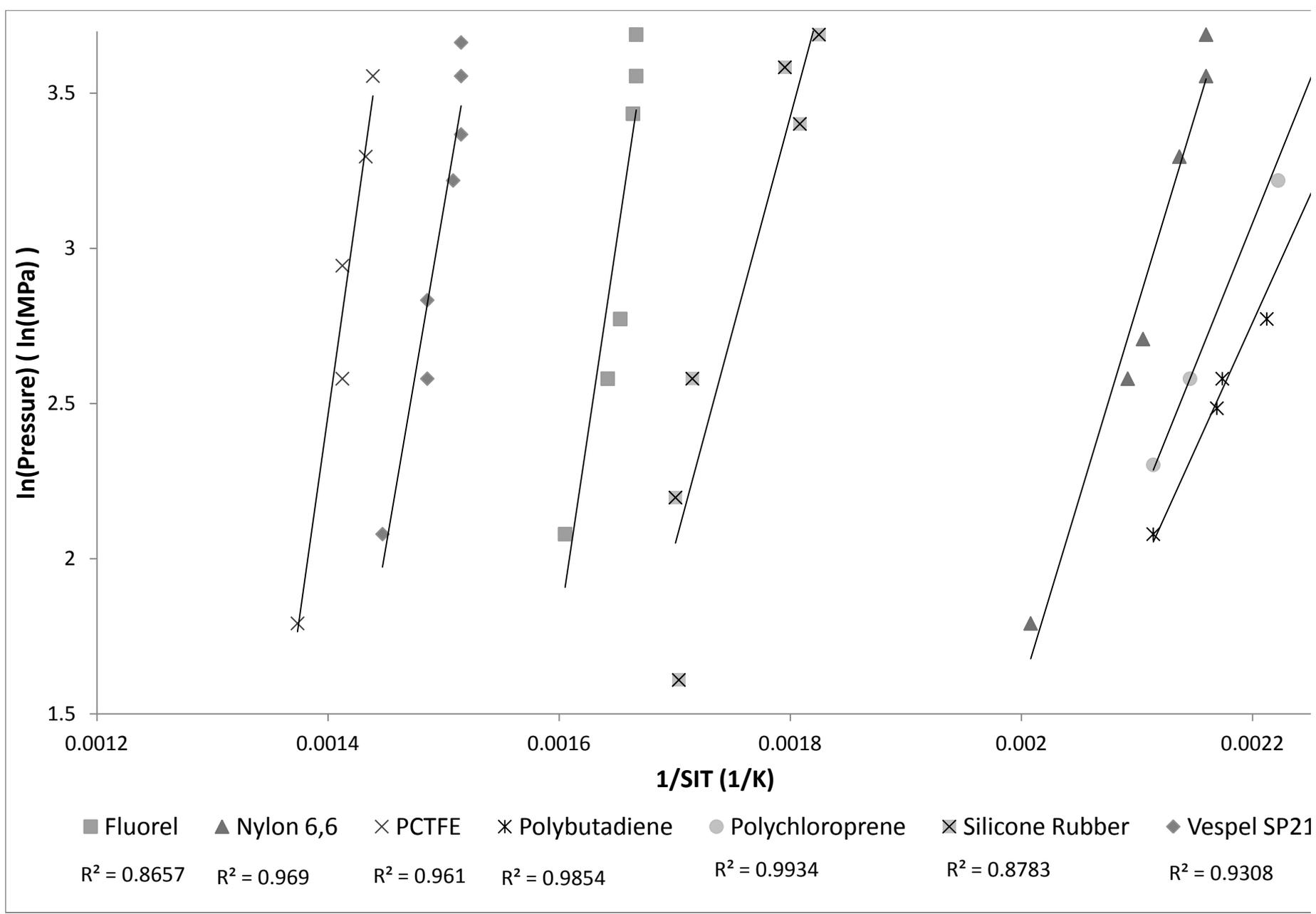boat

Nitrogen in

Figure 2
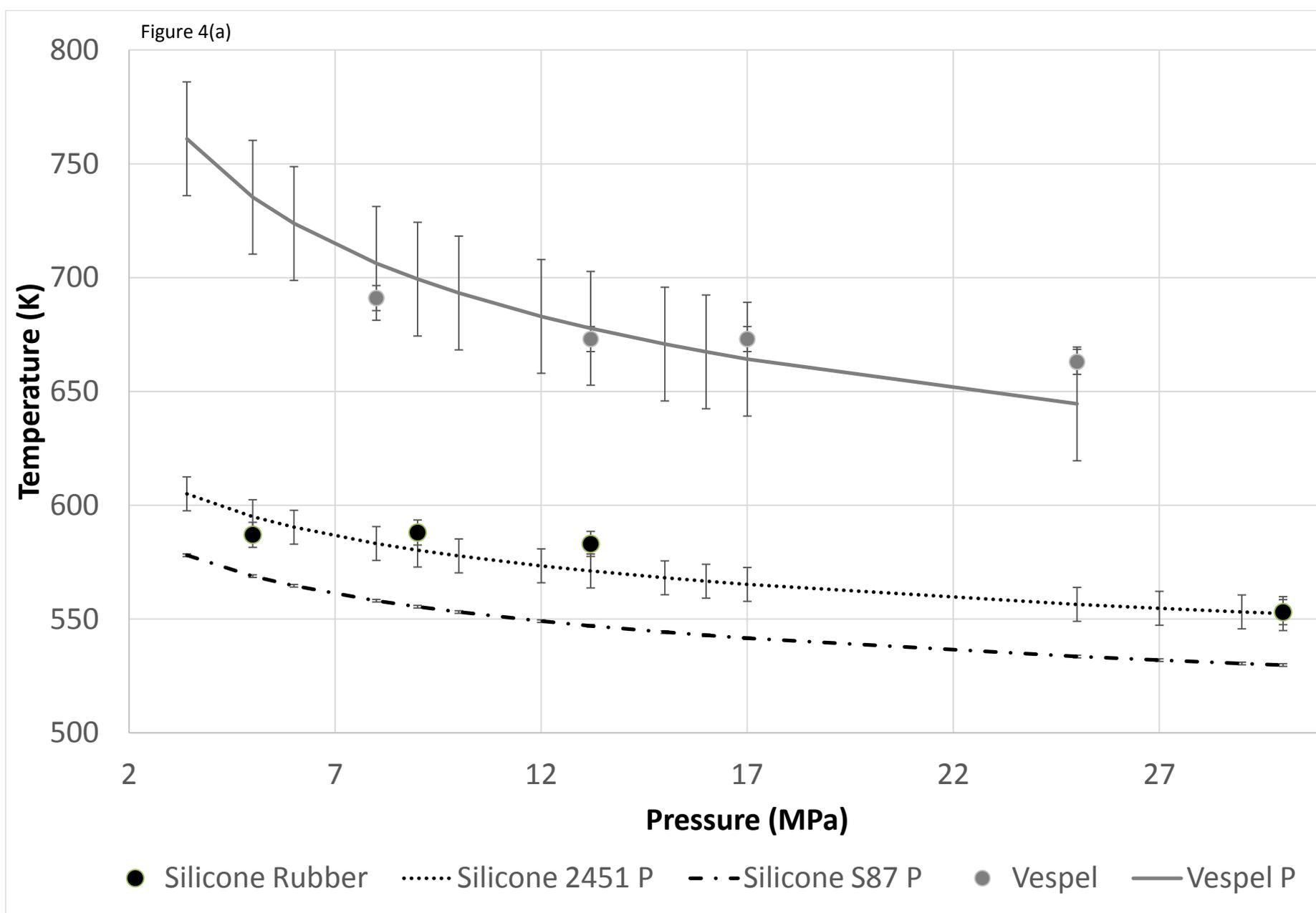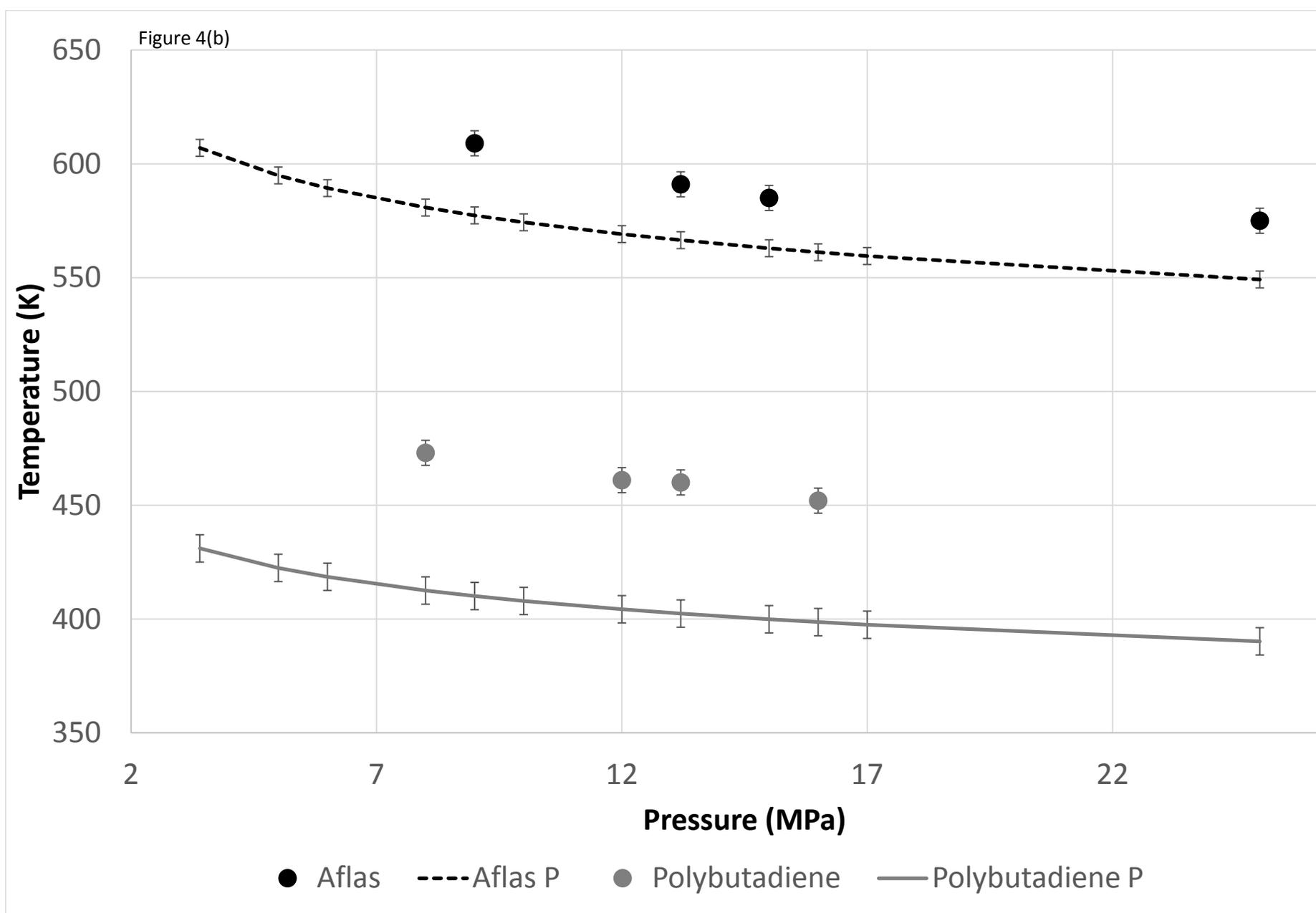**Click here to download high resolution image**

Figure 3

Figure 4(a)

Figure 4(b)

Figure 4(c)