IDENTIFICATION OF VOLATILE ORGANIC COMPOUNDS IN EARLY STAGES OF FIRE FROM COMMERCIAL PRODUCTS

BY

KATHRYN DICKENS

A thesis submitted in partial fulfilment for the requirements for the degree of Master of Science(by Research) at the University of Central Lancashire

November 2016

uclan
University of Central Lancashire

STUDENT DECLARATION FORM

Concurrent registration for two or more academic awards

Either *I declare that while registered as a candidate for the research degree, I have not been a registered candidate or enrolled student for another award of the University or other academic or professional institution

Material submitted for another award

Either *I declare that no material contained in the thesis has been used in any other submission for an academic award and is solely my own work

(state award and awarding body and list the material below):

** delete as appropriate*

Collaboration

Where a candidate's research programme is part of a collaborative project, the thesis must indicate in addition clearly the candidate's individual contribution and the extent of the collaboration. Please state below:

Signature of Candidate ______________________

Type of Award ______**Master of Science (by research)**_________

School __________________**PSC**______________________________

Abstract

Building products, such as insulation materials, are ubiquitous in daily life, but there is a lack of published research on their thermal behaviour and volatiles released in the early stages of a fire. In both analytical and applied applications, knowledge about the chemical processes taking place during pyrolysis is essential. Many techniques have been used to study the thermal degradation of polymers with some having general applicability for polymer characterisation, whilst others including thermal volatilisation analysis, pyrolysis mass spectroscopy and analysis by infrared spectroscopy are used to look at the formation of specific molecules or groups in degrading products as well as changes in their concentrations.

A number of different insulation materials (expanded polystyrene, phenolic foams, polyisocyanurate foams, polyurethane foams and wool-based insulation materials) were analysed via X-Ray Fluorescence, Energy Dispersive X-Ray analysis and a CHNS elemental analyser to provide a brief overview of their elemental composition and allow likely decomposition products to be predicted. The materials were then thermally degraded in both air and inert environments via thermogravimetric analysis, differential scanning calorimetry, micro-scale combustion calorimetry and pyrolysis to identify the decomposition temperatures and points of significant heat and volatile release. The released volatiles were then analysed via Gas Chromatography-Mass Spectrometry and gas phase Fourier Transform Infrared Spectroscopy. The data was analysed in terms of toxicity.

The study found that some common insulation materials released volatiles which have been linked to various health problems. Acute asphyxiants such as hydrogen cyanide, carbon monoxide and carbon dioxide were identified from the FTIR analysis of decomposition in air, while carcinogenic and potentially carcinogenic volatiles, such as benzene and various polycyclic aromatic hydrocarbons, were identified amongst the released volatiles from the GCMS analysis.

From the tests it was found that expanded polystyrene decomposed in two steps in air at approximately 320 and 420°C and one step in nitrogen at approximately 420°C. Styrene was identified as the main product released from both FTIR and py-GCMS studies in both environments. Two phenolic foams showed very similar decomposition, with two steps in air at approximately 310

and 520°C and a number of small decomposition steps in nitrogen. From the py-GCMS studies the strongest signals were obtained from di- and tri-methylphenol isomers (1,3, 2,4 2,5 and 3,6-dimethylphenol and 2,4,5-trimethylphenol), and from the FTIR analysis 1,4-dioxane and sulphur dioxide. The polyisocyanurate and polyurethane foams also showed similar decomposition steps with mostly three degradation steps in air (Around 200, 350 and 550°C for PIR and around 170, 320, and 500°C for PUR samples) and two degradation steps in nitrogen (~200 and ~320°C for PIR and ~200 and ~350°C for PUR). The volatiles released via py-GCMS included two phosphorus based volatiles, tris(2-chloro-1-methylethyl)ester phosphoric acid and bis(2-chloro-1-methylethyl)-3-chloropropylphosphate, indicative of the presence of a fire retardant, while different isocyanates and hydrogen cyanide were identified from FTIR. The fibre materials largely showed very little decomposition, with no real steps identified in either air or nitrogen and no real peaks of heat release. Despite this a known carcinogenic compound, benzene, was identified in the py-GCMS results from one of the fibre samples along with other products that could suggest some fibre samples were treated with phenolic filler however it is not conclusive.

Table of Contents

Acknowledgements

I would like to thank the following people for their assistance, without which this would not have been possible:

First and foremost I am deeply grateful to my supervisor Dr Anna Stec for many things, but most of all for her patience, kindness and support throughout this work.

Professor Richard Hull, who offered guidance and welcome tangential discussions throughout this work.

Jim Donnelly, who can fix anything and find any attachment, and Tamar Garcia-Sorribes, who has endless good ideas, for their friendship and support during my time at UCLan, along with Sal Tracey, who keeps the entire department running and is always there when you need her.

Antony and Fiona, who offered help, support and always something to make me laugh in the office, as well as Artur, who showed infinite patience with my maths questions and Mariëlle, for all the coffee, boxes and hamkas.

Finally to all my friends and family for their love and support, in particular Charlotte, who kept me going with coffee and Sam, whom I owe many coffees, for answering my endless grammar questions.

In memory of Cooper

רומג ליז :אוה השוריפ ךדיאו ,הלוכ הרותה לכ איה וז .דיבעת אל ךרבחל ינס ךלעד

Abbreviations

CHNS Analysis – Carbon, Hydrogen, Nitrogen, Sulphur Analysis

CO – Carbon Monoxide

CO_2 – Carbon Dioxide

DSC – Differential Scanning Calorimetry

EDAX – Energy Dispersive X-Ray Analysis

EPA – Environmental Protection Agency (US)

EPS – Expanded Polystyrene

FTIR – Fourier Transform Infrared Spectroscopy

GCMS – Gas Chromatography Mass Spectrometry

HBDD - Hexabromododecane

HBCD – Hexabromocyclododecane

HBr – Hydrogen Bromide

HCl – Hydrogen Chloride

HCN – Hydrogen Cyanide

IARC – International Agency for Research on Cancer

MCC – Microscale Combustion Calorimetry

NO – Nitrogen Oxide

NO_2 – Nitrogen Dioxide

PAHs – Polycylic Aromatic Hydrocarbons

PF Foam – Phenolic Foam

PF Resin – Phenolic Resin

PIR Foam – Polyisocyanurate Foam

PS – Polystyrene

PU- Polyurethane

PUF – Flexible Polyurethane Foam

PUR Foam – Rigid Polyurethane foam

Py-GCMS – Pyrolysis Gas Chromatography Mass Spectrometry

SW – Stone wool

TBBPA - Tetrabromobisphenol A

TGA – Thermogravimetric Analysis

TGA-FTIR – Thermogravimetric Analysis coupled with Fourier Transform Infrared Spectroscopy

VOC – Volatile Organic Compound

XRF – X-Ray Fluorescent Spectroscopy

List of Figures

List of Tables

1. AIMS AND OBJECTIVES

This study aims to investigate the thermal decomposition of insulation materials via identification of the temperatures at which decomposition occurs, and which volatiles are released at different stages of degradation. This study uses thermogravimetric analysis and gas phase Fourier Transform Infrared spectroscopy (TGA-FTIR) alongside Differential Scanning Calorimetry (DSC) and Pyrolysis Gas Chromatography Mass Spectrometry (py-GCMS) in order to identify the volatile organic compounds (VOCs) released in the early stages of fire. The materials undergo elemental composition analysis in order to provide basic information on the materials' composition before proceeding with decomposition analysis. Thermal decomposition is carried out by TGA, DSC and Microscale Combustion Calorimetry (MCC). FTIR allows for the volatiles released across the whole decomposition range to be identified. Finally, various GCMS methods are used, tested and optimised in order to find the most suitable method for py-GCMS analysis of different insulation materials. Py-GCMS analysis is carried out in helium and air over a large temperature range, and repeated in helium for specific temperature ranges (determined from the TGA-FTIR and DSC results) to identify pyrolysates. The main identified volatiles are then assessed in terms of toxicity.

2. INTRODUCTION

Insulating materials have a wide range of applications that mean they are a constant presence in everyday life. They are used in buildings, in construction, in carpets, electrical appliances, toys and clothing amongst other products.[1,2,3] They can be used to meet weight and noise reduction targets as well as to provide heat insulation.[1] It is important to study the pyrolysis products, both with and without the addition of fire retardants, in addition to different thermal decomposition conditions. This enables an understanding of the effects that these can have on the composition of the smoke released the early smouldering stages of fire and the chemistry of the fuel entering the flame zone, as well as in long-term smouldering scenarios such as waste fires.

There is limited information on volatiles and material behaviour in the early stages of fire. The breakdown of any materials can cause the formation of acute asphyxiants such as carbon monoxide (CO), hydrogen cyanide (HCN), or irritants such as hydrogen chloride (HCl), hydrogen bromide (HBr) and nitrogen oxides (NO, NO_2).[4] Additionally, aromatic compounds such as polycylic aromatic hydrocarbons (PAHs) and chronic toxicants such as benzene and other organoirritants can be formed and released.

Three types of non-flaming early fires have been defined by ISO in relation to toxic hazards as shown in Table 1.[5]

Fire Stage	Heat /kW m^{-2}	Max Temp /°C		Oxygen %		$\frac{V_{CO}}{V_{CO_2}}$	Combustion Efficiency %
		Fuel	**Smoke**	**In**	**Out**		
Non-flaming							
1a. Self-sustained smouldering	n.a.	450 - 800	25 - 85	20	0 - 20	0.1 – 1	50-90
1b. Oxidative, external radiation	-	300 - 600		20	20		
1c. Anaerobic external radiation	-	100 - 500		0	0		

Table 1 - Adopted ISO 19706 classification of non-flaming fire stages from ISO 19706[5]

Non-flaming thermal decomposition occurs when a polymer reaches a sufficient temperature to thermally break down, known as pyrolysis (usually between 100-500°C). The simplest pyrolysis (anaerobic external radiation, Table 1) generally occurs in inert atmospheres. Most polymeric materials will decompose, under these conditions, into a small range of organic compounds generally consisting of those similar to the parent monomers or polymers. If the temperature of the surface is raised further, to around 300°C, then thermal decomposition by oxidative pyrolysis can occur, with the products consisting of larger quantities of partly decomposed organic molecules, higher molecular weight PAHs, carbon monoxide and smoke particulates.[6,7,8]

2.1. Building materials and their pyrolysis products

Building products, such as insulation materials, are ubiquitous in daily life, but there is a lack of published research on thermal behaviour and released volatiles in early stages of fire. In this study, some of the most commonly used building materials were tested, falling into two broad categories: foam based materials and inorganic fibrous materials. The foam-based materials were polystyrene, phenolic foam, polyisocyanurate foam and polyurethane foam. These materials are all commonly found as insulation materials in the structures of modern buildings themselves as well as in a wide variety of functions within homes and businesses. The inorganic fibrous materials included mineral, stone and glass wools.

2.1.1 Polystyrene

Polystyrene is a widely used plastic polymer made from styrene monomers. It comes in two forms, an expanded foam material and a solid material. The foam has many common uses, as an insulation material, in packaging and also for single use cases such as food containers.[9–15] According to the EPA, it is the fourth largest thermoplastic product by production volume.[9] In the form of expanded polystyrene (EPS), it has a density of between 10–50kg/m^3, depending on manufacturer's specifications.[15] However, EPS as an insulation material has also been linked to fast spreading fires, and in its raw form has relatively high flammability and low thermal stability, meaning it often incorporates fire retardants in an attempt to increase its safety and suitability as a building insulation material.[12] Of these, the most common are brominated fire retardants, most commonly hexabromocyclododecane (HBCD) in EPS.[14,16,17]

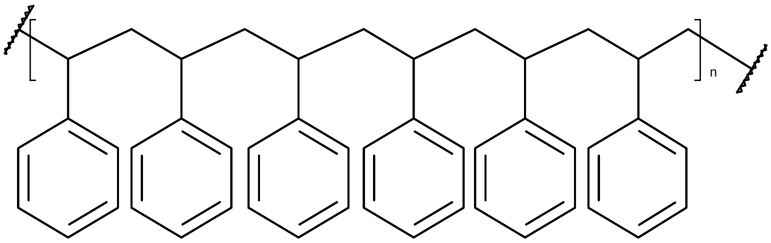


Figure 1: Chemical structure of polystyrene

The thermal degradation of polystyrene (Figure 1) has been extensively studied and is widely accepted to be a two-step process in air, with the first and largest step occurring between 250-500°C and a second, relatively small, step occurring between 450-575°C.[18,19] It is thought that the degradation of PS takes place in what is known as an unbuttoning reaction with radicals formed during the initial thermal scission taking part in the reversal of the polymerisation process.[18,19,20] However, under nitrogen it was discovered that the reaction took place in one step between 250-500°C.[19,21] Kannan *et al.*[19] performed an in-depth study into the thermal decomposition of EPS specifically under different gaseous environments and their results agreed with the studies on PS, suggesting that the decomposition of the granulated and expanded polystyrene takes place in a very similar manner.

As the decomposition behaviours of PS and EPS are almost identical, it follows that the products released when PS decomposes are likely to be similar to those of EPS. In 1989, Cullis *et al.* carried out a detailed study into the pyrolysis products formed from PS. They found that below 300°C pyrolysis did not occur at a noticeable level, and at higher temperatures the dominant product was styrene.[13,22] The average yield for styrene was between 42-45% and more recent studies have supported this research, meaning that the main product released during the thermal decomposition of PS is the styrene monomer.[18,20,2,22,12] Small amounts of other products can also be detected. A summary of the other products identified from several different pyrolysis studies of polystyrene is shown in Table 2.

Publication	Conditions used	Products Identified
Thermal Degradation of Polystyrene in Different Environments[13]	Thermogravimetry at 300°C in dynamic nitrogen, followed by analysis using MS and IR spectroscopy for the highly volatile products and GCMS for the less volatile products.	Styrene, toluene, alpha-methylstyrene, styrene dimer and trimer.
Thermal Degradation of Polystyrene Composites[23]	Direct pyrolysis mass spectrometry with an initial heating rate of 5°C/min to 50°C, followed by 10°C/min to 650°C then a 5 minute hold.	Styrene, benzene, toluene (in addition to some hydrocarbons only identified by molecular formula).
A Thermal Degradation Study of Insulation Materials Extruded Polystyrene[12]	Py-GCMS from room temperature to 700°C at 10°C/min in an inert environment	Styrene, toluene, alpha-methylstyrene, styrene dimer
Impact of Brominated Flame Retardants on the Thermal Degradation of High-Impact Polystyrene[17]	Thermogravimetric analysis in a helium environment, followed by GC-MS. Samples were decomposed from 50-700°C at a rate of 5°C/min.	Styrene, Toluene, alpha-methylstyrene, 1,3-diphenylpropene, styrene dimer, diphenylpropene, diphenylpentadiene, diphenylpentene, diphenylhexadiene, methylphenylnaphthalene, styrene trimer, triphenylhexadiene, quaterphenyl

Table 2: Summary of pyrolysis studies of polystyrene

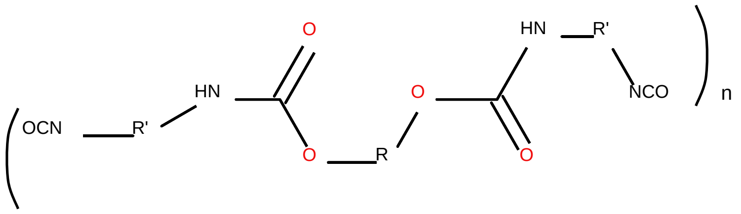
As styrene is consistently the main product released, it is also worth considering the decomposition products of styrene itself. In particular, studies have been carried out to investigate the release of PAHs from the decomposition of styrene under pyrolysis. Westblad *et al.* performed an in-depth study into this by batch combusting styrene which detected more than 50 PAHs released from styrene with 16 being considered to have had a significant yield. [11]

16 PAHs with significant yield as identified by Westblad *et al.*[11]	The samples were pyrolysed between 300-1000°C across 2 furnaces in air. The volatiles were captured in a resin, extracted using methylene chloride, and then identified via GCMS.	indene, naphthalene, biphenyl, acenaphthalene, fluorine, phenanthrene, anthracene, fluoranthene, acephenanthrylene, pyrene, benzo[g,h,i]fluoranthene, cyclopenta[c,d]pyrene, benzo[b]-flouranthene, benzo[a]pyrene, perylene, benzo[g,h,i]perylene

Table 3: PAHs with significant yield from styrene

2.1.2 Polyurethane foam

Polyurethane (PUR) foam (Figure 2) is a widely used polymer that is particularly popular in the furnishings market. It is also available as a rigid foam for thermal insulation and a flexible foam and is created from a reaction between a polyol and a diisocyanate to form the urethane bonds which act as a repeating unit.[24–26] Closed cell foams have gas bubbles trapped within their polymer matrix are rigid, whereas open cell foams have air "tunnels" within the matrix forming flexible foams as they have greater flexibility or elasticity.[24–26,31] One broad categorisation was that rigid PUR foam is formed with methyl diphenyl isocyanate while flexible PU foam uses toluene diisocyanate, however many modern flexible foams are formed using methyl diphenyl isocyanate.[27] They have an average density of 30-80 kg/m^{3,} with the variation due to the differing compositions, additives and monomers used by manufacturers.[15] Flexible PU foam is most commonly used in mattresses, sofas and chairs, which make up nearly 30% of the total PU foam market, whereas rigid foam is more commonly found in insulation panels.[24,26] The polyurethane foam market as a whole was estimated to be worth around £266 billion in 2013, and further growth is predicted.[25] Flexible PU foam is known to be particularly susceptible to smouldering due to the open cell structure.[24] Traditionally both rigid and flexible PU foam have incorporated halogenated fire retardants.[28] However in recent years these are being replaced by phosphorus-based fire retardants due to health concerns.[29,30,31] The current market-leading fire retardants used to treat rigid foams such as PUR and polyisocyanurate foam (PIR) are tris(2-chloroethyl) phosphate (TCEP) and tris(1-chloro-2-propyl) phosphate (TCPP), in addition to other related compounds. [28]



R and R' represent hydrocarbon groups which change based on manufacturer specification.

Figure 2: General structure of PU foam

Both types of PU foam consist of nitrogen, oxygen, carbon and hydrogen atoms. The hydrocarbon chains (R and R') can be expected to produce hydrocarbons on decomposition, whilst the linkage groups can produce aldehydes, ketones, acids, amines, cyanides, esters and phenols. In addition, CO and HCN are found to be the main gases released from oxidative decomposition of PU foam.[32] The difference in temperatures and number of degradation steps between these studies suggests that the degradation of PUR foam is highly dependent on the specific composition of the foam (as represented by the R groups in Figure 2 and on the crosslinks between the chains) and thus can vary between manufacturers, but normally consists of various chain length hydrocarbons.

Jiao *et al.* studied the thermal degradation of rigid PUR foam via thermogravimetric analysis.[33] They found that in air the degradation was a three step process. Initial weight loss occurs between 110-190°C, with the next step at around 200°C. The final step occurs between 350-500°C. The products identified during this degradation are highlighted in Table 4.[33]

Herrera *et al.* also tested the thermal degradation of flexible PU in nitrogen and in air and found that it decomposed in two to four steps under nitrogen), and three steps in air.[32] A further study on flexible PUR foam found that it first decomposes into isocyanates and polyols formed by the monomers, and polyol decomposition occurs at around 280°C in oxygen and 330°C in nitrogen.[24] This study also highlighted that flexible PUR foam can be particularly susceptible to smouldering.[24] No specific volatiles were identified.

However a study carried out in 2014 by Terakado *et al.* found that for flexible PU foam tested in an inert atmosphere there are two steps, at 250 and 400°C, and for rigid PUR foam only one that occurred between 300-370°C.[34]

Study	Conditions	Products identified
Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS[33]	TGA heated from room temperature to 800°C at 10°C per minute.	Carbon dioxide, polyols, aliphatic ether alcohols, isocyanates, amines, benzyl alcohols and vinyl ethers.

Table 4: Summary of pyrolysis studies of PUR foam

2.1.3 Polyisocyanurate foam

Polyisocyanurate foam (PIR foam), Figure 3, is very similar in composition to PUR, but contains a higher proportion of isocyanates, leading to the formation of isocyanurate groups (Figure 3) within the PU structure. It has characteristically better thermal stability and more fire resistance than PUR foam as the isocyanurate linkage is much stronger than that of the urethane group in PIR foam, whilst keeping the same average density of between 30-80 kg/m^3.[15,35,36] A study by Liggat *et al.* found that the isocyanurate group decomposed at around 300°C[35]. It is relatively rare for PIR foam to be made up of purely isocyanurate linkages, as this results in a very friable foam, therefore it is found that most commercially available foams are a PUR-PIR mixture.[28,35] A thermal decomposition study of a PIR foam discovered that there was an initial small mass loss at 85°C, followed by rapid decomposition at 240°C with the highest rate of mass loss occurring at 280°C.[37] No data on the specific volatiles released was given.

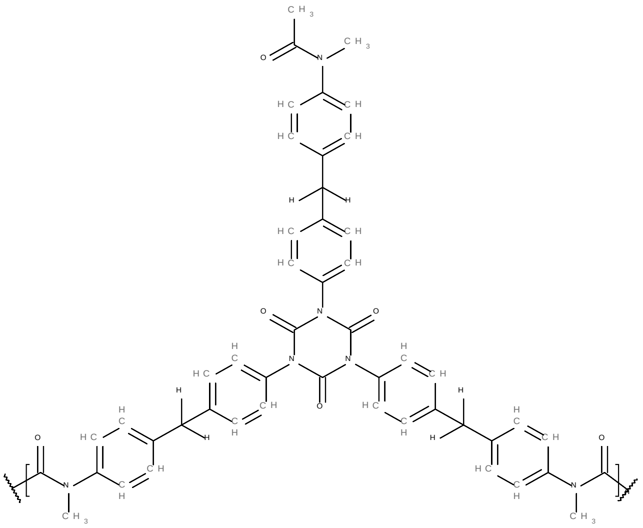


Figure 3: Generic chemical structure of PIR

Based on the composition of PIR foam, the expected degradation compounds are hydrocarbons, ketones, polyenes, esters, benzenes, cyanides, isocyanides and diisocyanides, with gases similar to those of PUR foam; HCN and CO. The isocyanurate ring structure is formed when an isocyanate undergoes cyclotrimerisation.[36] As most commercially available PIR foams contain varying amounts of polyurethane linkages, it is to be expected that many of the products released during the thermal decomposition of PUR could also be released during the decomposition of PIR with the exact proportions heavily dependent on the PIR-PUR ratio of each individual foam. However, there have not been many detailed studies carried out into the decomposition products of either pure PIR foam or the PIR-PUR mixes with the existing studies broadly concentrating on the rigidity and stability of the material and the general kinetics of decomposition.

2.1.4 Phenolic foam

Phenolic (PF) foam displays superior flame resistance in comparison to the other foams discussed, as well as being highly thermally stable.[38] As it has relatively high thermal conductivity, PF has traditionally been used where fire resistance is the critical requirement including in the aerospace and naval industries and as a building material.[38,39] The density of PF is, on average, between 30-40 kg/m^3, allowing for minor variations between manufacturers.[15]

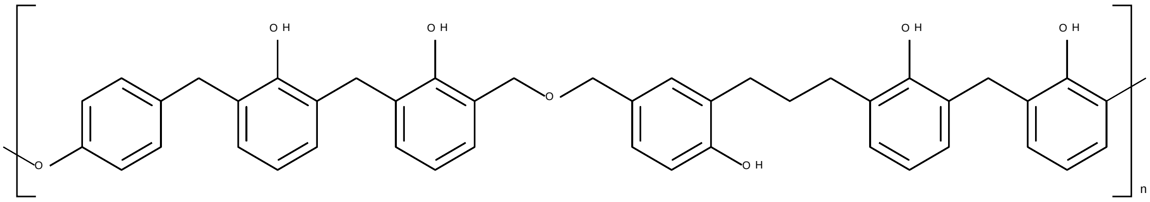


Figure 4: Generic chemical structure of one unit of phenolic foam

Based on the composition of phenolic foam, Figure 4, the primary degradation products are likely to be carbon, hydrogen and oxygen containing compounds, such as hydrocarbons, polyenes, ketones, aldehydes, phenols, alcohols, enols, esters or benzenes. A literature review carried out in 1988 by Johnston *et al.* showed that the major products during pyrolysis in air and nitrogen are carbon monoxide, carbon dioxide and methane, with less than 5% each of formaldehyde and volatile organic compounds such as phenols, methyl phenols and dimethyl phenols.[40] When pyrolysis was carried out at temperatures below 400^{o}C then carbon dioxide, water and formaldehyde were the main products, whereas formaldehyde was not produced beyond 400^{o}C. Between 400-800^{o}C the products comprise of aromatic compounds and gaseous products whereas over 800^{o}C the gases are the dominant products.[40] PF foam is believed to produce relatively low amounts of toxic gases during combustion compared to other insulation materials.[38]

The main volatile products released from PF foam and PF resins are broadly similar across most studies, with various isomers of di- and trimethylphenols being particularly ubiquitous.[41,42,43] In addition to PF itself, phenolic resins are commonly used as binders in mineral wool products to increase the insulation properties of the material.[41,42] It is believed that these produce similar products to phenolic foam itself, with a study on several types of phenolic resins showing that the main products are gaseous compounds such as carbon monoxide, carbon dioxide, ethane and methane.[40] There were also small amounts (less than 5% by weight) of volatile organic compounds such as benzene, toluene, propanols, butanols and dimethylbenzenes found, with phenols identified between 500-1000°C in air.[40]

A study by Jiang *et al.* showed the decomposition mechanism of a phenolic-formaldehyde resin, and released pyrolysis products.[43] They found that when PF resin is pyrolysed between 400-750°C that phenols and methyl phenol derivatives are always the main products.[43] A list of volatiles released by PF resin during their testing is shown in Table 5.

Study	Conditions	Products identified
Phenolics: A Literature Review of Thermal Decomposition Products and Toxicity[40]	A summary of other works	Carbon monoxide, carbon dioxide, methane, formaldehyde, phenol, methylphenols, dimethylphenols
The Pyrolysis Mechanism of Phenol Formaldehyde Resin[43]	Pyrolysis carried out in a pyrolysis device in helium between 400-750°C, volatiles analysed via GC-MS.	Carbon dioxide, Carbon monoxide, Benzene, Toluene, o-Xylene, p-Xylene, Mesitylene, Phenol, o-Cresol, p-Cresol, 2,6-Dimethylphenol, 2,4-Dimethylphenol, Naphthalene, 2,4,6-Trimethylphenol, 2-Methylnaphthalene, Diphenylmethane, 3-Methylbiphenyl, Xanthene, 1,2-Dimethyl naphtho[2,1-b]furan, Anthracene, Methanone, Dimethyl-9H-Xanthene, Trimethyl-9H-Xanthene

Table 5: Pyrolysis products of PF foam and PF resin

2.1.5 Stone wool and glass wool

As stone wool is classified as non-combustible, but contains a pyrolysable binder to hold the involatile "stone" compounds together, there is wide variation of pyrolysis products due to the use of different binders by different manufacturers. [1] There are few reports on the pyrolysis products of the individual binders. It is also difficult to generate a general structure or to anticipate any thermal degradation processes. However, some types of mineral wool are manufactured using phenolic resins as a binder which have been investigated in terms of pyrolysis properties, as explained in the previous section.

Glass wool can also be classified as having low combustibility or being non-combustible dependant on the content of the binder used. It can lose a small amount of its weight due to a pyrolysable binder, typically around 5% or less, however its contribution to fuel load is negligible.[15] Similarly to stone wool, there are few published studies on the degradation products of glass wool and it is also difficult to present a representative structure as it varies with different manufacturers.

2.2 Thermal and analytical methods used for generation and analysis of pyrolysates

Different thermal techniques will enable a more comprehensive evaluation of the compounds released when commercial products undergo thermal degradation in conditions designed to reproduce those of early-stage fires. The effluents from each of the commonly used insulation materials can be then analysed. There are many techniques used to study the thermal degradation of polymers. Some techniques have general applicability for polymer characterisation and others are more specific, correlating degradation temperatures with the released volatiles.[44] Each stage of decomposition that occurs prior to gasification needs to be properly understood on the microscale. Microscale techniques such as thermogravimetric analysis (TGA) combined with Fourier transform infrared spectroscopy (FTIR) (TGA-FTIR), differential scanning calorimetry (DSC), microscale combustion calorimetry (MCC) and pyrolysis gas chromatography-mass spectrometry (py-GCMS) are the most efficient and effective screening tools to identify decomposition steps and released products for complex mixtures of materials.[45] The individual stages of polymer decomposition, which are the key to understanding fire behaviour, can be identified alongside complex processes like heat transfer, polymeric chain breakdown, volatile fuel formation and gasification.[46] They also provide essential insight into both decomposition and fuel production chemistry.

The most common methods reported in literature to monitor these parameters as a function of reaction time are thermogravimetric analysis and pyrolysis to initiate the thermal decomposition and gas chromatography-mass spectrometry and gas phase Fourier transform infrared spectroscopy to analyse the products.[44,45,46,47,48] These are summarised briefly below.

Thermal decomposition methods

Thermogravimetric analysis is an established technique for studying polymer decomposition, including polymers that have been treated with fire retardants. In TGA the mass of a polymer sample is constantly measured whilst the polymer is heated at a fixed rate in a specific atmosphere, either air or inert. The samples are heated in crucibles on a balance beam within a sealed furnace.[49]

The initial mass loss can be attributed to the volatile compounds in the polymer, such as any absorbed water, evaporating off, and then the later mass loss is caused by the decomposition of the polymer, allowing the thermal stability of the sample to be determined. As decomposition can be carried out in both air and inert environments, it is possible to compare the temperatures decomposition occurs at and relative mass loss for each environment.[50]

Differential Scanning Calorimetry is a technique used to measure the thermal transitions of a polymer such as melting point and glass transition temperaturez. A reference pan is heated alongside the sample pan and they are heated at a constant rate. When the polymer undergoes a change, the temperature of that pan reflects the endo- or exothermic process occurring and the difference in energy required to equalise this is monitored. The energy change is displayed as a function of temperature and can be used to quantify the energy change.[48]

Microscale combustion calorimetry, Figure 5, is used to characterise the flammability properties of a polymeric material via the micro-scale use of oxygen depletion calorimetry. It can determine the heat release rate of a compound, the pyrolysis temperature, the char yield and the heat of combustion. A small amount, less than 3 mg, of sample is pyrolysed in the specimen chamber and the products of this pyrolysis are swept by a purge gas into the combustor, where they react with oxygen and the heat of combustion is calculated.[51] The oxygen consumption is converted by the MCC software to represent heat release data as a function of temperature. The pyrolysis gas can either be nitrogen, which is used as the standard to reproduce fire conditions, or air which produces results comparable to a bomb calorimeter.[52]

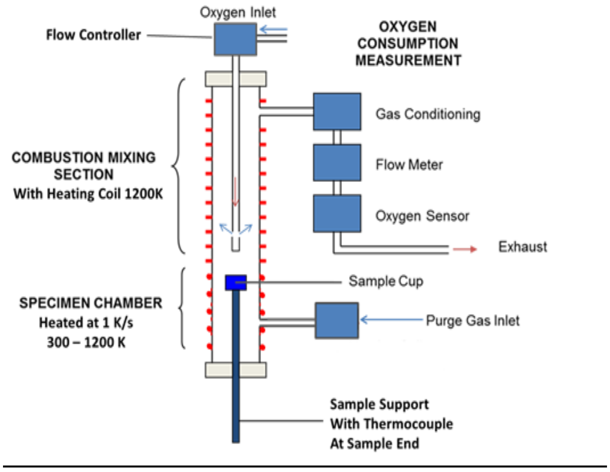


Figure 5: Adapted diagram of the Microscale Combustion Calorimeter[48]

As shown above, the sample is supported on thermocouple- containing stand. The reactant (O_2) gas flows through the top of the MCC and out at the base of the combustion mixing section.

Identification of volatiles

Pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) involves a sample being heated at a controlled rate in a controlled atmosphere for thermal decomposition to occur. The volatiles are then separated via gas chromatography, eluting down a capillary column lined with a suitable involatile liquid.[47] The resulting separated components then are transferred to the mass spectrometer where they are ionised and fragmented, and the resulting chromatogram and the mass spectrum each peak represents can be then matched against a computer database to accurately identify individual components of pyrolysates. [47] It can be carried out in both helium and air environments.[47]

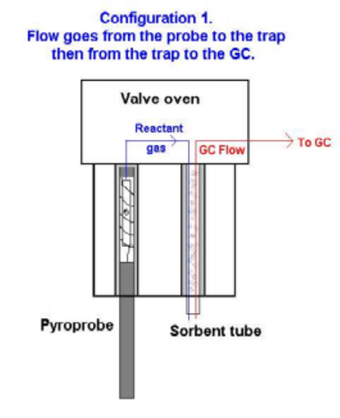


Figure 6: Pyroprobe diagaram

A small amount of sample, around 1 mg, is inserted into a tube inside the pyroprobe (Figure 6) and heated rapidly. The flow of reactant gas pushes the volatiles produced on heating firstly into a trap (sorbent tube), where they are held for a short period of time, then into the GC, as shown by the arrows.

The volatiles enter the GC via the sample inlet and are separated along the column before being transferred into the MS, with lower molecular weight volatiles generally reaching the MS faster than larger volatiles. The MS uses an ion source to ionise the volatiles into fragments of their original molecule. The fragments are then identified by the detector, which outputs the information to the computer. The fragmentation for each GC peak can be compared against a library to identify the volatile behind each peak.[53]

Gas phase Fourier Transform Infrared spectroscopy is another useful method for volatile identification. It uses infrared absorption over the range of wavelengths displayed as a conventional 2D spectrum. Molecules that have a dipole moment and asymmetry produce a characteristic spectrum that is unique to that molecule.[47] However since many components will be present simultaneously, deconvolution of the spectra is a challenging and time-consuming process. Gas-phase FTIR has been developed to identify and quantify a wide range of volatiles released from different fire scenarios and can identify many of the volatiles released with a high degree of accuracy.[12] When coupled to a TGA, the FTIR is set to perform scans over the entire heating range, providing data for several decomposition steps in one run. [47] A potential problem with FTIR analysis is that some compounds can strongly absorb IR radiation to the extent that they overlap with, and in some cases entirely mask, other released products. One of the most common examples of this problem is water.[54]

Elemental composition investigation

In addition, techniques which help with the identification of elemental composition can prove useful when carrying out analysis to identify products released from a decomposing polymer, by proving or disproving the presence of specific elements.

X-Ray fluorescence spectroscopy (XRF) is a technique used to analyse the elemental composition of given materials.[55] When a material is targeted with an X-Ray, an electron is ejected from a lower energy shell and an electron from a higher shell replaces it. The difference in the energy produced as the electron moves to the lower level is released as a characteristic secondary X-Ray, allowing for the elements present to be identified. The main limitation of XRF is that lighter elements cannot be identified such as carbon, oxygen and nitrogen and depending on the specific target each system uses for analysis, there is the potential for wavelength overlap causing problems identifying further elements such as chlorine.[56]

Energy dispersive X-ray spectroscopy (EDAX) is used alongside a scanning electron microscope (SEM). As the electron beam from the SEM interacts with the material, X-Rays are produced in characteristic ranges for each material. This allows for the elements present to be identified and quantified in terms of relative amounts present. [57] However, lighter elements such as nitrogen (with an atomic mass below 14 amu) cannot be identified and depending on the coating used to enhance conductivity other elements may be problematic, commonly carbon or gold.

Carbon, Nitrogen, Hydrogen and Sulphur analysis (CHNS analysis) involves combusting a material at high temperatures in an oxygen rich environment. During this carbon, nitrogen and sulphur are converted to their oxides and dioxides and hydrogen is converted to water and these combustion products are identified using a thermal conductivity detector.[58]

3. EXPERIMENTAL PROCEDURES

This chapter will focus on the use of TGA-FTIR and py-GCMS to identify the volatile organic compounds released in the early stages of fire. The materials were investigated by elemental composition analysis in order to gain some basic knowledge about the materials before proceeding with decomposition analysis. Thermal decomposition was carried out using thermogravimetric analysis, differential scanning calorimetry and microscale combustion calorimetry. Gas phase Fourier transform infrared spectroscopy will additionally allow for the volatiles released across the whole decomposition range to be identified. Finally, pyrolysis-gas chromatography-mass spectrometry methods will be investigated and optimised in order to find the most suitable conditions for decomposition of the insulation materials. Py-GCMS analysis was carried out in helium and air over a large temperature range, and repeated in helium for specific temperature ranges (determined from the TGA-FTIR and DSC results) to identify pyrolysates.

3.1 Materials

A summary table of the materials tested is given in Table 6. The abbreviations in the table are used throughout the experimental section of this work.

Sample name	Sample name used in this work	Picture	Density
Expanded Polystyrene	EPS		17kg/m^3
Phenolic Foam	PF1		35kg/m^3
Phenolic Foam 2	PF2		36kg/m^3

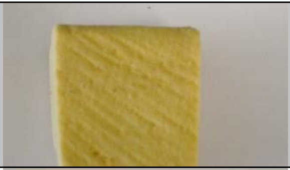
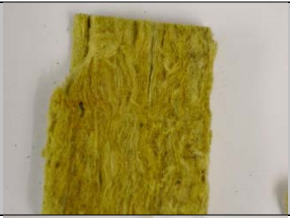
Polyisocyanurate Foam	PIR1		33kg/m^3
Polyisocyanurate Foam 2	PIR2		33kg/m^3
Polyisocyanurate Foam 3	PIR3		34kg/m^3
Polyurethane Foam	PUR1		34kg/m^3
Polyurethane Foam 2	PUR2		35kg/m^3
Stone wool	SW1		170kg/m^3
Stone wool 2	SW2		45kg/m^3
Stone wool 3	SW3		110kg/m^3
Earthwool	EW		15kg/m^3
Glass wool	GW		87kg/m^3

Table 6: Identification of materials tested

3.1.2 Elemental analysis

Elemental composition of the insulation materials was determined by X-Ray Fluorescence spectrometry (XRF), Energy Dispersive X-Ray analysis (EDAX) and CHNS analysis. The presence of chlorine was identified via EDAX analysis as the wavelength overlaps with that of the rhodium target used by the XRF system. Additionally bromine and phosphorus present challenges for the XRF system due to similar overlapping. The identification of Au in some of the EDAX samples is due to the usage of a gold coating in order to enhance the conductivity of the material and obtain better results. As both EDAX and XRF analysis are unable to quantify the presence of nitrogen, CHNS analysis was also performed. A summary of the specific equipment used as well as sampling procedures is given in Table 7 and the compositions obtained are summarised in Table 8.

Testing	Equipment details	Procedure
XRF	Bruker Handheld XRF Tracer IV-SD	0.25 mg of sample is scanned at 25 Kv, 35 µA. The samples are weighed and placed on a stand for scanning.
EDAX	FEI Company Quanta series 200 SEM/EDAX, with an xT microscope system	Samples are coated in gold and placed on a carbon tape for analysis
CHNS	ThermoScientfic Flash CHNS/O analyser	2-3 mg of sample is placed into a tin capsule and dropped into an oxidation/reduction reactor which is held at 950°C. When the sample oxidises exothermically, the released elemental gases are separated and then analysed by a thermal conductivity detector.

Table 7: Elemental analysis procedure

3.1.3 TGA-FTIR and MCC experimental procedure

Mettler Toledo STARe System TGA/DSC 2 LF/1100 was used for the thermogravimetry and differential scanning calorimetry analysis in both air and nitrogen environments. Between 2-5mg of each sample was decomposed, with a heating rate 10°C min^{-1} with a flow rate of 25cm^{3} min^{-1} from ambient to 700°C, to record mass loss and heat flux changes.

The microscale combustion calorimetry testing was carried out on an MCC with between 2-3 mg of sample heated to 700°C at 1°C/second and 10°C/minute in both inert and air environments according to the ASTM D7309 standard.

FTIR was carried out on a Thermo Nicolet iS50 FTIR, set to a resolution of 1 cm^{-1} with a DGTS detector and a scan rate of 10 average spectra. The gas cell and heated lines were both heated to 280°C. All testing was carried out in duplicate. FTIR spectra were analysed against the HR Nicolet Vapour Phase and TGA Vapour Phase libraries using OMNIC 9.3.32 software. Library spectra, recorded at 4 cm^{-1}, for the 10 most commonly identified products are presented in Figure 10 and Figure 11.

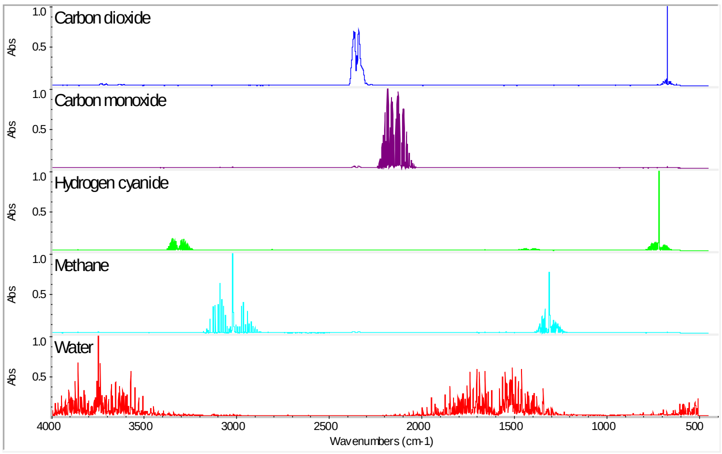


Figure 10: FTIR library spectra for carbon dioxide, carbon monoxide, hydrogen cyanide and water

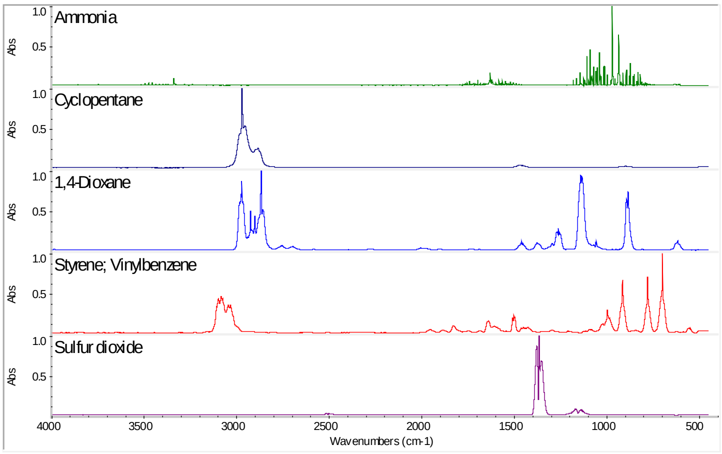


Figure 11: FTIR library spectra for ammonia, cyclopentane, 1,4-dioxane, styrene and sulfur dioxide

One frequently encountered issue was that isocyanic acid, methyl isocyanate and carbon dioxide all absorb at similar wavelengths, Figure 12, and distinguishing between them proved difficult. Where there was reasonable doubt, the peaks are unassigned. The spectra shown below are gas phase spectra obtained at 4 cm^{-1} resolution and as such may show slight differences in comparison to the data obtained in this testing.

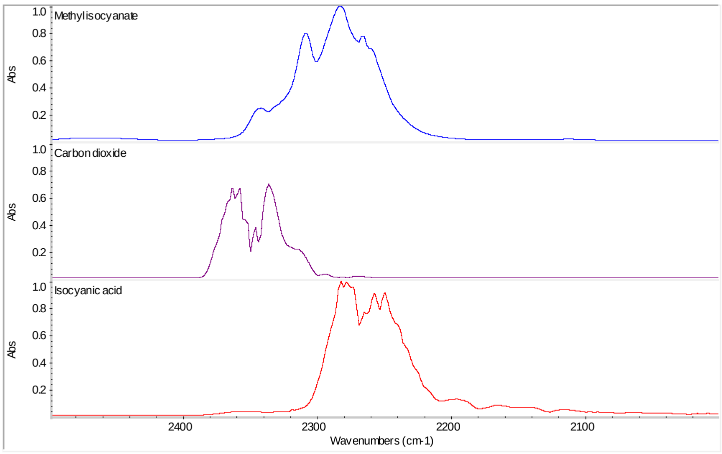


Figure 12: FTIR library spectra for carbon dioxide, methyl isocyanate and isocyanic acid

3.1.4 Optimisation of py-GCMS method

In order for analysis by pyrolysis gas chromatography-mass spectrometry to be performed on the volatiles, it was first necessary to ensure that the gas chromatography-mass spectrometry method that was suitable. A number of GCMS methods were selected from literature, shown in Table 24. Polystyrene was chosen as the target polymer, as the decomposition mechanism has been thoroughly studied and is well-understood, with distinctive products formed and released. In addition, the main product released during the decomposition of polystyrene is styrene itself, which provides a distinct peak and mass spectra that makes it ideal as a benchmark. The pyrolyser conditions given below were kept the same for all the tests. The details of each method used are shown in Table 24. Methods A-J were literature based methods that had shown success in identifying volatiles from materials similar to those in this study, methods K, L and M are in-house developed methods. Methods A and G-I are based on EPA methods 8720D[59] and 8260C[60].

All py-GCMS tests were carried out on a CDS 5000 series pyroprobe 5200 attached to a Turbomass GC and Thermoscientific MS system. Approximately 0.8mg of the material to be tested was inserted into a quartz tube, with both ends then sealed with quartz wool. The samples then were inserted into the platinum filament of the pyrolyser, and was heated at 10°C per minute from the lower temperature to the higher temperature of the range selected. The range used was 300-800°C. The decomposition products were captured on a trap which was held at 50°C. When the pyrolyser program was finished, the trap was heated to 280^{o}C for 2 minutes, after which the gas was transferred to GC, with the transfer line at 310^{o}C. The GCMS methods used are specified in the table below. The samples were analysed based on the NIST library and the chromatograms labelled with retention times only.

	Method A[59]	Method B[61]	Method C[61]	Method D [61]	Method E [61]	Method F[62]	Method G[59]	Method H[59]	Method I[60]	Method J[63]	Method K	Method L	Method M
Mass range	35-650	35-650	35-650	35-650	35-650	41-650	45-650	50-650	41-650	41-650	41-650	29-650	29-600
Scan time (min)	0.59	0.59	0.59	0.59	0.59	1.22	1.32	1.22	0.59	0.59	0.59	0.59	0.59
Ion source (°C):	250	250	250	250	250	250	250	250	250	250	250	250	250
Oven Program													
Initial Temp(°C).:	38	40	120	120	120	100	40	100	130	45	40	45	50
Initial Hold:	2 min	4 min	8 min	2 min	0 min	0min	4min	2min	0min	4min	2min	0.8min	2min
Ramp 1:	10°C/min to 220°C, hold for 5 min	8°C/min to 320°C, hold for 8 min	8°C/min to 3000°C, hold for 6 min	5°C/min to 300°C, hold for 6 min	4°C/min to 290°C, hold for 5 min	12°C/min to 210°C	10°C/min to 320°C, hold 8 min	8°C/min to 210°C	4°C/min to 290°C	8°C/min to 300°C, hold for 6 mins	40°C/min to 140°C	45°C/min to 200°C	10°C/min to 280°C, then hold for 5 min
Ramp 2	30°C/min to 300°C					2°C/min to 260°C, hold for 3 min		2°C/min 280°C, hold for 3 min			7C/min to 200°C	2.5°C/min to 225°C, then 3°C/min to 266°C, 5°C/min to 300°C, then 10°C/min to 320°C and hold for 4.5min	
Run time	32.89min	47.00min	36.50min	44.00min	47.50min	33.13min	40.02min	53.76min	46.02min	43min	15.00min	41.52 min	28.80

Table 8: GCMS used methods for PS optimisation

The chromatograms obtained from each method are shown below in Figure 34 and Figure 35, and the volatiles identified are shown below. As can be seen from Figure 34 and Figure 35 the quality of the chromatograms produced is quite different for all selected methods. Some chromatograms showed large initial peaks (around the 2 minute mark) which come from air and these peaks were disregarded from the analysis. The main visible peak, typically between 6 to 8 minutes, on most of the chromatograms was assigned to styrene.

The best separation was identified in methods G, I, L and M. However, methods G and I showed significantly fewer volatiles than were expected and so the two best methods selected were L and M. As Table 9 shows that the most comprehensive ranges of volatiles were identified by methods L and M.

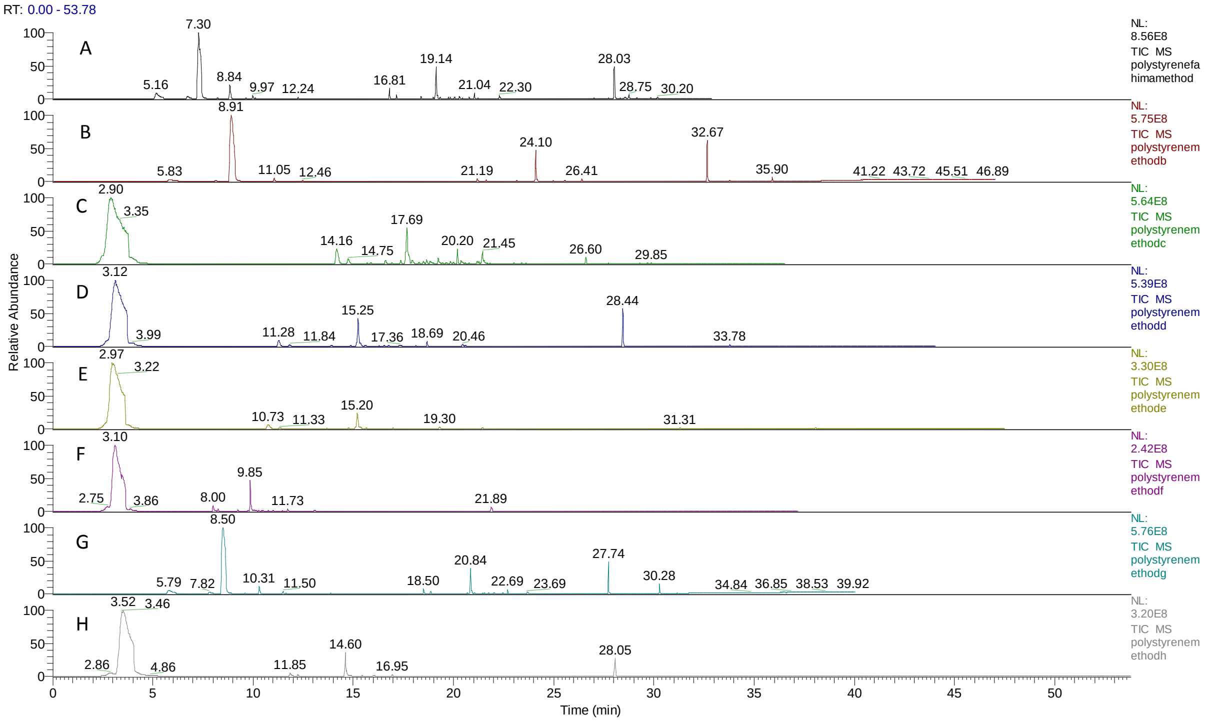


Figure 10: Comparison of PS pyGCMS chromatograms from methods A-H

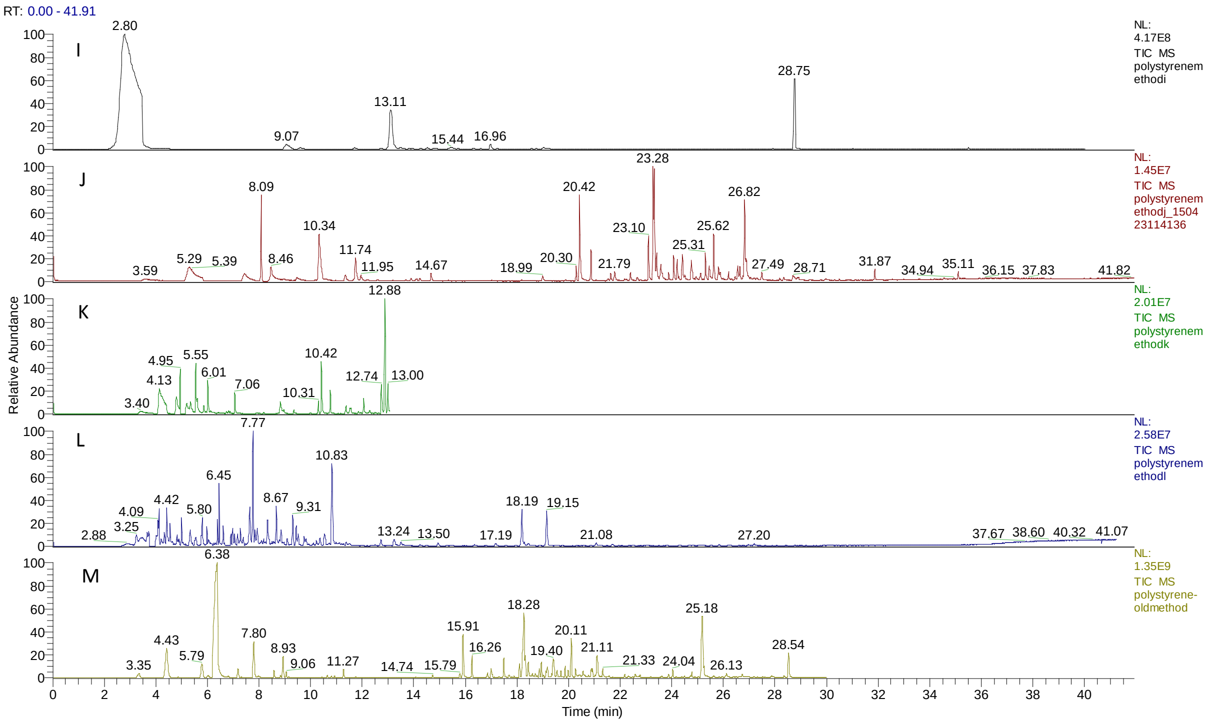


Figure 11: Comparison of PS pyGCMS chromatograms from methods I-M

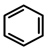
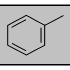
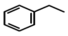
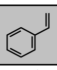
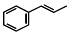
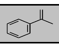
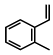
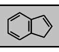
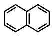
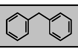
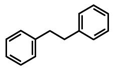
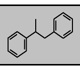
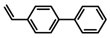
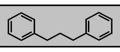
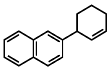
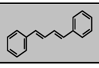
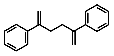
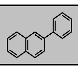
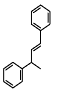
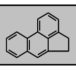
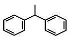
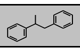
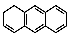
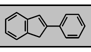
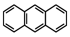
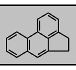
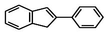
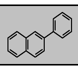
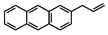
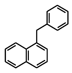
Name	MW	Structure	Method												
			A	B	C	D	E	F	G	H	I	J	K	L	M
Benzene	78				x	x	x	x	x	x	x		x		x
Toluene	92		x	x					x					x	x
Ethylbenzene	106			x								x	x	x	x
Styrene	108		x	x	x	x	x	x	x	x	x	x	x	x	x
1-propenylbenzene	118														x
Alphamethylstyrene	118		x					x	x		x	x	x	x	x
O-methyl styrene	118											x	x		x
Indene	116		x				x		x			x	x	x	x
Naphthalene	128		x									x	x	x	x
Diphenylmethane	168														x
Bibenzyl	182				x	x						x			x
Alphamethylbibenzyl	196														x
4-vinylbiphenyl	180														x
1,3-diphenylpropane	196														x
1,2,3,4-tetrahydro-2-phenylnaphthalene	208														x
1,4-diphenyl-1,3-butadiene	206														x
2,5-diphenyl-1,5-hexadiene	234											x		x	x
2-phenylnaphthalene	204											x	x		x
1,3-diphenylbutene	208			x								x		x	x
4,5-dihydroacephenanthrylene	204													x	
S-diphenylethane	182													x	
Alphamethylbibenzyl	196													x	
Dihydroanthracene	180													x	
2-phenyl-1h-indene	192													x	
Anthracene	178													x	
4,5-dihydroacephenanthrylene	204													x	
2-phenyl-1h-indene	192													x	
2-phenylnapthalene	204													x	
2-allylanthracene	218													x	
1-benzylnapthalene	218													x	

Table 9: Comparison of volatiles identified from PS during pyGCMS optimisation testing

All methods were evaluated using several factors; the quality and reliability of chromatograms, the range of elutants identified and their time efficiency.

Only two methods were identified to meet these criteria: L and M. Two different materials, PIR1 and PUR1, were then tested in order to evaluate the suitability of the two selected methods in order to further analyse the quality of the chromatograms as well as the range of identified elutants. Chromatograms for these two methods and materials are presented in Figure 12 and Figure 13 below, and the volatiles identified are presented in Table 9.

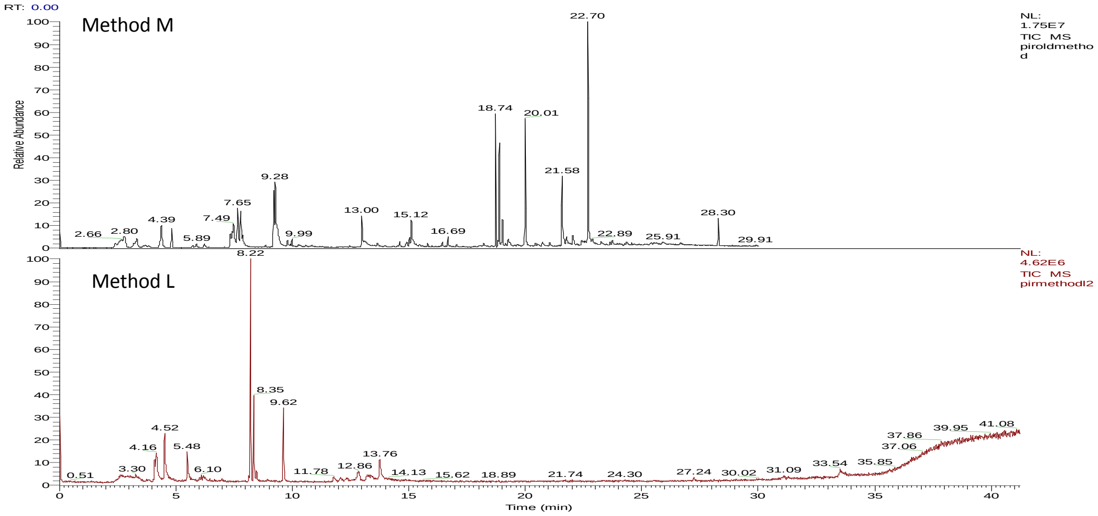


Figure 12: PIR1 pyGCMS chromatograms for methods M and L

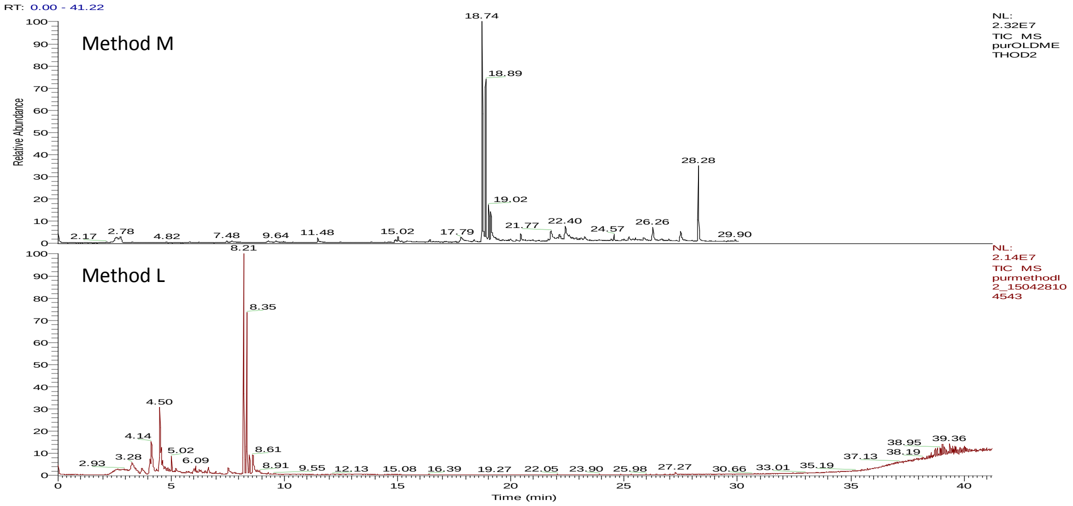
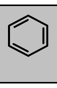
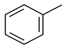
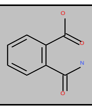
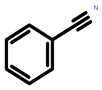
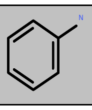
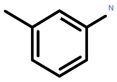
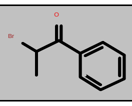
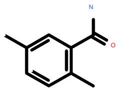
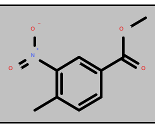
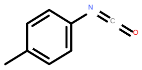
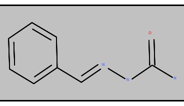
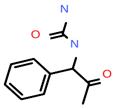
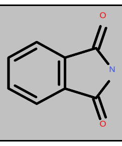
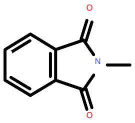


Figure 13: PUR1 pyGCMS chromatograms for methods M and L

As can be seen, a far greater range of volatiles was identified from method M, as well as being more time efficient. It can be concluded that for PIR testing, method M is the best method.

Similarly to PUR1, for PIR1 method L continued for a significant amount of time after the last volatiles eluted, as shown above. Additionally, the separation in method M was judged to be better than method L, and like for PIR1, method M was selected to be the best method.

Py-GCMS			
Compound	Analysed Materials (o= method L, x = method M)		
	Structure	PIR 1	PUR 1
Benzene		x	
Toluene			o
Phthalic acid		xo	
Cyanobenzene		x	
Aniline		x	o
3-methylbenzenamine		x	
1-benzoyl-1-bromoethane			x
N-2-dimethylbenzenamide			x
Methylesterp-toluic acid			x
1-isocyanato-4-methylbenzene		o	
2-(phenylmethylene)-hydrazinecarboxamide		o	
1-acetyl-3-benzyl urea			o
Phthalimide		x	
N-methylphthalimide		o	

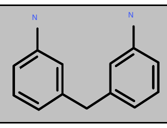
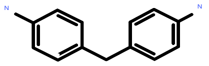
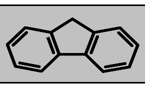
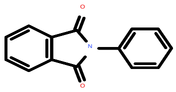
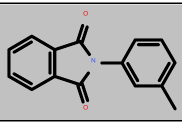
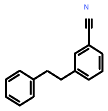
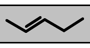
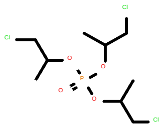
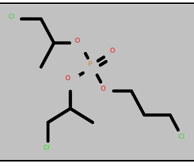
3-(3-aminobenzyl)-phenylamine			x
4-4’-methylenedianiline			xo
Fluorene		x	
N-phenylphthalimide		xo	
2-(3-methylphenyl)-isoindole-1,3-dione		xo	
3-(2-phenylethyl)benzonitrile		o	
(trans) 2-pentene		x	x
Tris(2-chloro-1-methylethyl)ester phosphoric acid		xo	xo
Bis(2-chloro-1-methylethyl)-3-chloropropylphosphate		x	xo

Table 10: Volatiles identified from pyGCMS optimisation for PIR and PUR

The results for PIR1 and PUR1 largely reflected those of polystyrene, with the main difference being slightly better separation of the chromatograms from method M than method L. As method L was longer than method M, extra attention was paid to this area of the chromatogram to monitor whether anything significant was released after method M stopped recording. However, similarly to PS results, nothing identifiable eluted in this time. In addition, the volatiles identified were similar to those expected based on the literature results for products produced during the decomposition of PUR1.

As method M showed the best time efficiency and superior product detection for the three materials tested, it was decided that method M was the most suitable method for the insulation material testing.

4. RESULTS

4.1 Elemental Analysis

Figure 7 and Figure 8 present the XRF results for all materials tested. All the significant peaks have been assigned, however there are some residual tail peaks that remain unidentified. The results of the XRF analysis show that phosphorus was identified in five of the materials tested: PIR, PIR2, PIR3, PUR and PUR2. Sulphur was identified in PF and PF2. One notable issue was around the presence of bromine in EPS. A small signal was detected, however the limits of detection of the XRF spectrometer meant it could not be fully confirmed.

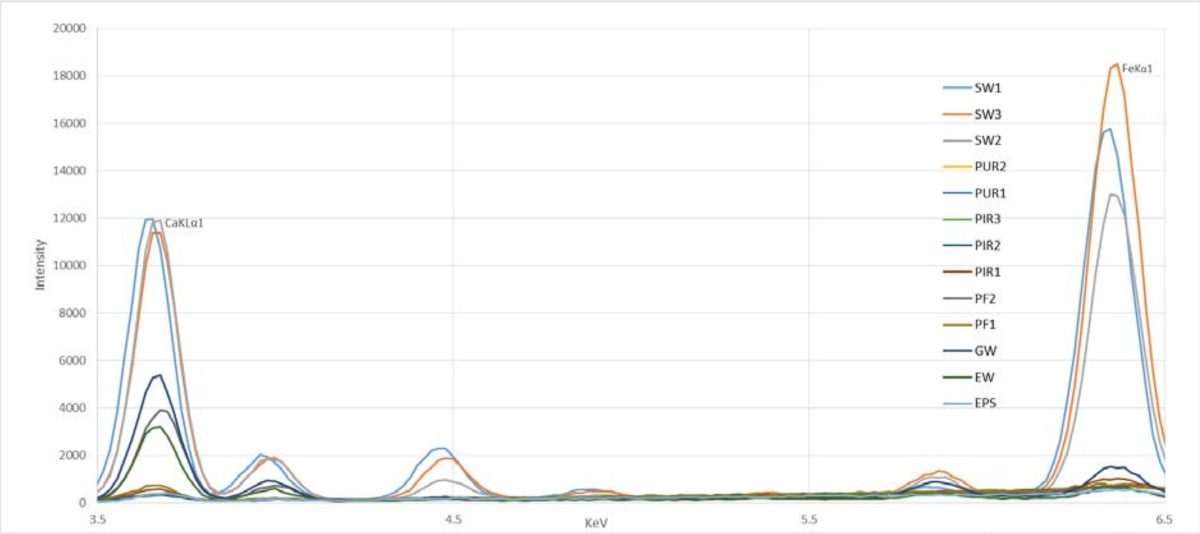


Figure 14: XRF analysis (scale from 3.5-6.5 KeV) of tested materials

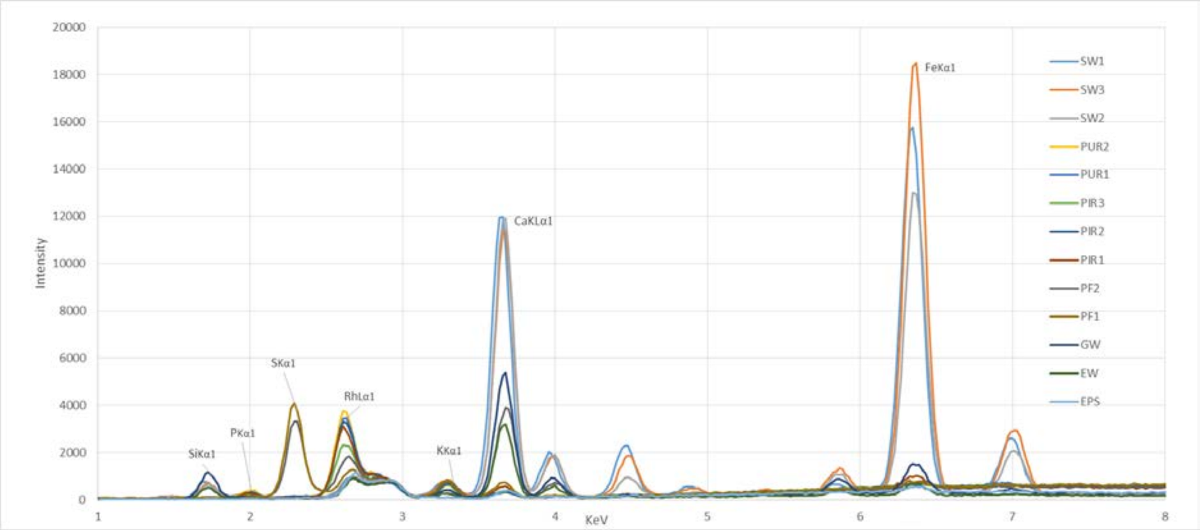


Figure 15: XRF analysis (scale from 1-8 KeV) of tested materials

Figure 16 presents the results from the EDAX analysis of the insulation materials. It is firstly important to note that in SW3 zinc and titanium were identified and in SW5 nickel was identified; however the peaks are covered by others overlaying them. The results are complementary to the XRF analysis, with bromine additionally being detected in EPS and chlorine in PF, PF2, PIR, PIR2, PIR3, PUR and PUR2 samples. One notable difference to the XRF analysis is that for PIR and PIR2, no phosphorus was identified which may be due to the amount present being lower than the detection limit. For the fibre based samples, SW, SW2, SW3, SW4 and SW5, Si was detected in each material, and Fe in SW, SW2 and SW3. A summary of all elements identified is presented in Table 11.

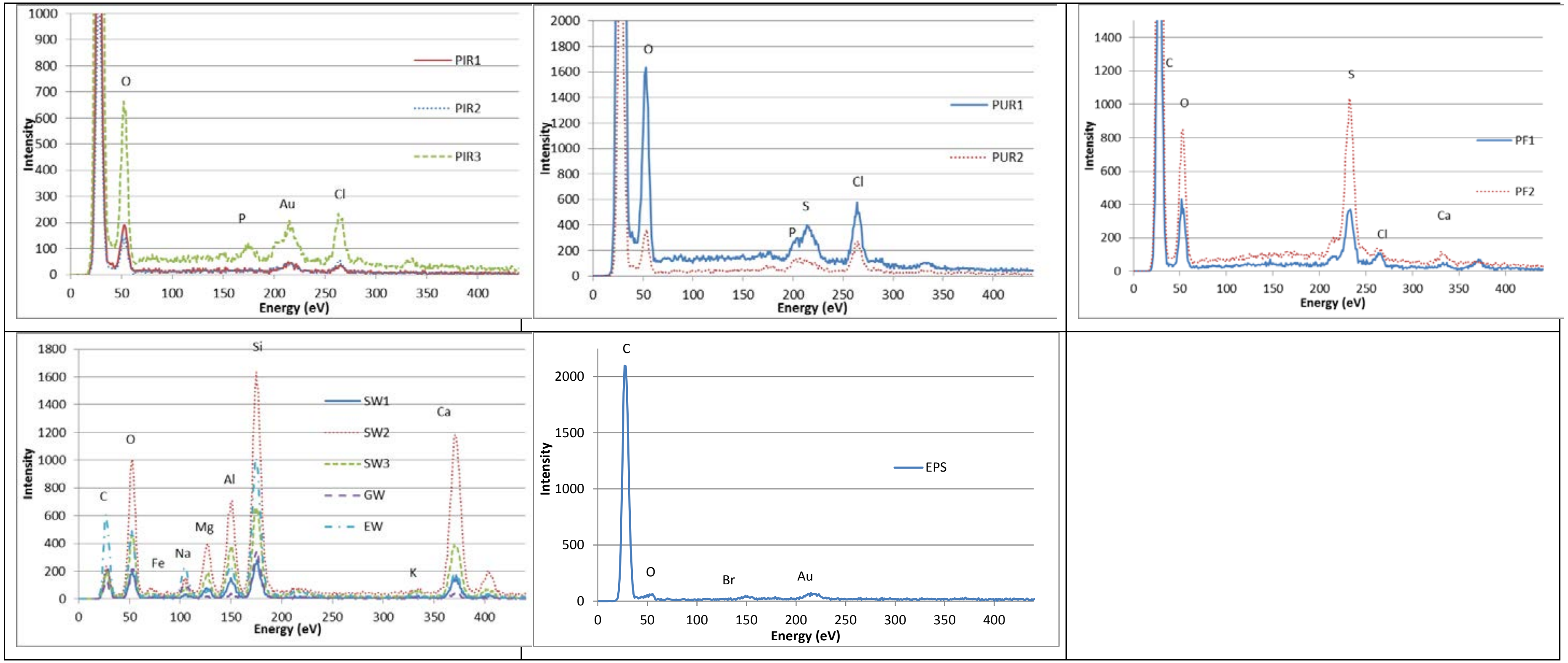


Figure 16: EDAX elemental analysis for all materials tested

	XRF and EDAX	**CHNS Analysis**			
Sample name	Elemental analysis results	% Carbon present	% Nitrogen present	% Hydrogen present	% Sulphur present
EPS	C,O, Br	88.73	1.35	7.87	0.5
PF	C,O, Cl, S, Ca	32.33	2.66	5.50	1.95
PF2	C, O, Cl, S	34.39	3.04	5.77	1.55
PIR	C, O, Cl	67.00	7.33	5.34	0.00
PIR2	C, O, P, Cl	65.63	6.68	5.38	0.00
PIR3	C, O, P, Cl	66.10	6.67	5.35	0.00
PUR	C, O, P, Cl	65.47	6.68	4.49	0.41
PUR2	C, O, P, Cl	67.25	7.62	5.51	0.16
SW	C,O, Si, K, Mg, Ca, Na, Al	1.81	1.47	0.35	0.00
SW2	C,O, Si, Mg, Ca, Na, Al	1.23	1.56	0.28	0.00
SW3	C,O, Si, K, Mg, Ca, Ti, Al, Fe, Zn	1.75	1.29	0.30	0.00
SW4	C,O, K, Mg, Ca, Na, Al, Ni	2.65	2.78	0.67	0.00
SW5	C, O, K, Na, Ca, Ni, Al	1.83	1.53	0.35	0.00

Table 11: Summary of elemental analysis for insulation materials

The presence of chlorine and phosphorus in several of the samples suggests that they contain a fire retardant. The similarity between the general composition of PIR and PUR foam, as well as the similarity in the elements detected suggests that they could contain similar fire retardants. The elements Si, K, Mg, Ca, Ni, Al, Ti, Fe and Zn are likely to be components of the mineral (stone or glass) fibre.

4.2 Thermal degradation studies of insulation materials

The results of the TGA-FTIR and MCC testing carried out on the materials detailed in section 3 are presented, grouped by material, below.

4.2.1 Thermal degradation studies of fibre samples

TGA, DSC and MCC analysis for the wool materials: SW1, SW2, SW3, EW and GW, is presented below.

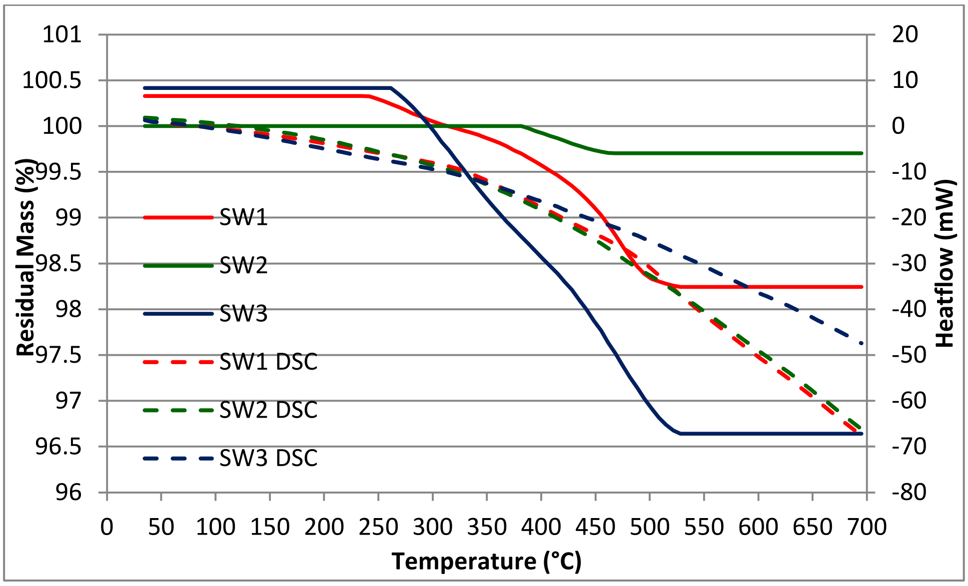


Figure 17: TGA and DSC results for SW1, SW2 and SW3 in air

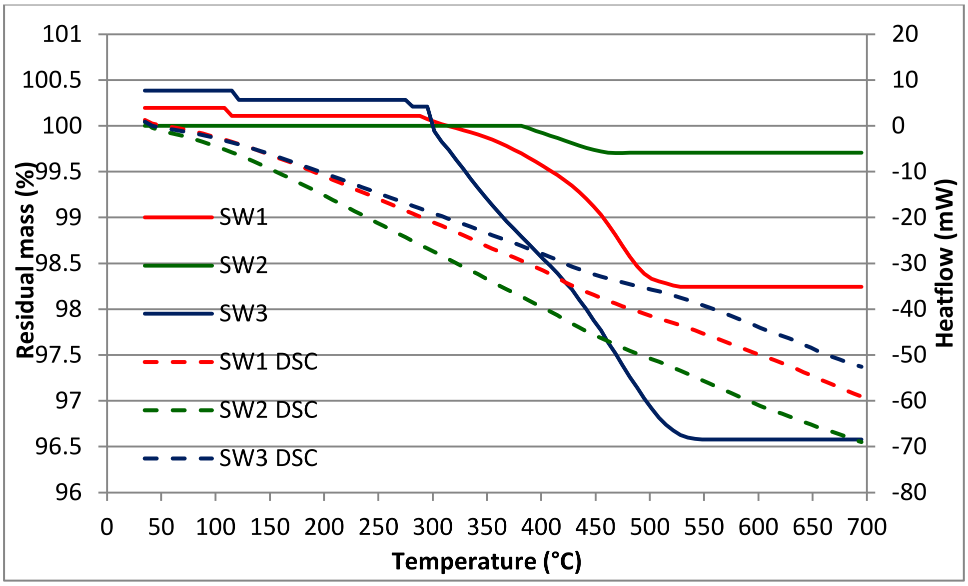


Figure 18: TGA and DSC data for SW1, SW2 and SW3 in nitrogen

There was very little decomposition for these three materials. SW3 showed the biggest change in mass, but the smallest change in heatflow, but none of the materials have any notable decomposition steps for the temperature range tested in air (Figure 17).

The results in nitrogen were similar to those in air for these three materials (**Error! Reference source not found.**), with very little mass loss or change in heatflow shown, and no notable decomposition steps identifiable.

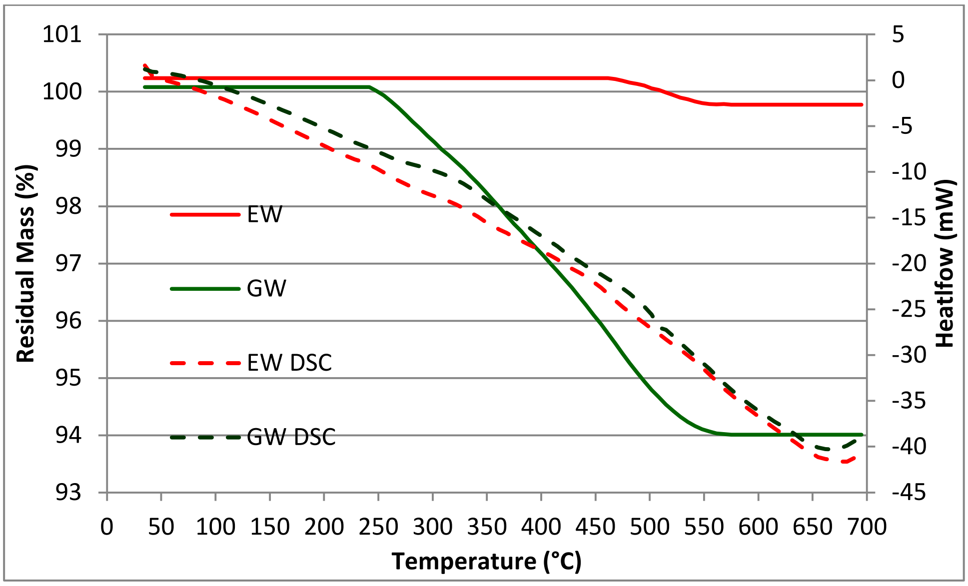


Figure 19: TGA and DSC data for EW and GW in air

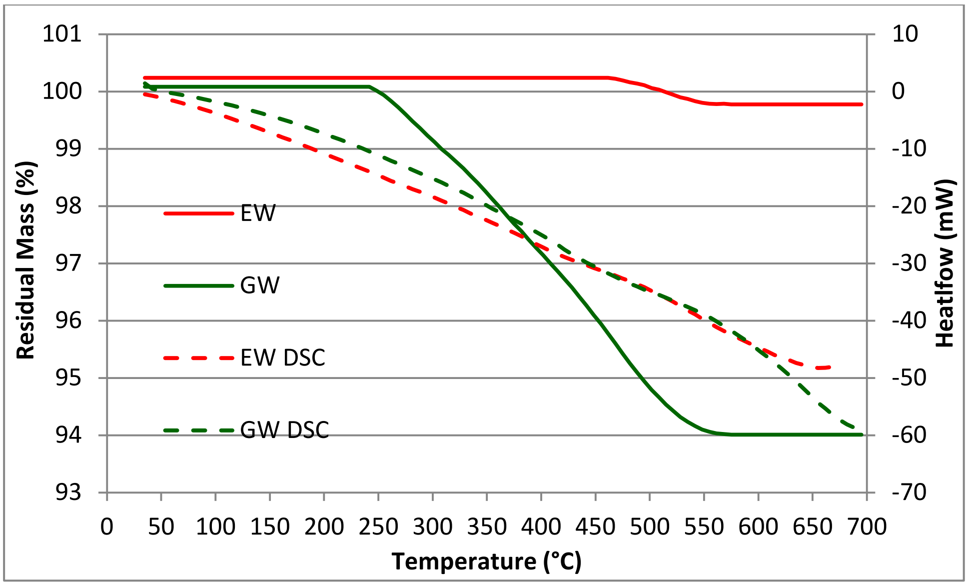


Figure 20: TGA and DSC data for EW and GW in nitrogen

Similarly to the other fibre materials, EW and GW show very little decomposition or change in heatflow, and it is not really possible to identify any decomposition steps in air or nitrogen for these materials.

Overall, very little mass loss occurred in air for any of these products during the TGA. The results were broadly similar in nitrogen with all materials except GW flattening out after around 500°C. There was no indication of any significant decomposition taking place from the results in N_2, and very little mass loss occurs across this temperature range in air for these materials. GW showed the highest mass loss, around 6%, with EW and SW2 losing less than 0.5% of their overall mass. The small amounts of mass loss that occurred all appear to be in one step. The DSC results also showed minimal heatflow for the materials.

As with the DSC results, the MCC results in air (Figure 21) show minimal fuel release, indicating that very little, if any, decomposition is occurring for the fibre materials. The results for SW3 in nitrogen tested on the MCC as shown below produced a higher HRR rate (Figure 22). This was an overall anomaly, as the rest of the wool materials produced similar results in both nitrogen and air environments. As there were no real decomposition steps identified in the thermal degradation studies, it is difficult to correlate the FTIR data to specific decomposition steps.

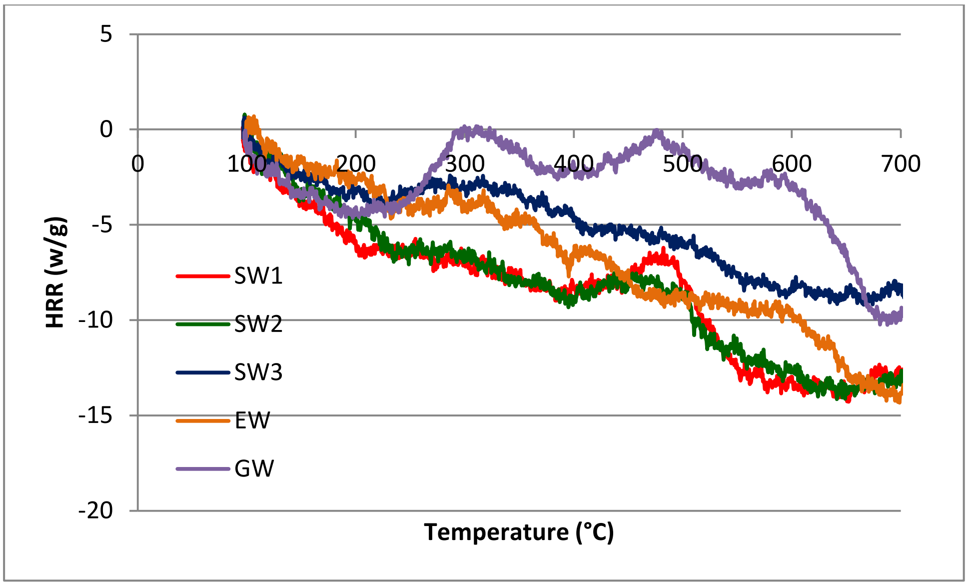


Figure 21: MCC data for wool materials in air

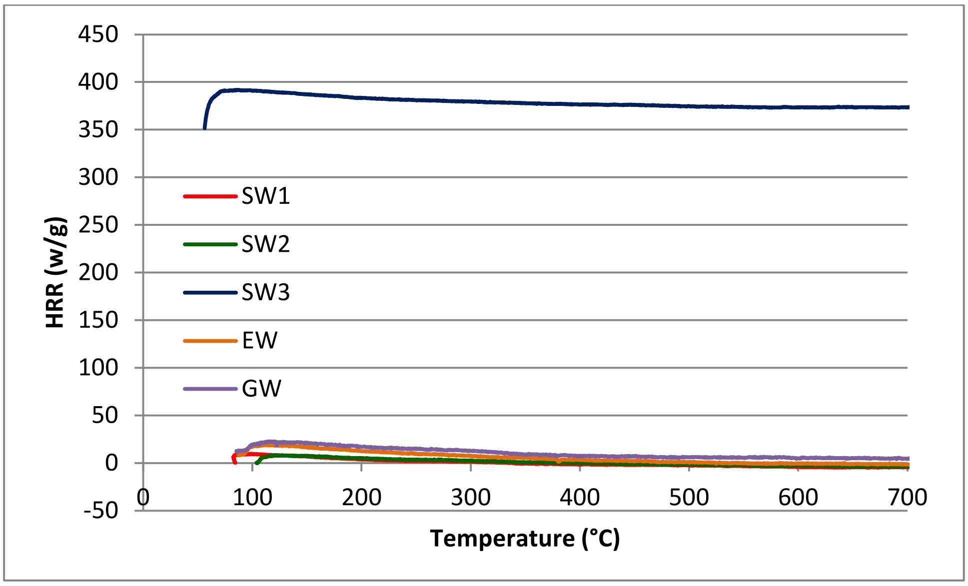


Figure 22: MCC data for wool materials in nitrogen

FTIR spectra and analysis is presented for the wool materials in Table 12.

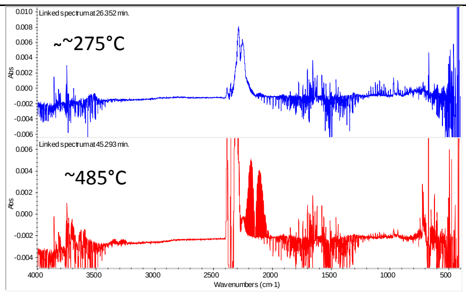
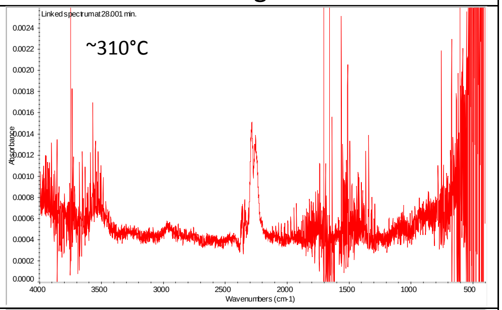
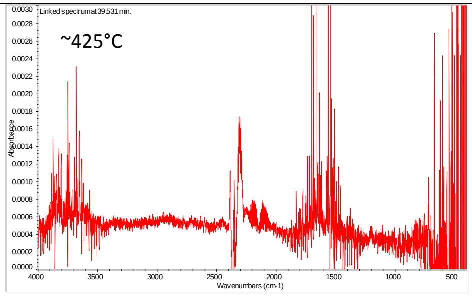
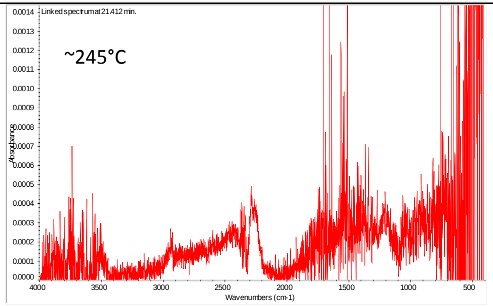
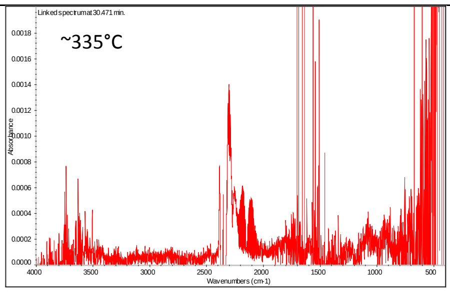
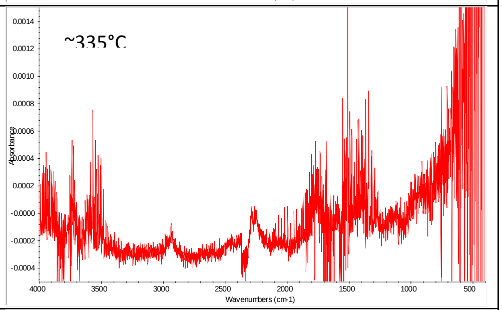
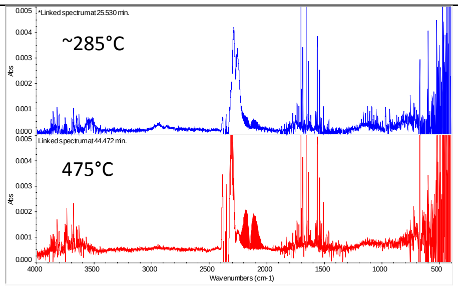
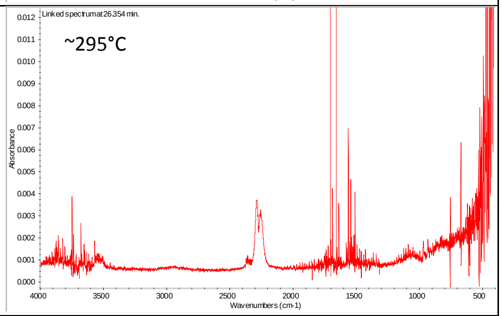
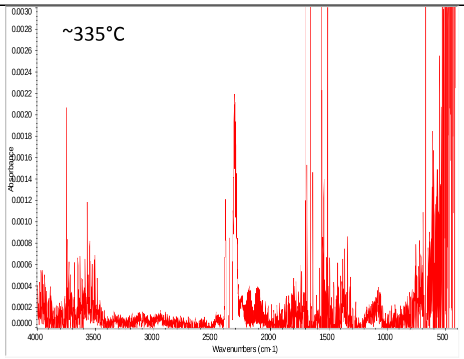
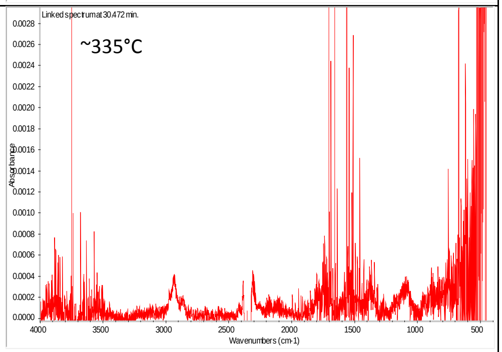
Material	Air	Nitrogen
SW1		
SW2		
SW3		
GW		
EW		

Table 12: FTIR spectra in air and nitrogen for the fibre materials

The main product identified for the fibre samples was water in nitrogen, and water and carbon monoxide were the main products in air. The air results are presented in Table 13 and the nitrogen results in Table 14. SW additionally produced ammonia in air, and SW5 produced ammonia in both air and nitrogen environments. For the GW sample, ammonia was identified in air and nitrogen, and a clear and positive identification of isocyanic acid was reached in air despite the general difficulties in identification for this region.

Materials	Identified Volatiles	Not Identified Volatiles
SW1	Water, carbon monoxide, ammonia	2200cm^{-1}
SW2	Water, carbon monoxide	2200cm^{-1}
SW3	Water, carbon monoxide	2200cm^{-1}
GW	Water, carbon monoxide, isocyanic acid, ammonia	2200cm^{-1}
EW	Water, carbon monoxide	2200cm^{-1}

Table 13: FTIR analysis for the fibre materials in air

As previously mentioned it is difficult to identify volatiles in the 2200cm^{-1} region, as methyl isocyanate, isocyanic acid and carbon dioxide all show strong absorbance in this region. However, for SW5, isocyanic acid was distinct and clearly identified.

Material	Identified Volatiles	Not Identified Volatiles
SW1	Water	2200 cm^{-1}
SW2	Water	2200 cm^{-1}
SW3	Water	2200 cm^{-1}
EW	Water	2200 cm^{-1}
GW	Water, ammonia	2200 cm^{-1}

Table 14: FTIR analysis for the fibre materials in nitrogen

4.2.2 Thermal degradation studies of phenolic samples

TGA, DSC and MCC results for both phenolic foams, PF1 and PF2, are presented below.

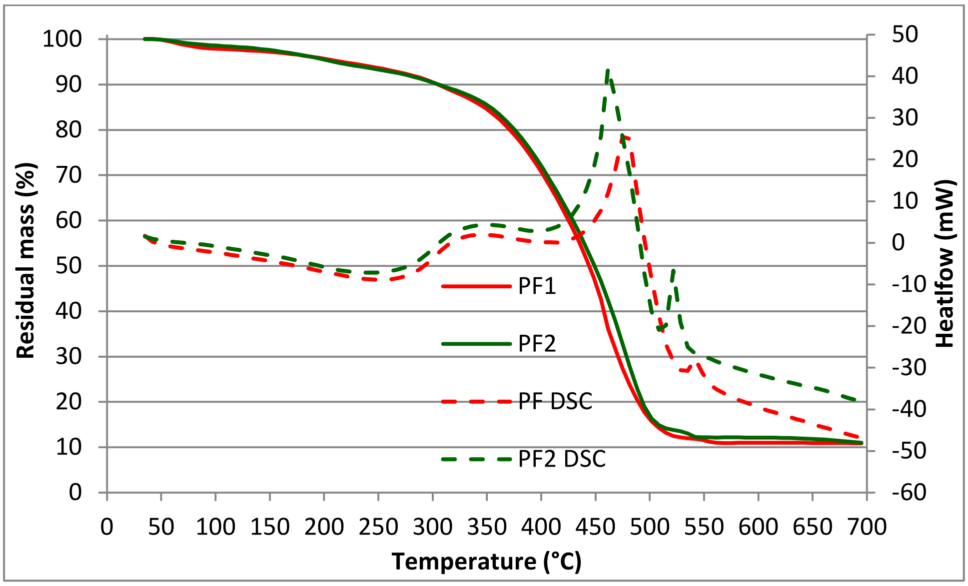


Figure 23: TGA and DSC data for phenolic materials in air

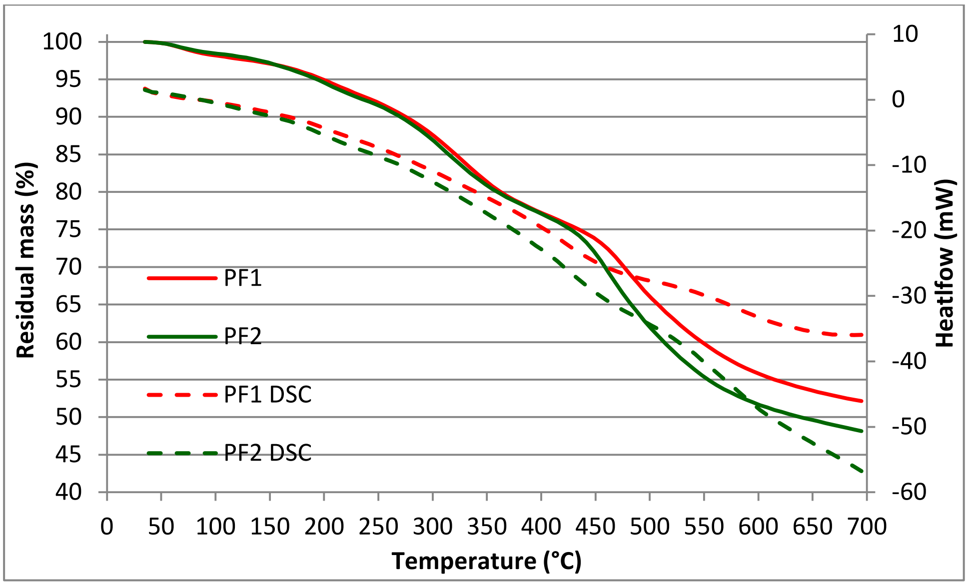


Figure 24: TGA and DSC data for phenolic materials in nitrogen

For both phenolic materials, decomposition in air from the TGA data appears to be a two-step process, Figure 19, with an initial TGA mass loss of around 8% occurring before 200°C followed by a 15% mass loss before 350°C and a further 75% mass loss between 350-500°C. According to the DSC data, an exothermic peaks occurs around 475°C for PF and 460°C for PF2 corresponding to the main mass loss stage, suggesting char oxidation.

The decomposition steps in nitrogen, Figure 24: TGA and DSC data for phenolic materials in nitrogen, for the phenolic materials were significantly smaller than in air. A residue of around 50% of the initial weight was left at the end of TGA testing for both the phenolic materials, compared to around 10% in air. The shape of the TGA curve indicates that this decomposition may also be a three step process, with small steps occurring at 150, 250, and 450°C, however no real spikes were observed in the DSC data for nitrogen. In addition, the first step until 350°C seems similar in both air and nitrogen environments, however the previously described char oxidation step is missing in nitrogen.

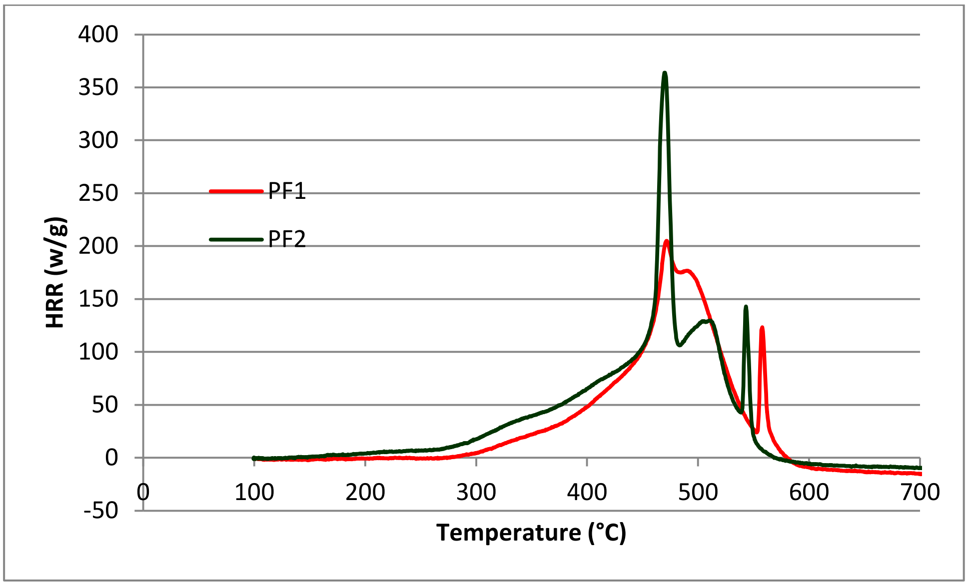


Figure 25: MCC results for phenolic materials in air

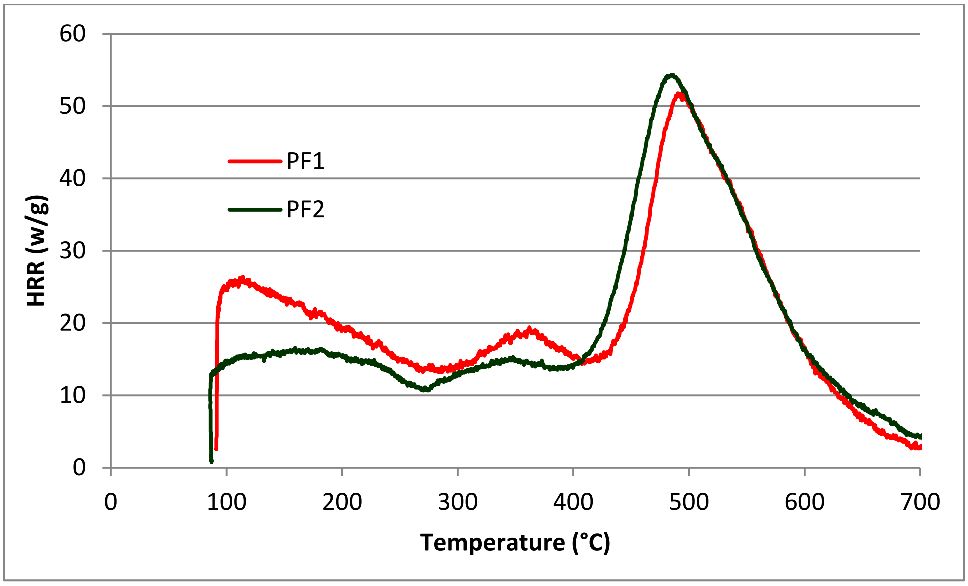


Figure 26: MCC results for phenolic materials in nitrogen

In air, the MCC data, Figure 25: MCC results for phenolic materials in air, shows two main areas of change for the phenolic materials, the first at around 470°C and the second between 540-550°C. This second peak could support the char oxidation theory.

In nitrogen, the MCC data Figure 26: MCC results for phenolic materials in nitrogen shows three small HRR peaks for both phenolic materials at 100°C, 360°C and just before 500°C. The results from the MCC testing also support the three step decomposition theory, with three distinct peaks of HRR across the temperature range.

The FTIR spectra obtained in nitrogen and air for the phenolic materials are shown below in Table 15 followed by summaries in Table 16 and Table 17. The thermal analysis had suggested that the decomposition of these foams was a three step process, and the FTIR data supported this conclusion, with three distinctly different stages identified.

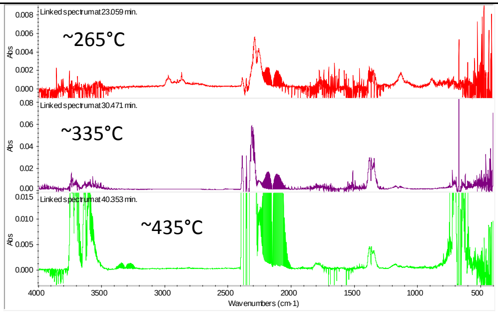
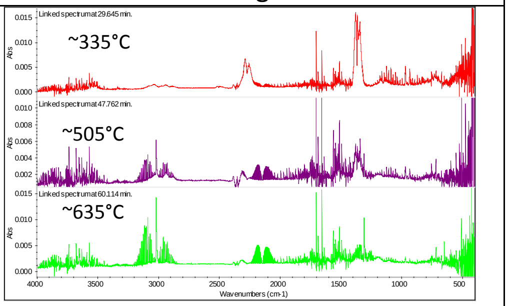
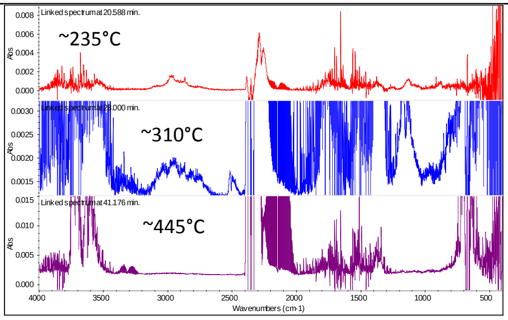
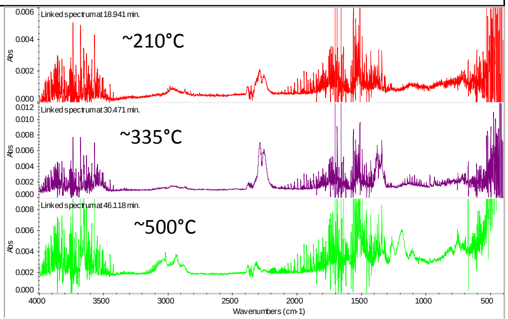
Material	Air	Nitrogen
PF1		
PF2		

Table 15: FTIR spectra in air and nitrogen from phenolic materials

Both PF1 and PF2 produced 1,4-dioxane and sulphur dioxide in air and nitrogen. Large amounts of methane were produced from PF1 in nitrogen; however PF2 did not show the same production. In addition, phenol was identified as a decomposition product from PF2 in nitrogen, but could not be identified from PF at the same point, suggesting these foams did decompose slightly differently. Despite the decomposition in air from the TGA and MCC data for these foams appearing to be a two-step process, three distinct spectra were identified from the FTIR testing, agreeing with the DSC data. This could possibly be due to the sensitivity of the FTIR in identifying products that do not evolve in significant enough quantities to cause notable mass loss, and could suggest that the decomposition in air is actually a three step process, as in nitrogen.

Material	**Identified Volatiles**	**Possible Volatiles**	**Not Identified Volatiles**
PF1	Carbon monoxide, water, sulphur dioxide, 1,4-dioxane		Small peak at 1300cm^{-1} 2200cm^{-1}
PF2	Carbon monoxide, carbon dioxide, water, sulphur dioxide, 1,4-dioxane		

Table 16: FTIR analysis for phenolic materials in air

Material	**Identified Volatiles**	**Possible Volatiles**	**Not Identified Volatiles**
PF1	Sulphur dioxide, ammonia, water, 1,4-dioxane, phenol, methane		2200cm^{-1}
PF2	Sulphur dioxide, ammonia, water, 1,4-dioxane, 2,6-dimethylphenol	Methane	2200cm^{-1}

Table 17: FTIR analysis for phenolic materials in nitrogen

4.1.3 Thermal degradation studies of polyisocyanurate materials

TGA, DSC and MCC results for PIR1, PIR2 and PIR3 samples are shown below.

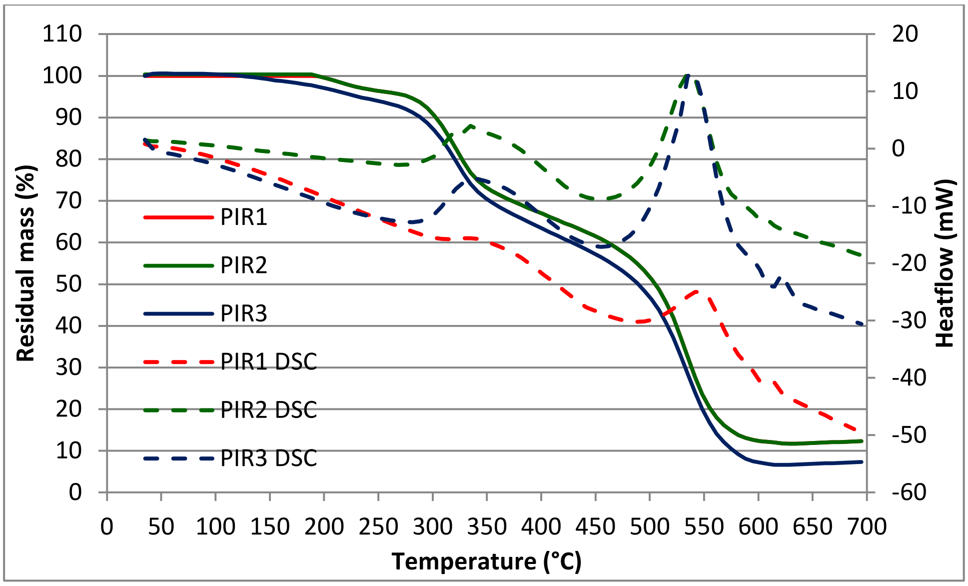


Figure 27: TGA and DSC results for polyisocyanurate materials in air

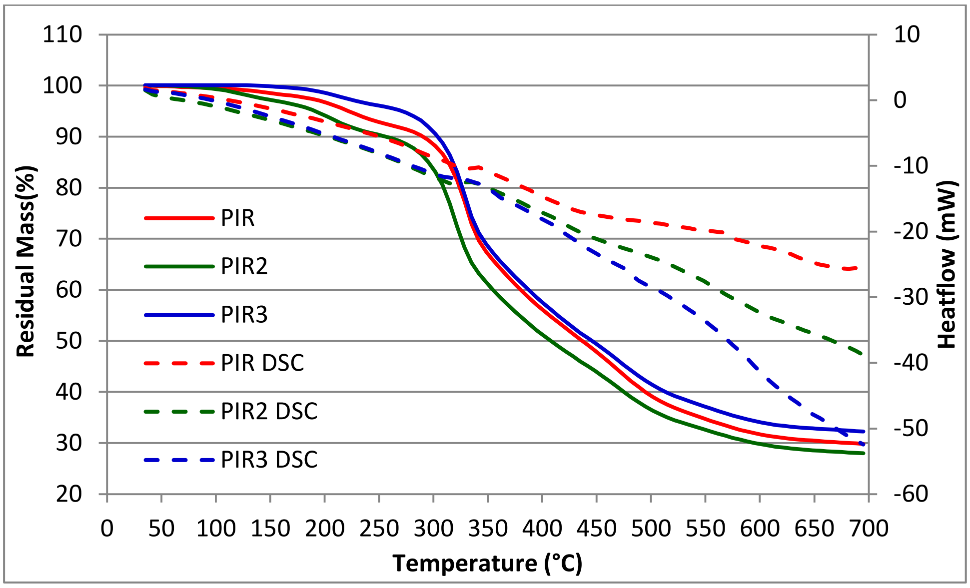


Figure 28: TGA and DSC results for polyisocyanurate materials in nitrogen

The TGA data for the decomposition of PIR1, PIR2 and PIR3 in air, Figure 27, suggest that there are three to four decomposition steps, with only a small amount of the initial mass (5-15%) left at the end of the testing. Decomposition starts at around 180°C with a small initial mass loss. The DSC data for PIR and PIR2 in air shows two heatflow peaks, whereas PIR3 shows three heatflow peaks. For all materials the biggest heatflow peak is identified at around 575°C.

The TGA data for the decomposition of the polyisocyanurate materials in nitrogen, Figure 28, show some significant differences to the data in air. Decomposition occurs in two steps with a relatively small initial step followed by a large second step. The initial step starts around 50°C later than in air. In addition, approximately 20% more of the initial mass is left after the testing than in air. PIR, PIR2 and PIR3 all have broadly similar DSC results in nitrogen, with only very small peaks in heatflow visible across a general downwards trend.

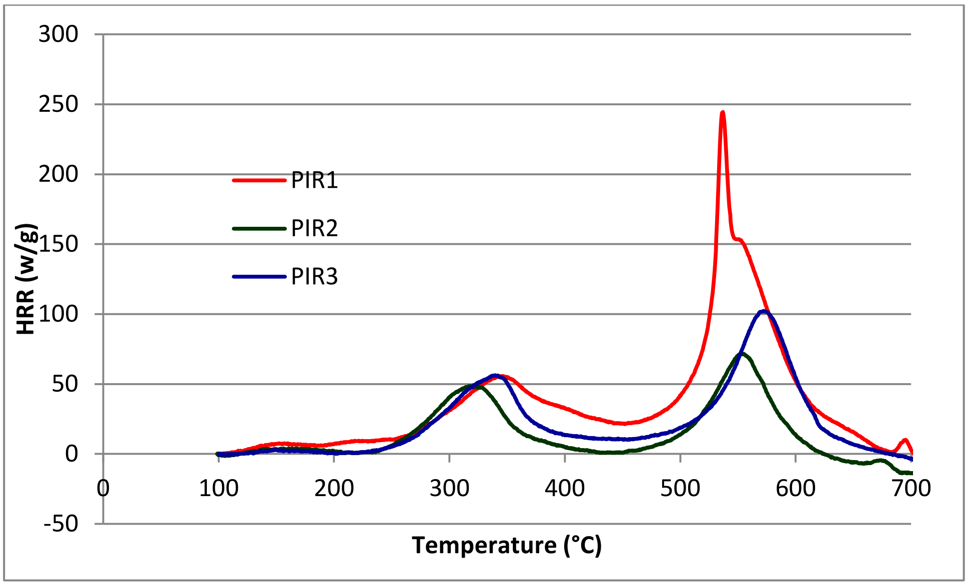


Figure 29: MCC results for polyisocyanurate materials in air

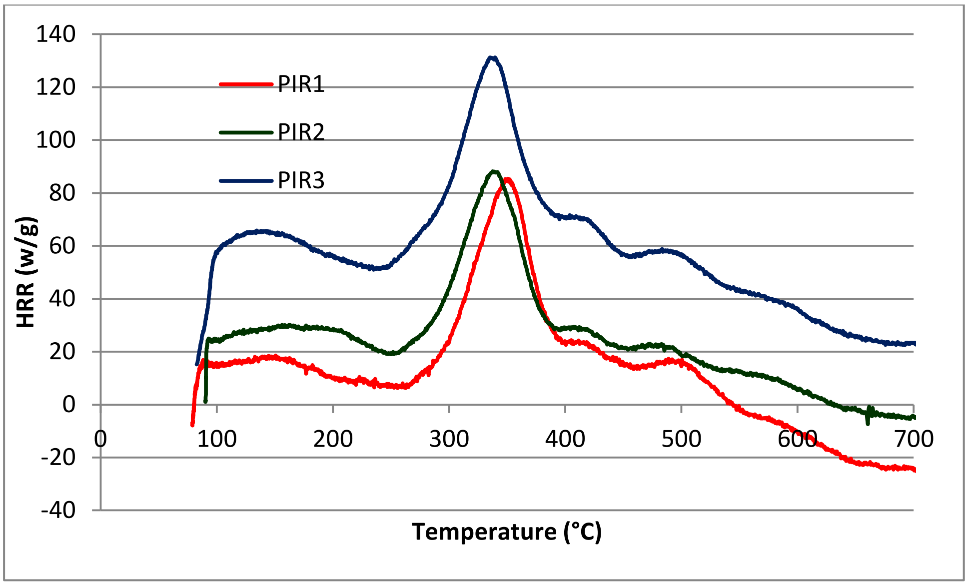


Figure 30: MCC results in nitrogen for polyisocyanurate materials

The point of peak heat release for the foams in air was around 550°C, Figure 29, with PIR1 and PIR3 showing three areas of heat release compared to PIR2 showing two. The point of peak heat release correlates with that shown from the DSC data in air above.

The point of peak heat released for these foams in nitrogen was around 350°C, Figure 30, almost 200°C earlier than in air, with an initial peak at around 150°C believed to be due to the release of a foaming agent as identified in the FTIR analysis below.

The FTIR spectra obtained in nitrogen and air for the polyisocyanurate materials are shown below in Table 18, followed by a summary of the FTIR analysis in Table 19 and Table 20. The thermal analysis for these materials suggested that decomposition occurs in three to four step processes, a conclusion that was supported by the FTIR data.

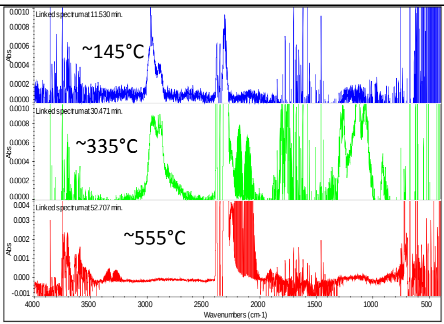
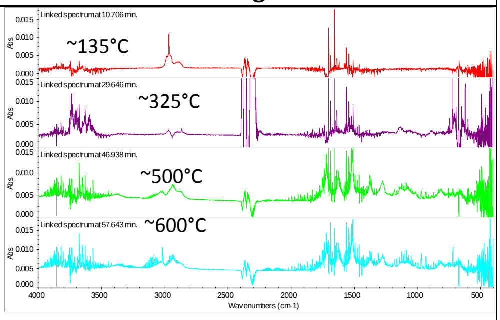
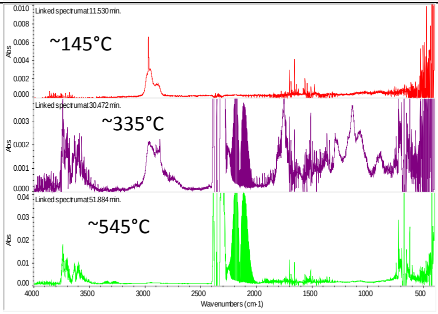
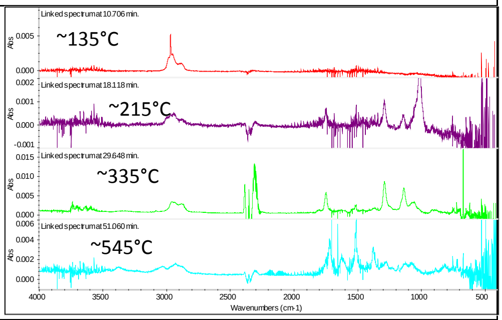
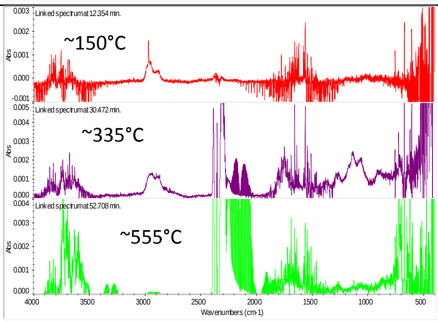
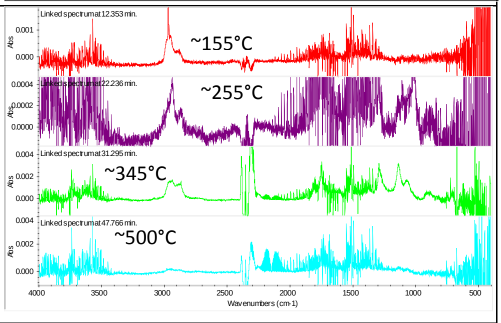
Material	Air	Nitrogen
PIR1		
PIR2		
PIR3		

Table 18: FTIR spectra of polyisocyanurate materials in air and nitrogen

As Table 19 shows, the degradation of the polymer polyol and urethane backbone is clearly visible in the changes of the spectra between the 1000-1500cm^{-1} wavelengths. The clearest example of this is in PIR2 in nitrogen, where you can see the change across the spectra at 18, 29 and 51 minutes reflecting the breakdown and formation of polyols – as covered in literature by Jiao *et al.*[33] Visible on the initial spectra for all of these materials (all taken at around 10 minutes into the test) is the release of cyclopentane, used as a blowing agent, and probably responsible for the initial HRR rate change on the MCC testing shown above. The other most common products for these materials were carbon monoxide, carbon dioxide and water, with hydrogen cyanide identified exclusively in air for PIR2 and PIR3. Additionally, 1,4-dioxane was released under both conditions, while methane and ammonia were only identified in nitrogen.

Material	Identified Volatiles	Possible Volatiles	Not Identified Volatiles
PIR1	Cyclopentane, water, carbon dioxide, carbon monoxide, hydrogen cyanide	1700cm^{-1} – Urethane monomer (cannot identify specific one) 1200cm^{-1} – Polyol (cannot identify specific polyol)	3000cm^{-1} 2200cm^{-1}
PIR2	Cyclopentane, water, carbon dioxide, carbon monoxide, hydrogen cyanide, 1-4-dioxane	1700cm^{-1} – Urethane monomer (cannot identify specific one) 1200cm^{-1} – Polyol (cannot identify specific polyol)	2200cm^{-1}
PIR3	Cyclopentane, water, carbon dioxide, carbon monoxide, hydrogen cyanide, 1-4-dioxane	1700cm^{-1} – Urethane monomer (cannot identify specific one) 1200cm^{-1} – Polyol (cannot identify specific polyol)	2200cm^{-1}

Table 19: FTIR analysis of polyisocyanurate materials in air

Material	Identified Volatiles	Possible Volatiles	Not Identified Volatiles
PIR1	Cyclopentane, water, carbon dioxide, carbon monoxide, hydrogen cyanide, methane, ammonia	1103cm^{-1} – Polyol (cluster around)1700cm^{-1} – Urethane monomer (cannot identify specific one) Pyridine Aniline	2200cm^{-1}
PIR2	Cyclopentane, carbon dioxide, carbon monoxide, water	1103cm^{-1} – Polyol (cluster around) 1700cm^{-1} – Urethane monomer (cannot identify specific one) Aniline	2200cm^{-1}
PIR3	Cyclopentane, carbon dioxide, carbon monoxide, water, 1-4, dioxane	1103cm^{-1} – Polyol (cluster around) 1700cm^{-1} – Urethane monomer (cannot identify specific one) Aniline	2200cm^{-1}

Table 20: FTIR analysis of polyisocyanurate materials in nitrogen

4.2.4 Thermal degradation studies of polyurethane materials

TGA, DSC and MCC results for PUR1 and PUR2 are presented below.

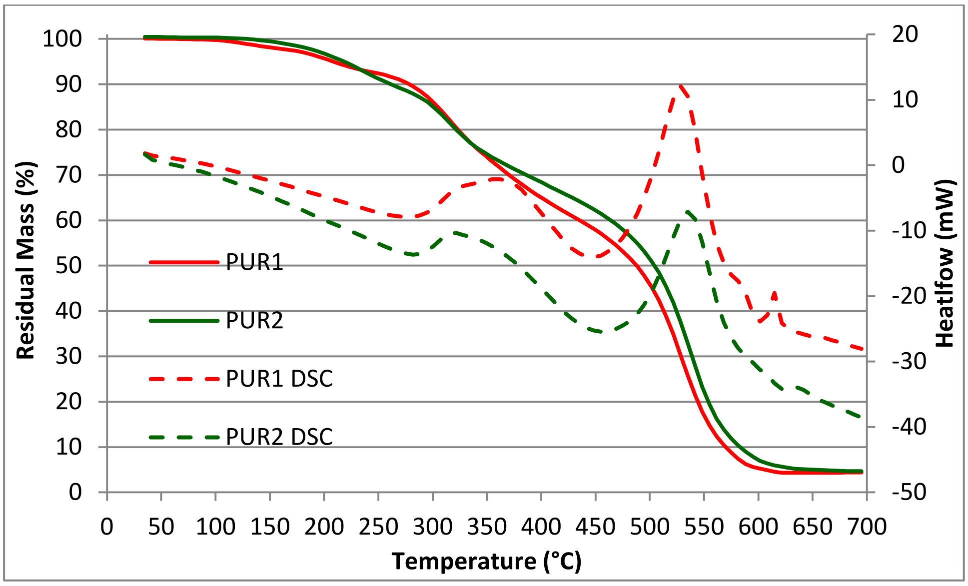


Figure 31: TGA and DSC results for polyurethane materials in air

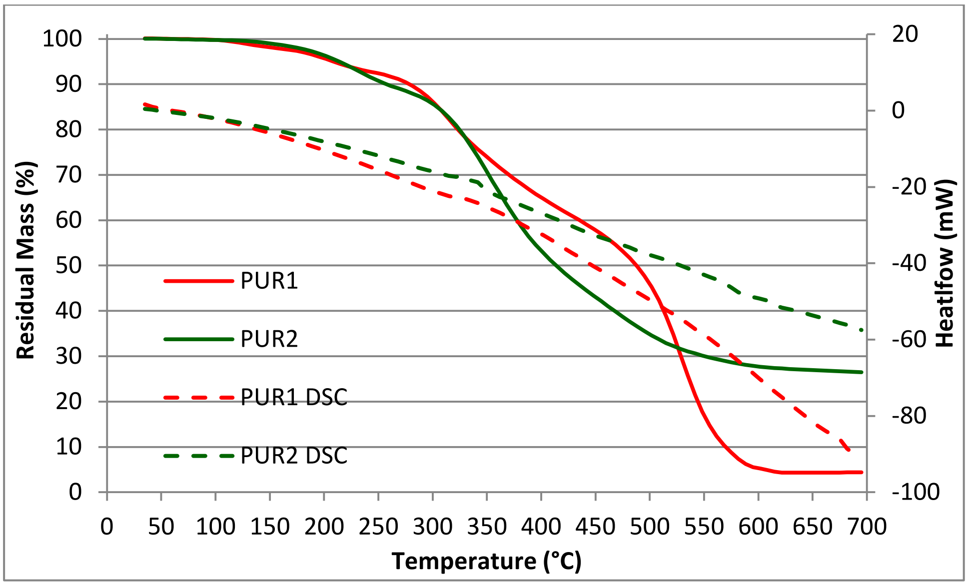


Figure 32: TGA and DSC data for polyurethane materials in nitrogen

For PUR1 and PUR2, from the TGA data, Figure 31, decomposition in air appears to be a three step process, with an almost complete mass loss by the end of testing. The first step occurs before 300°C followed by steps at around 375°C and 475°C. In air, the peak point of heat release according to the DSC data obtained for PUR1 and PUR2 is around 550°C, towards the end of the mass loss, with PUR1 showing three heatflow spikes whilst PUR2 only shows two.

The decomposition of PUR1 and PUR2 in nitrogen, Figure 32, appears to be a two-step process, with between 26-30% of the initial mass remaining once testing is complete. Similarly to in air, the first step occurs before 300°C, however in nitrogen it is followed by one larger step ending at around 570°C.

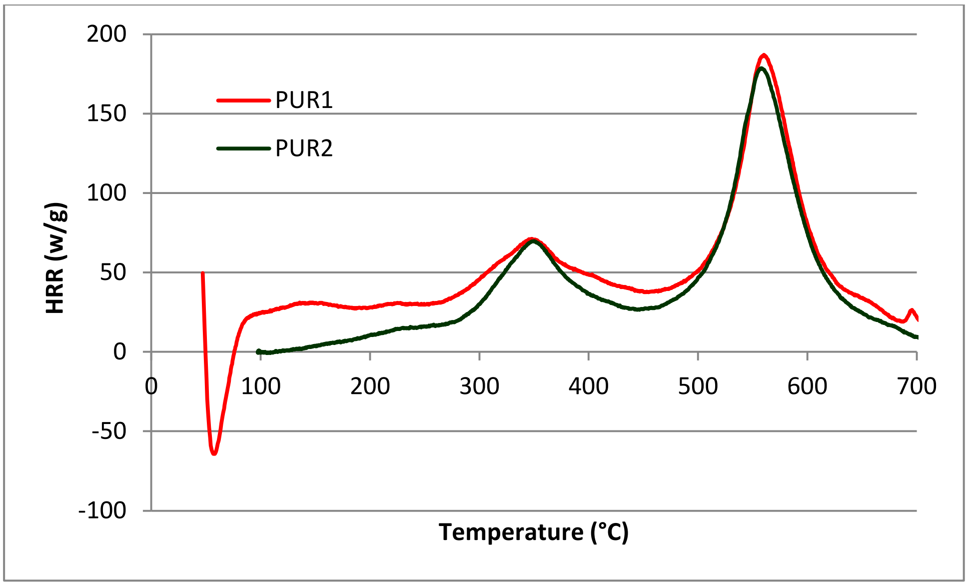


Figure 33: MCC results in air for polyurethane materials

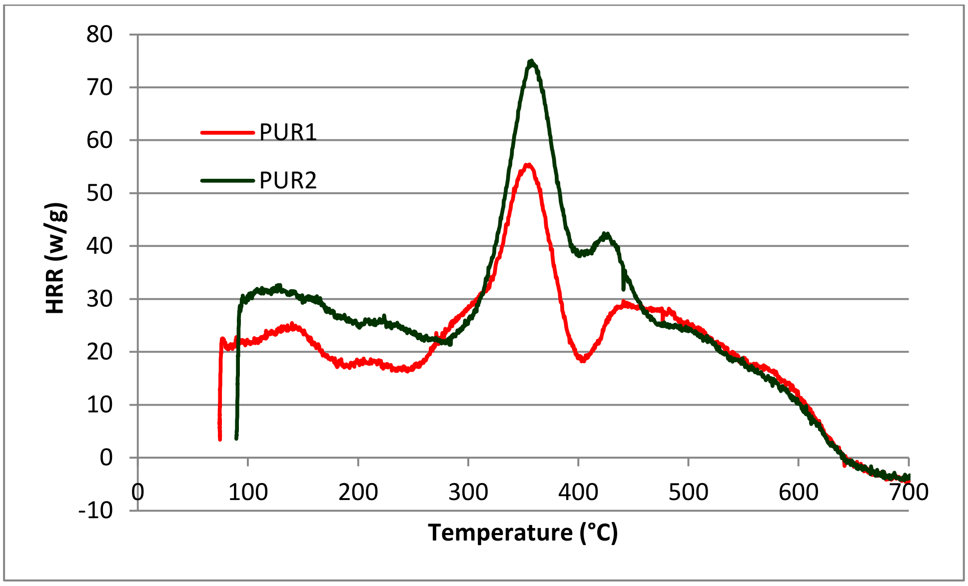


Figure 34: MCC results in nitrogen for polyurethane materials

The point of peak heat release according to the MCC data in air, Figure 33, for PUR1 and PUR2 is 575°C.

The MCC data for PUR1 and PUR2 in nitrogen, Figure 34, suggests that the main peak of heat release occurs at 375°C, significantly earlier than the result obtained in air.

The FTIR spectra obtained in nitrogen and air for the polyurethane materials are shown below, Table 21, followed by summary tables of the FTIR analysis (22 and 23), which broadly supports the conclusions drawn on decomposition steps by the thermal analysis above.

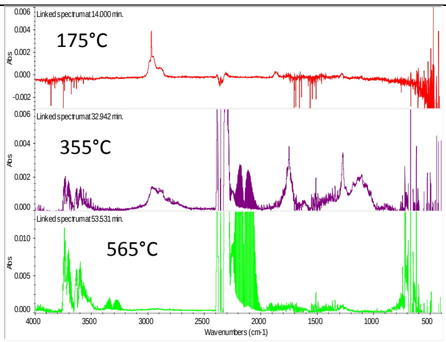
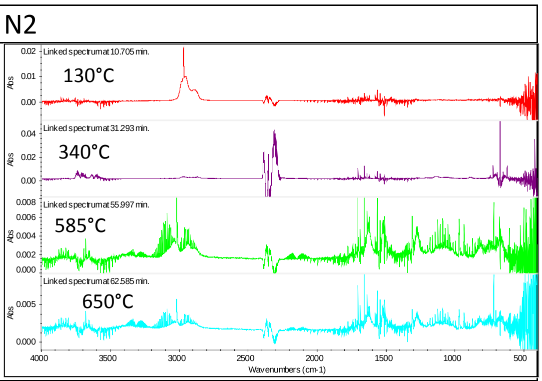
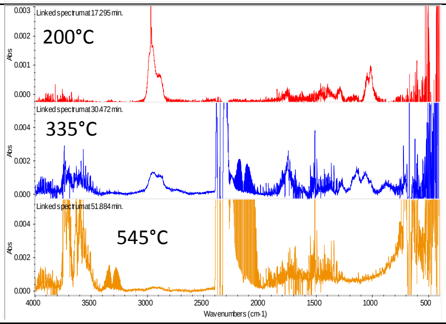
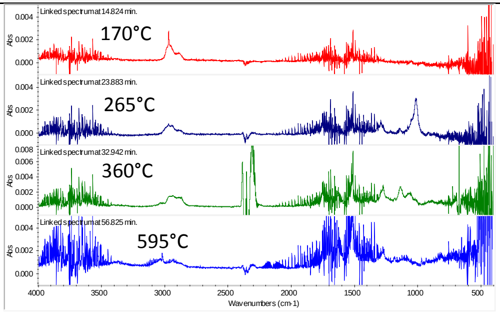
Material	Air	N2
PUR1		
PUR2		

Table 21: FTIR spectra in air and nitrogen from polyurethane materials

Similarly to the spectra in Table 18 for PIR1, PIR2 and PIR3, the spectra for PUR1 and PUR2 show the release of cyclopentane early in the testing. Additionally, the breakdown of the polymer backbone is again visible, with the formation and decomposition of polyol and urethane compounds, as also described by Jiao *et al.*[33] The possible identification of chloroethoxyethanol in air could point to the materials containing a fire retardant, although a definite identification could not be made. Similarly to the PIR foams, hydrogen cyanide was produced only in air whereas in nitrogen, 1,4-dioxane, methane and ammonia could be identified, with also aniline highlighted as a possible volatile.

Material	Identified Volatiles	Possible Volatiles	Not Identified Volatiles
PUR1	Cyclopentane, water, carbon dioxide, carbon monoxide, hydrogen cyanide	$1103cm^{-1}$ – Polyol $1600cm^{-1}$ – Chloroethoxyethanol $1700cm^{-1}$ – Urethane monomer (cannot identify specific one)	$2200cm^{-1}$
PUR2	Cyclopentane, water, carbon dioxide, carbon monoxide, hydrogen cyanide	$1103cm^{-1}$ – Polyol $1600cm^{-1}$ – Chloroethoxyethanol $1700cm^{-1}$ – Urethane monomer (cannot identify specific one)	$1200cm^{-1}$ $2200cm^{-1}$

Table 22: FTIR analysis for polyurethane materials in air

Material	Identified Volatiles	Possible Volatiles	Not Identified Volatiles
PUR1	Cyclopentane, carbon dioxide, carbon monoxide, water, 1-4, dioxane, methane, ammonia	Aniline $1103cm^{-1}$ – Polyol (Cluster around) $1700cm^{-1}$ – Urethane monomer (cannot identify specific one)	$2200cm^{-1}$
PUR2	Cyclopentane, carbon dioxide, carbon monoxide, water, methane, ammonia	$1103cm^{-1}$ – Polyol (Cluster around) $1700cm^{-1}$ – Urethane monomer (cannot identify specific one)	$2200cm^{-1}$ $3000cm^{-1}$

Table 23: FTIR analysis for polyurethane materials in nitrogen

4.2.5 Thermal degradation studies of expanded polystyrene

TGA, DSC and MCC data is presented for EPS below.

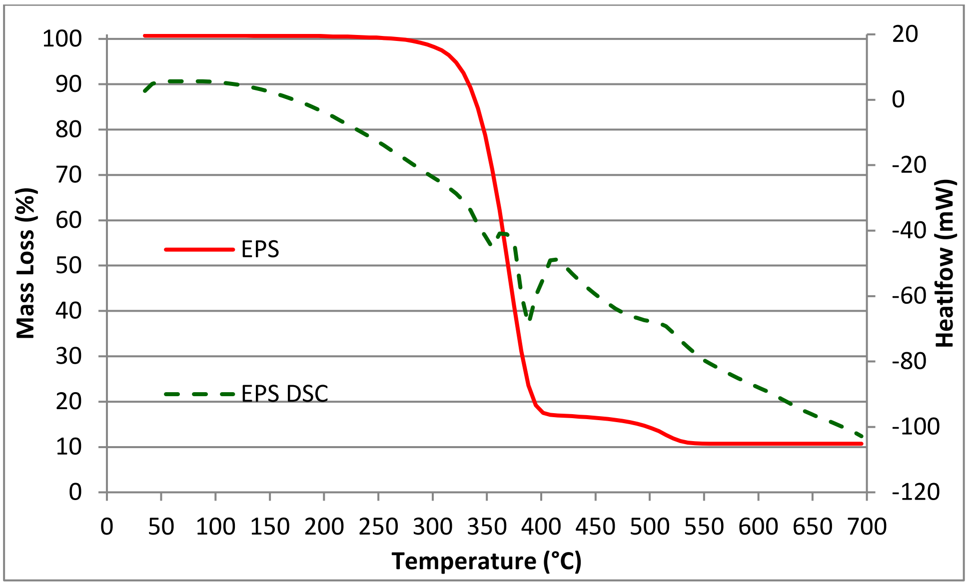


Figure 35: TGA and DSC results in air for EPS

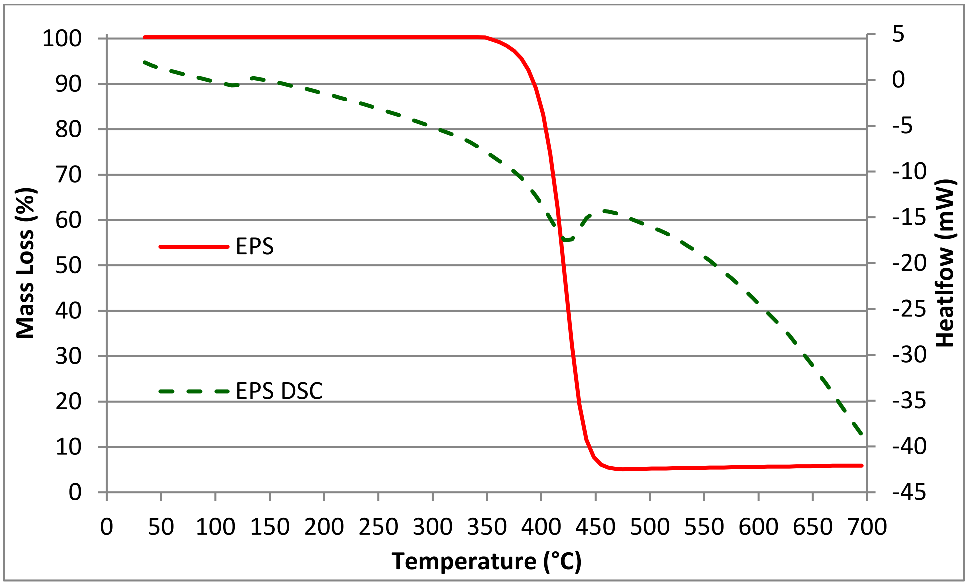


Figure 36: TGA and DSC data for EPS in nitrogen

The TGA data for EPS in air suggest that it is a two-step process, Figure 35 with an initial large decomposition occurring between 300-400°C followed by a relatively small step between 450-

520°C. After testing was complete, around 10% of the initial mass remained. The DSC data in air for EPS shows two potential peaks of heatflow change.

EPS loses slightly more of its total mass in nitrogen than in air (92% vs 90%), Figure 36, in a smooth one step process starting at around 350°C and finishing at 450°C. There is one peak of significant heatflow change for EPS in nitrogen.

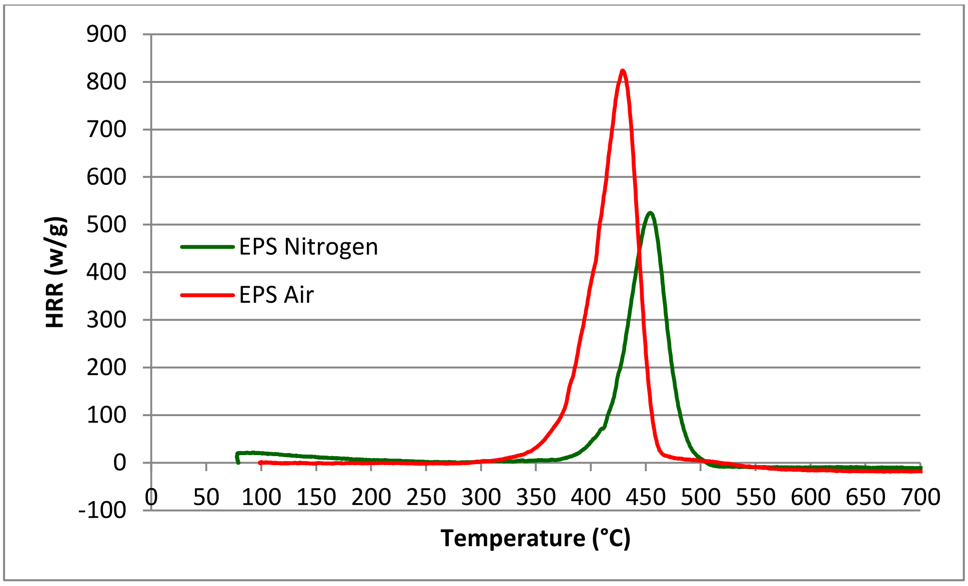


Figure 37: MCC data for EPS

The MCC data in air for EPS, Figure 35, shows that the main peak of heat release is around 420°C, and there is only one change in HRR across the temperature range tested.

The peak heat release for EPS in nitrogen is at 450°C with only one real peak.

The spectra obtained in nitrogen and air for EPS are shown below, Table 24, followed by summary tables of the FTIR analysis, Table 25 and Table 26, with decomposition in one stage in nitrogen and two stages in air.

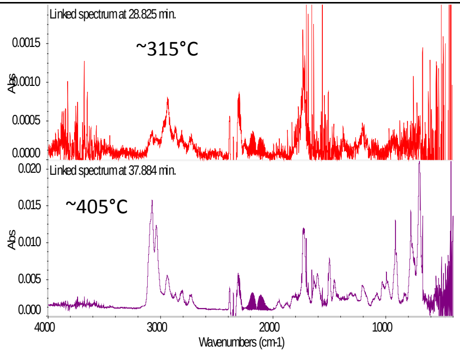
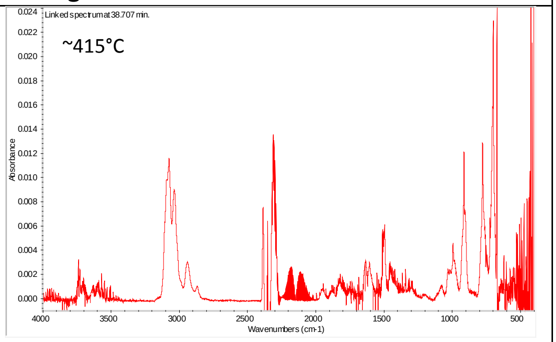
Material	Air	Nitrogen
EPS		

Table 24: FTIR spectra in air and nitrogen for EPS

As expected the main product identified from EPS in both air and nitrogen is styrene. 1-phenylhexane is also identified. In air, diphenylacetone was also identified, as well as water. Carbon dioxide and carbon monoxide were common to both environments. This is not what would be expected for EPS in nitrogen, however the presence of oxygen in the elemental analysis could mean that any fire retardant EPS may contain has oxygen.

Material	**Identified Volatiles**	**Possible Volatiles**	**Not Identified Volatiles**
EPS	1-phenylhexane, carbon monoxide, styrene, carbon dioxide, water	p-tolualdehyde	If not p-tolualdehyde, peak at 1200cm^{-1}

Table 25: FTIR analysis for EPS in air

Material	**Identified Volatiles**	**Possible Volatiles**	**Not Identified Volatiles**
EPS	1-phenylhexane, carbon monoxide, styrene, carbon dioxide, water	p-tolualdehyde	If not p-tolualdehyde, peak at 1200cm^{-1}

Table 26: FTIR analysis for EPS in nitrogen

4.3 Py-GCMS analysis of pyrolysates for insulation materials

The samples were inserted into the platinum filament of the pyrolyser, and was heated at 10°C per second from 300-300°C. The decomposition products were captured on a trap which was held at 50°C. When the pyrolyser program was finished, the trap was heated to 280°C for 2 minutes, after which the gas was transferred to GC, with the transfer line at 310°C. Following py-GCMS method optimisation, the GCMS method used was method M, as detailed in Table 24. The samples were analysed based on the NIST library and the chromatograms labelled with retention times only.

The chromatograms from the initial testing in air are presented below for all tested materials.

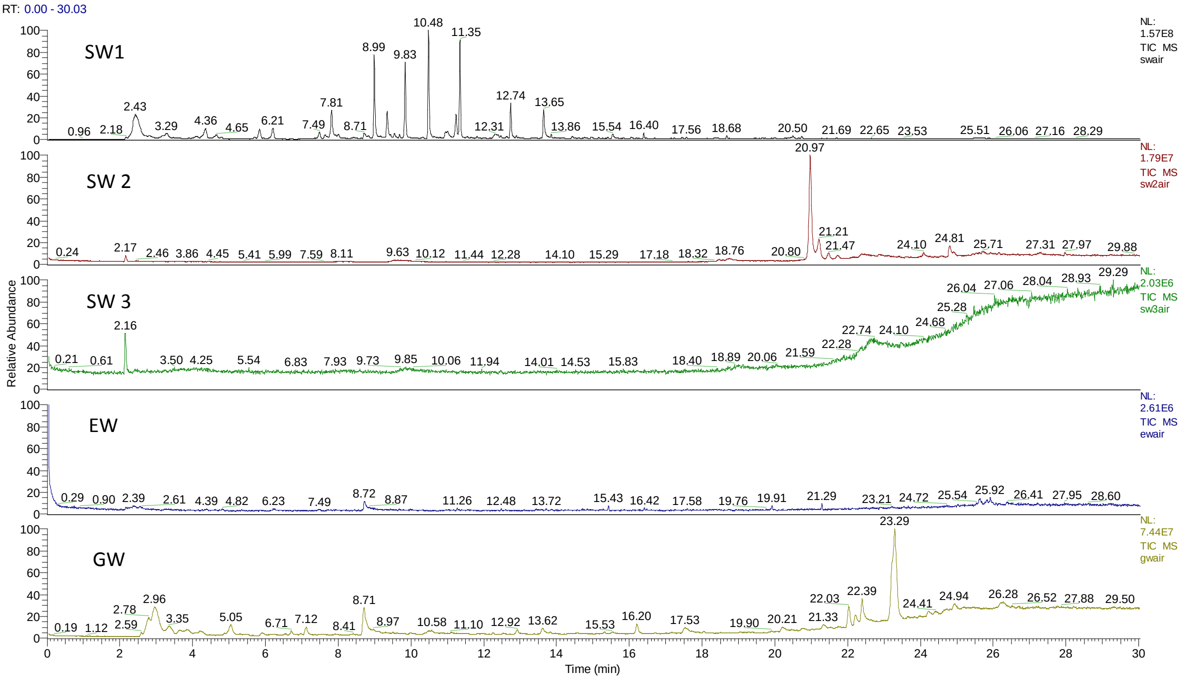


Figure 38: PyGCMS chromatograms in air for fibre materials

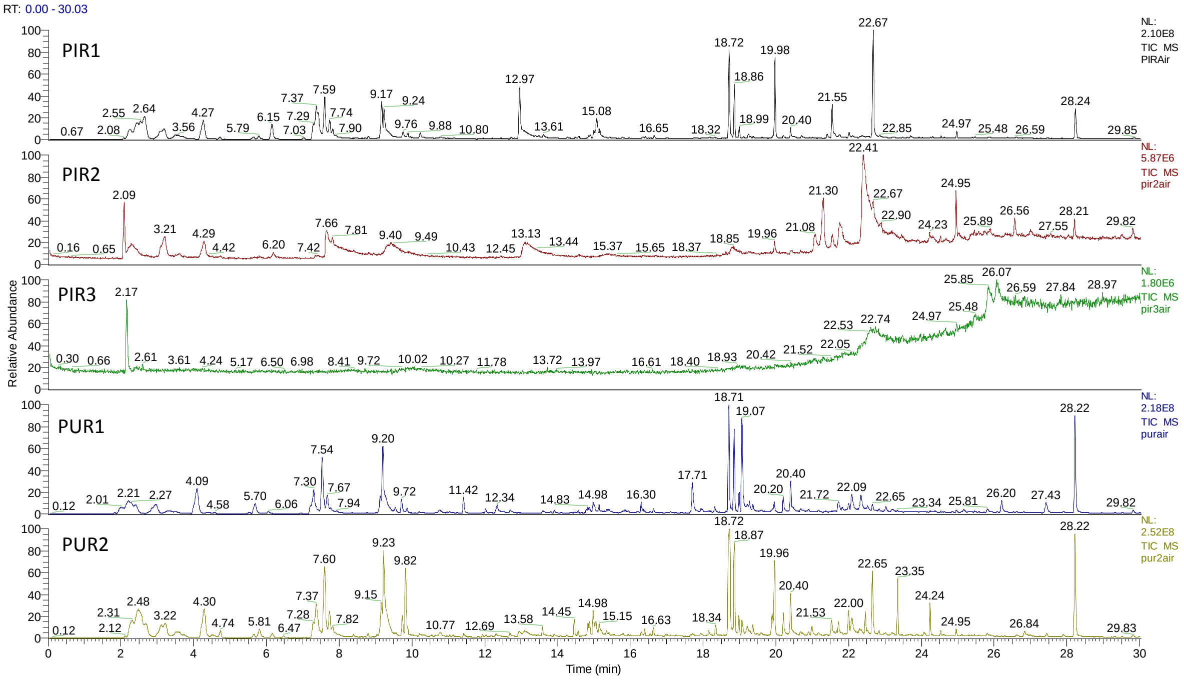


Figure 39: PyGCMS chromatograms in air for polyisocyanurate and polyurethane materials

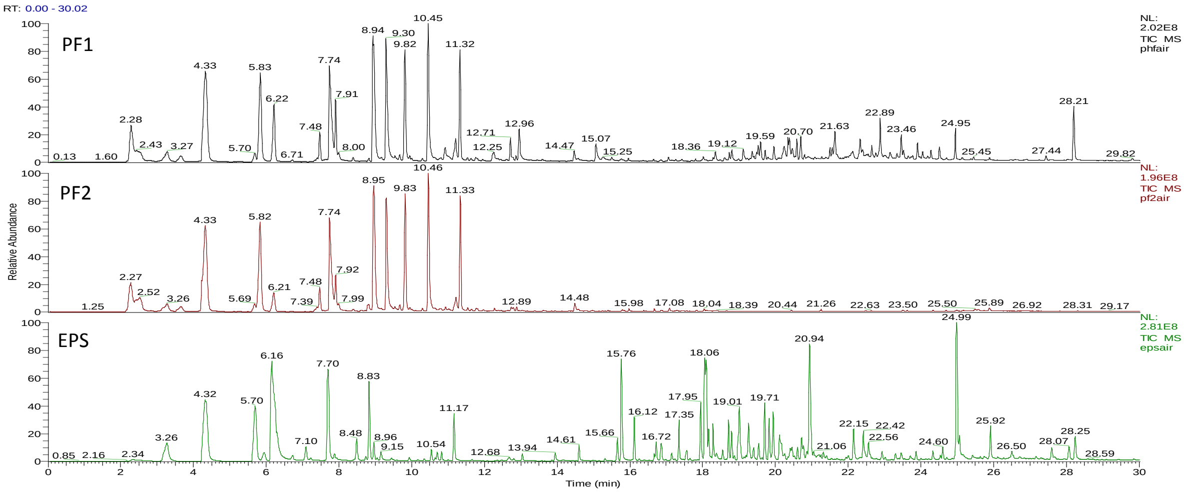


Figure 40: PyGCMS chromatograms for phenolic materials and EPS in air

In air, Figures 38-40, EPS produces a wide range of peaks across the time range. PF1 and PF2 show similar chromatograms, suggesting they have very similar compositions, as do PIR1 and PIR3, with PIR2 showing slightly less similarity. PUR1 and PUR2 produce almost identical chromatograms, also suggesting they are similar in composition. Despite the material differences, SW presents a similar chromatogram to the ones produced by PF1 and PF2. Few peaks were produced from SW2, SW3, EW and GW in air.

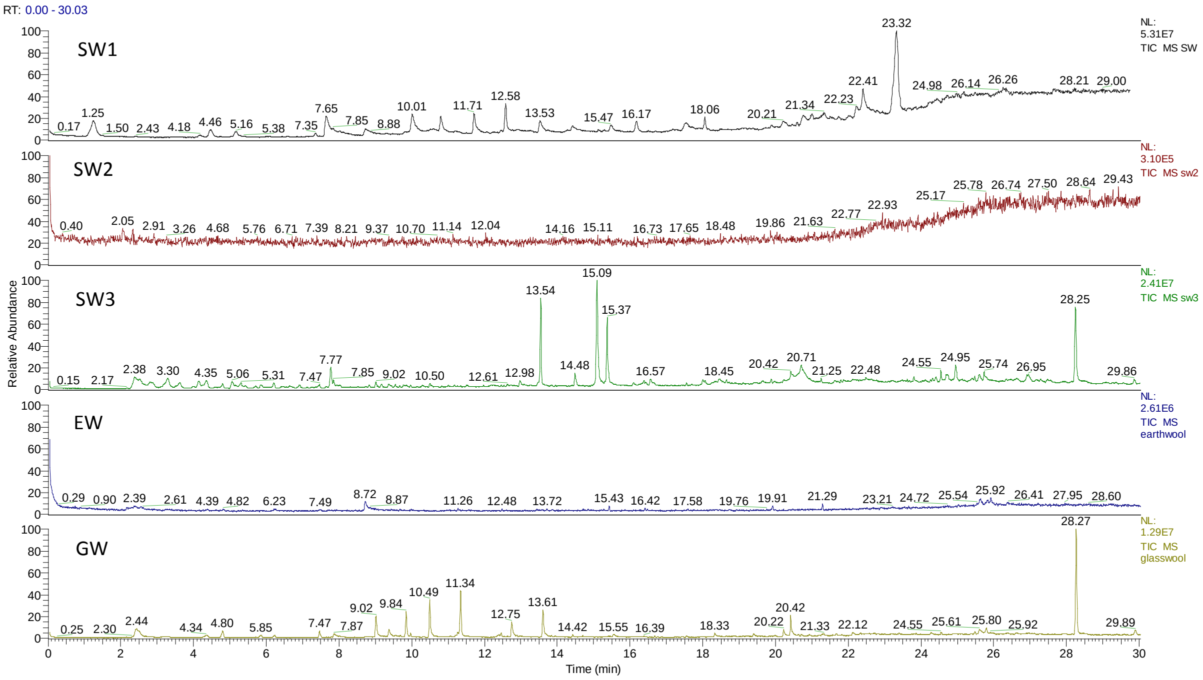


Figure 41: PyGCMS chromatograms in helium for fibre materials

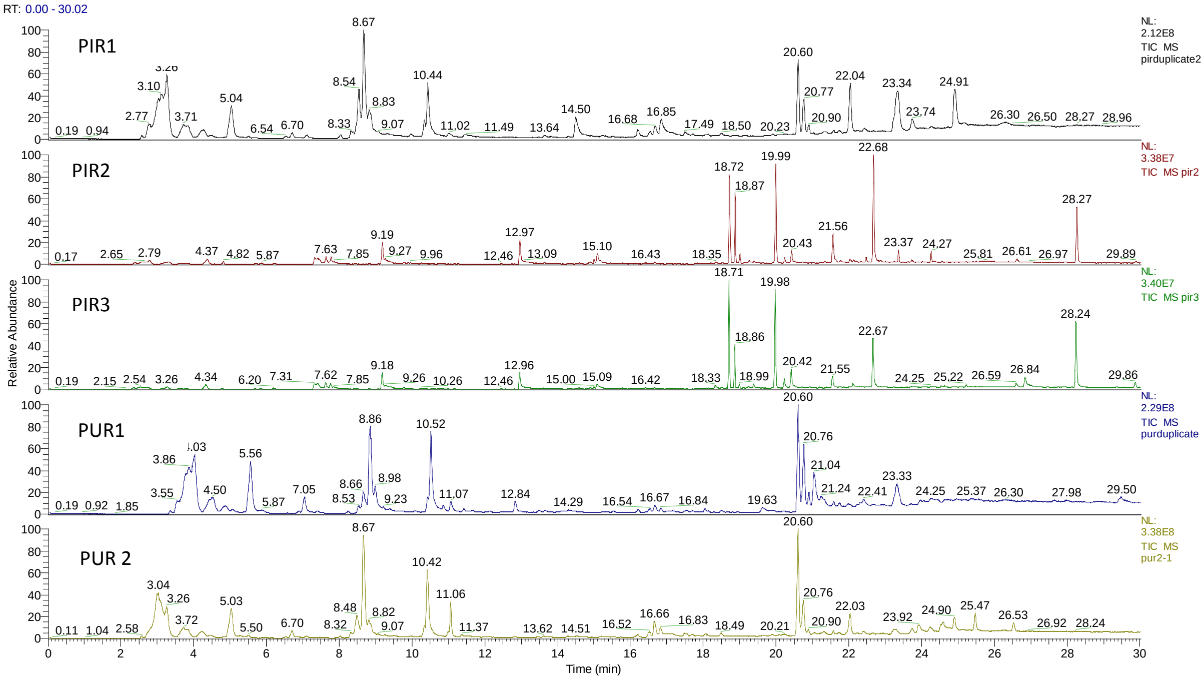


Figure 42: PyGCMS chromatograms in helium for polyisocyanurate and polyurethane materials

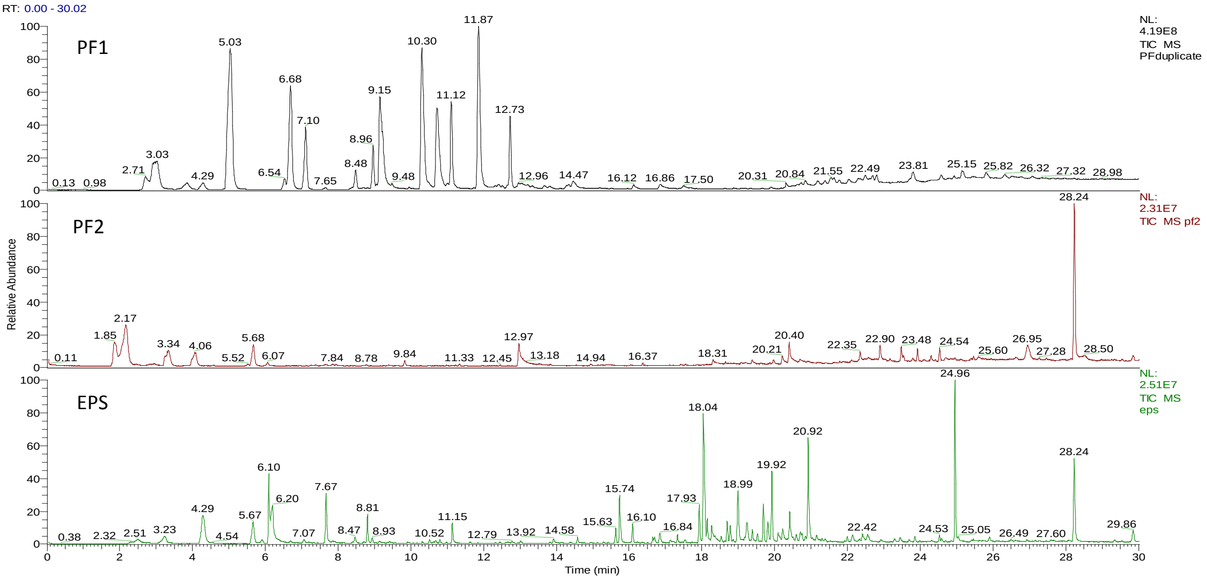


Figure 43: PyGCMS chromatograms in helium for phenolic materials and EPS

In helium, Figures 41-43, EPS produces a wide range of peaks across the time range. PF1 and PF2 show similar chromatograms, suggesting they have very similar compositions, as do PIR and PIR3, with PIR2 showing slightly less similarity. Again, PUR1 and PUR2 show similar chromatograms, while SW1 resembles the chromatograms produced by PF.

As shown in Table 28, which presents identified volatiles from this testing, the general pattern was that more volatiles were released in air than in helium. GW was an exception to this, with very few volatiles released in air, but a considerable number in helium. EW released no identifiable volatiles in air or in helium, while the peaks from SW2 could only be identified as long chain silica compounds, possibly due to the interaction between the Si identified in SW2 via EDAX analysis and the column. Based on their lack of volatiles released in this testing, as well as the lack of decomposition shown when these materials were tested via TGA in the previous section, it was decided to exclude them from the optimised temperature runs.

Based on the TGA data obtained in the previous section, optimised temperatures were selected for 11 of the 13 materials tested in helium and the tests run in duplicate. The only setting that was changed was the temperature of the pyroprobe.

	Helium (°C)
EPS	350-450
PF1	250-550
PF2	250-550
PIR1	200-600
PIR3	200-600
PIR2	200-600
PUR1	250-600
PUR2	250-600
SW1	200-600
SW2	N/A
Glass wool	250-700
SW3	250-700
Earthwool	N/A

Table 27: Temperatures optimised from TGA data used for pyGCMS testing

The chromatograms obtained for these optimised temperatures are displayed below.

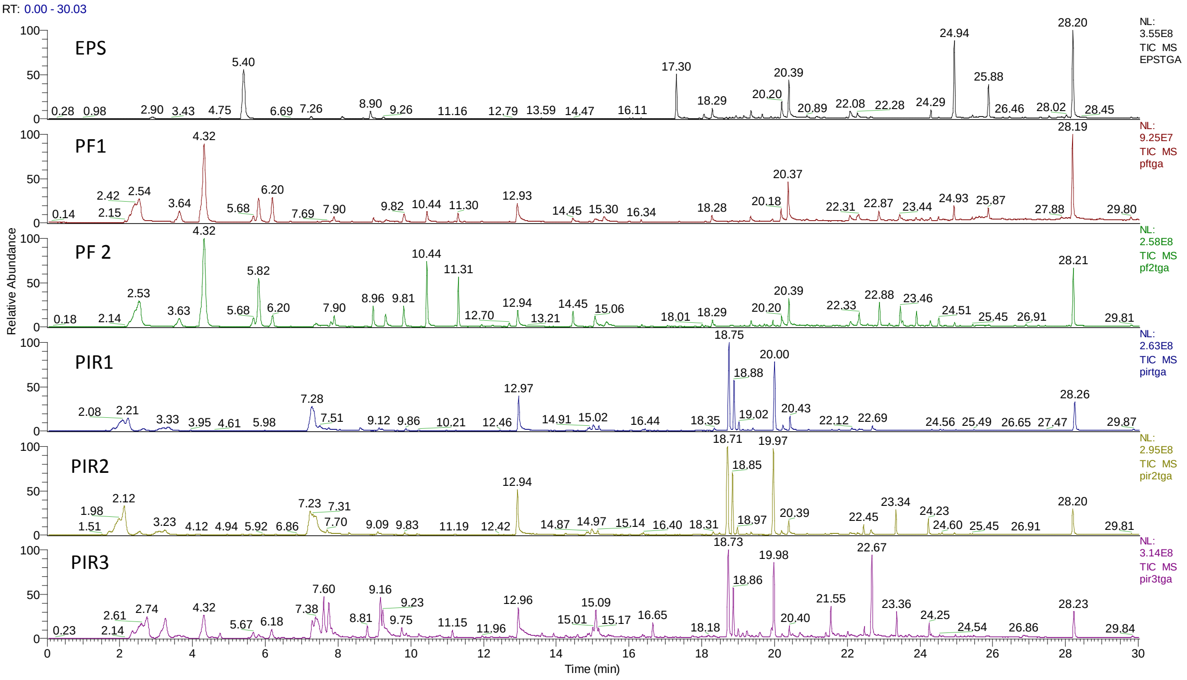


Figure 44: PyGCMS chromatograms for optimised temperatures for EPS, PF, PF2, PIR, PIR2 and PIR3

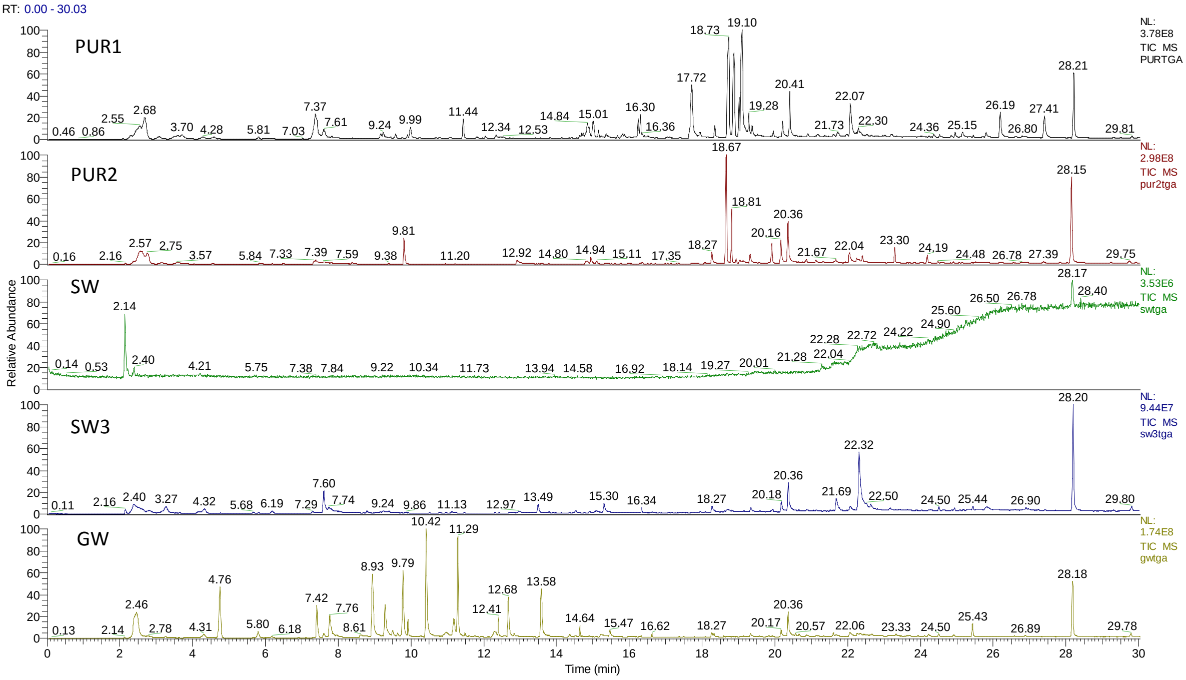


Figure 45: PyGCMS chromatograms for optimised temperatures for PUR, PUR2, SW, SW3 and SW5

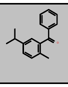
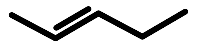
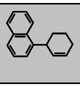
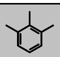
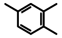
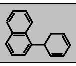
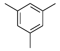
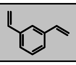
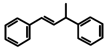
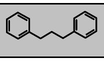
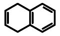
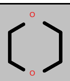
The chromatograms from the optimised temperatures show generally better separation, but fewer products are identified than in those from the full range.

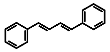
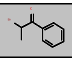
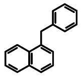
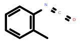
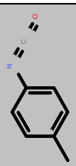
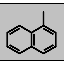
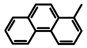
Table 28 shows the pyrolysate products classified in terms of carcinogenicity according to the International Agency for Research on Cancer classification, which are split into 5 groups explained below[19]:

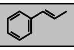
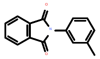
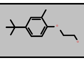
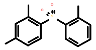
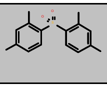
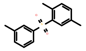
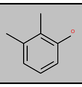
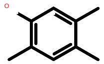
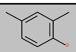
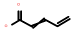
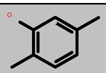
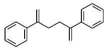
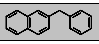
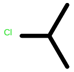
- Group 1: carcinogenic to humans.
- Group 2A: probably carcinogenic to humans.
- Group 2B: possibly carcinogenic to humans.
- Group 3: not classifiable as to carcinogenicity in humans.
- Group 4: probably not carcinogenic to humans.

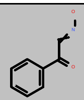
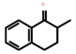
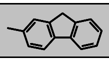
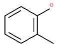
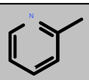
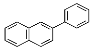
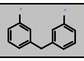
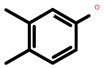
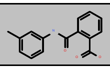
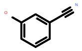
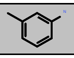
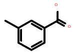
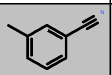
Further information is added on acute and long term toxicity based on ratings using the Globally Harmonised System of Classification and Labelling of Chemicals (GHS). The individual ratings are known as H-Statements and in the table below both the text descriptor and statement number are provided. An example of this is eye irritation (Category 2) H315 which indicates that a compound causes acute eye irritation.

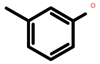
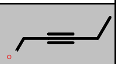
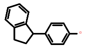
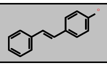
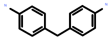
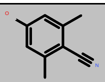
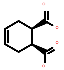
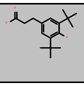
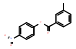
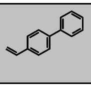
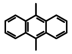
Compounds displayed in red are polycyclic aromatic hydrocarbons, which can have environmental concerns additionally to the toxicity concerns.

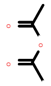
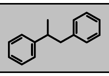
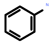
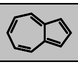
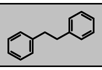
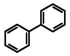
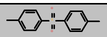
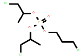
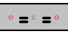
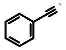
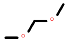
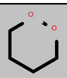
Py-GCMS (Helium = x air = o, additional temperature range in helium = ☐)															
Compound	Materials														Acute/Chronic Toxicity Classification
	Structure	PF1	PIR1	PUR1	EPS	PF2	PIR2	PIR3	PUR2	SW1	EW	GW	SW2	SW3	
(5-isopropyl-2-methylphenyl)(phenyl)methanone		o													No data available
(Trans) 2-pentene			xo□	x□			x□	x□	x□						IARC – Not Classified as carcinogenic Skin irritation (Category 2) Eye irritation (Category 2) Specific target organ toxicity - single exposure (Category 3) [80]
1,2,3,4-tetrahydrophenylnaphthalene															No data available
1,2,3,6-tetrahydrophthalimide														x	No data available
1,2,3-trimethylbenzene		o													IARC – Not Classified as carcinogenic Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335 [85]
1,2,4-trimethylbenzene		xo				o□				xo					IARC – Not Classified Acute toxicity, Inhalation (Category 4), H332 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335
1,2-dihydro-4-phenylnaphthalene					o										No data available
1,3,5-trimethylbenzene		x													IARC – Not Classified as carcinogenic Eye, skin and respiratory irritant[75]
1,3-diethenylbenzene															No data available
1,3-diphenylbutene					x□										No data available
1,3-diphenylpropane					x□										IARC – Not Classified as carcinogenic Not a hazardous substance[90]
1,4-dihydronaphthalene															No data available
1,4-dioxane						x									IARC – 2B Eye irritation (Category 2), H319 Carcinogenicity (Category 2), H351 Specific target organ toxicity - single

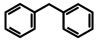
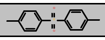
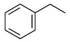
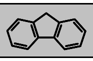
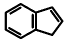
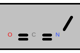
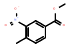
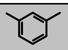
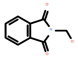
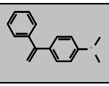
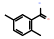
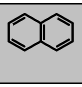
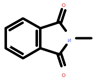
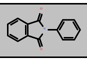
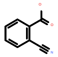
															exposure (Category 3), Respiratory system, H335
1,4-diphenyl-1,3-butadiene					o□										IARC – Not classified Skin irritation (Category 2) Eye irritation (Category 2) Specific target organ toxicity - single exposure (Category 3)[74]
1-benzoyl-1-bromoethane				x□											No data available
1-benzylnapthalene					o										No data available
1-chloropropene									xo						IARC – Group 3 Acute toxicity, Oral (Category 3), H301 Acute toxicity, Inhalation (Category 3), H331 Acute toxicity, Dermal (Category 3), H311 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Germ cell mutagenicity (Category 2), H341 Carcinogenicity (Category 2), H351 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335 Specific target organ toxicity - repeated exposure (Category 1), Nervous system, Liver, Kidney, H372
1-isocyanato-2-methylbenzene		o													No data available
1-isocyanato-4-methylbenzene				xo	xo		xo□	x□	xo						IARC – Not classified Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 4), H312 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Respiratory sensitisation (Category 1), H334 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335
1-methylhydrouracil										xo		x□			No data available
1-methylnapthalene															No data available
1-methylphenanthrene		xo□			o										No data available

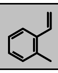
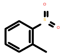
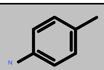
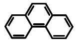
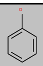
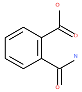
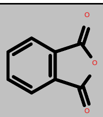
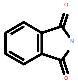
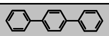
1-propenylbenzene															Not classified
2-(3-methylphenyl)-isoindole-1,3-dione			xo□												No data available
2-(4-tertbutyl-2-methylphenoxy)-ethanol							xo□	x□	xo						No data available
2,2,4’-trimethyldiphenylsulphone						x□									No data available
2,2’,4,4’-tetramethyldiphenylsuphone		xo□				x									No data available
2,3’,5-trimethyldiphenylsulphone		xo□													No data available
2,3-dimethylphenol						o				xo		x□		x	IARC – Not Classified as carcinogenic[83] Toxic by ingestion and skin absorption[84]
2,4,5-trimethylphenol		xo□				o□				xo		x□			IARC – Not Classified as carcinogenic Corrosive[78]
2,4-dimethylphenol		xo□				o□				xo					IARC – Not Classified as carcinogenic Acute toxicity, Dermal (Category 3), H311 Acute toxicity, Oral (Category 3), H301 Skin corrosion (Category 1B), H314[77]
2,4-pentadienoic acid						x									IARC – Not classified Not a hazardous substance
2,5-dimethylphenol		o													IARC – Not classified Skin corrosion (Category 1B), H314 Acute toxicity, Dermal (Category 3), H311 Acute toxicity, Oral (Category 3), H301
2,5-diphenyl-1,5-hexadiene					xo										No data available
2-benzylnapthalene					o										No data available
2-chloropropane			o	o		xo									IARC – not classified Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 4), H312 Acute toxicity, Oral (Category 4), H302

2-Isonitrosoacetophenone				o											IARC – Not classified Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 4), H312 Acute toxicity, Oral (Category 4), H302
2-methyl-1-tetralone														x	No data available
2-methylfluorene					xo										No data available
2-methylphenol		xo□				o□				xo		x□			IARC – Not Classified as carcinogenic Acute toxicity, Dermal (Category 3) Acute toxicity, Oral (Category 3) skin corrosion (Category 1B)[76]
2-methylpyridine														x	IARC – Not classified Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 3), H311 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335
2-phenylnaphthalene					xo										Not Classified as carcinogenic Not known to be harmful[92]
3-(3-aminobenzyl)-phenylamine			x	xo□				xo	xo						No data available
3,4-dimethylphenol		x□				□						x□			IARC – Not Classified as carcinogenic Acute toxicity, Dermal (Category 3), H311 Acute toxicity, Oral (Category 3), H301 Skin corrosion (Category 1B), H314[77]
3'-methylphthalanilic acid							x□	x□	xo						IARC – Not classified Eye irritation (Category 2), H319
3-hydroxybenzonitrile							x□								No data available
3-methylbenzenamine			xo□												No data available
3-methylbenzoic acid				o											No data available
3-methylbenzonitrile				o											IARC – Not classified Skin irritation (Category 2) Eye irritation (Category 2) Specific target organ toxicity - single exposure (Category 3)

3-methylphenol		xo□				o□				xo						IARC – Not Classified Acute toxicity, Oral (Category 3), H301 Acute toxicity, Dermal (Category 3), H311 Skin corrosion (Category 1B), H314
3-pentyn-1-ol														x		IARC – Not classified Skin irritation (Category 2) Eye irritation (Category 2) Specific target organ toxicity - single exposure (Category 3)
4-(2,3-dihydro-1h-inden-yl)-phenol		xo□														No data available
4-(2-phenylethenyl)-phenol		x														No data available
4-4’-methylenedianiline				xo□					xo□							IARC – Not classified Skin sensitisation (Category 1), H317 Germ cell mutagenicity (Category 2), H341 Carcinogenicity (Category 1B), H350 Specific target organ toxicity - single exposure (Category 1), H370 Specific target organ toxicity - repeated exposure (Category 2), H373
4-cyano-3,5-dimethylphenol		xo								xo						IARC – Not Classified Acute toxicity, Oral (Category 4) Eye irritation (Category 2) Skin irritation (Category 2) Skin sensitization (Category 1)
4-cyclohexene-1,2-dicarboxylicacid														x		IARC – Not classified Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335
4-hydroxy-3,5-ditertbutylphenylpropionicacid														x		No data available
4-nitrophenylester m-toluic acid				o												No data available
4-vinylbiphenyl																IARC – Not Classified No data available for acute toxicity in humans[93]
9,10-dimethylanthracene					o											IARC – Not Classified Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 4), H312 Respiratory sensitisation (Category 1), H334 Skin sensitisation

															(Category 1), H317
9-acrinylmethanol									xo						No data available
Acetic anhydride												x□			IARC – Not classified Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 3), H331 Skin corrosion (Category 1B), H314
Alphamethylbibenzyl					xo										No data available
Aniline			xo□	o□			xo□	xo□	xo□						IARC – 3[70] Toxic if ingested, inhaled or on skin contact[71]
Azulene															No data available
Benzene		o□	xo□	o□	xo	o□	xo□	xo□	xo					□x	IARC – 1 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319[64]
Bibenzyl					xo										IARC – Not Classified as carcinogenic Not classified for acute toxicity[89]
Biphenyl					ox										IARC – Not classified Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335
Bis (4-methylphenyl) sulphone						x□									No data available
Bis(2-chloro-1-methylethyl)-3-chloropropylphosphate			xo□	xo□			xo□	xo□	xo□						No data available
Carbon dioxide							o							o	No data available
Cyanobenzene			xo□	o□			xo□		xo□					x	No data available
Cyclopentane			xo□	xo□			x□	xo□	xo□						IARC-Not classified as carcinogenic Acute toxicity, Dermal (Category 4), H312 Acute toxicity, Oral (Category 4), H302 Skin irritation (Category 2), H315
Dimethoxymethane								x	xo□						IARC – Not classified Eye irritation (Category 2), H319
Dioxane						o									IARC – 2B Eye irritation (Category 2), H319 Carcinogenicity (Category 2), H351 Specific target organ toxicity - single

															exposure (Category 3), Respiratory system, H335
Diphenylmethane					xo										IARC – Not Classified as carcinogenic Not known to have toxic effects[91]
Di-p-tolylsulphone		xo□													No data available
Ethylbenzene					xo										IARC – Not Classified as carcinogenic Acute toxicity, Inhalation (Category 4), H332[87]
Fluorene			xo□						xo□						IARC – Group 3
Indene					xo										IARC - Not Classified as carcinogenic[81] Aspiration hazard (Category 1), H304[82]
Methyl Isocyanate										xo					IARC – Not Classified as carcinogenic[94]
Methylesterp-toluic acid				xo□											No data available
m-xylene		xo□		□		□o		□	□	□					IARC - 3 Acute toxicity, Inhalation (Category 4) Acute toxicity, Dermal (Category 4) Skin irritation (Category 2)[69]
n-(hydroxymethyl)-phthalimide							xo□	x□	xo						No data available
N,N-dimethyl-4-(phenylethenyl)-benzeneamine		xo□					x□								No data available
N-2-dimethylbenzenamide				xo□											No data available
Naphthalene					xo										IARC – 2B Carcinogenicity (Category 2) Acute toxicity, Oral (Category 4)[67]
N-methylphthalimide		xo				o□								x	IARC – Not classified Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335
N-phenylphthalimide			xo□												IARC – Not classified Not classified for toxicity
O-cyanobenzoic acid		o													IARC – Not Classified as carcinogenic Acute toxicity, Inhalation (Category 4) Acute toxicity, Dermal (Category 4) Acute toxicity, Oral (Category 4) Skin irritation (Category 2) Eye irritation (Category 2) Specific target organ toxicity - single

														exposure (Category 3)[86]
o-methylstyrene					xo									IARC – 2B Irritant – eye, skin, respiratory[66]
O-tolylsulphone		xo□												No data available
P-aminotoluene				o										IARC – Not Classified as carcinogenic Acute toxicity, Inhalation (Category 3), H331 Acute toxicity, Dermal (Category 3), H311 Acute toxicity, Oral (Category 3), H301 Eye irritation (Category 2), H319 Skin sensitisation (Category 1), H317[88]
Phenanthrene		xo□			xo									IARC – Group 3 Acute toxicity, Oral (Category 4), H302 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335
Phenol		o				o				xo		x□		IARC - 3 Acute toxicity, Inhalation (Category 3) Acute toxicity, Dermal (Category 3) Acute toxicity, Oral (Category 3) Skin corrosion (Category 1B)[73]
Phthalic acid		x□	xo□			□	xo□	xo□	xo□				x□	IARC – Not Classified Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335
Phthalic anhydride		o				x								IARC – Not classified Acute toxicity, Oral (Category 4) Skin irritation (Category 2) Serious eye damage (Category 1) Respiratory sensitization (Category 1) Skin sensitization (Category 1) Specific target organ toxicity - single exposure (Category 3)
Phthalimide		x	xo□						□				x	IARC – Not classified Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008
P-terphenyl					o									IARC – Not classified Skin irritation (Category 2) Eye irritation (Category 2) Specific target

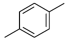
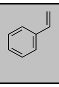
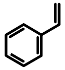
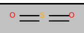
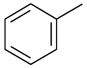
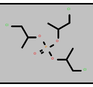
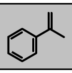
														organ toxicity - single exposure (Category 3)
p-Xylene		xo□		o□		xo□	□	□	□	xo				IARC - 3 Acute toxicity, Inhalation (Category 4) Acute toxicity, Dermal (Category 4) Skin irritation (Category 2)[69]
Styrene			o		xo□									IARC – 2B Acute toxicity, Inhalation (Category 4) Skin irritation (Category 2)[65]
Styrene (Dimer)														IARC – 2B Eye irritation (Category 2) Acute toxicity, Inhalation (Category 4) Skin irritation (Category 2) [65]
Sulphur dioxide		o				xo								IARC - 3 Acute toxicity, Inhalation (Category 3) Skin corrosion (Category 1B)[72]
Toluene		o□	□	o	xo	xo□	xo	xo	xo	xo		x□		x□	IARC – 3 Skin irritation (Category 2), H315 Specific target organ toxicity - single exposure (Category 3)[68]
Tris(2-chloro-1-methylethyl)ester phosphoric acid			xo□	xo□			xo□	xo□	xo□					No data available
Z-stilbene					ox									IARC – Not Classified as carcinogenic Skin irritation (Category 2) Eye irritation (Category 2)[79]
α-methylstyrene					xo									IARC – 2B Irritant – eye, skin, respiratory[66]

Table 28: Py-GCMS analysis of insulation materials for all temperatures and environments tested

As can be seen from Table 28, benzene, a compound classified by IARC as carcinogenic, was released from 9 of the 13 insulation materials tested, and was more commonly found in air than in nitrogen. Additionally, 6 compounds believed to be possibly carcinogenic to humans by IARC were identified through the testing: dioxane, styrene, styrene dimer, 1,4-dioxane, α-methylstyrene and o-methylstyrene. Several polycyclic aromatic hydrocarbons were identified including naphthalene, phenanthrene, fluorene and indene which are on the EPA's list of priority PAHs. All PAHs identified are highlighted in red in Table 28, with EPS producing the largest number of PAHs of the materials tested.

The main product released from EPS under all conditions was styrene. For PIR1, PUR1, PIR2, PUR2 and PIR, the main products released were aniline and phthalic acid along with two chlorophosphate compounds, tris(2-chloro-1-methylethyl)ester phosphoric acid and bis(2-chloro-1-methylethyl)-3-chloropropylphosphate, which are fire retardant additives. Stereoisomers of di and trimethylphenol, such as 1,4-dimethyl phenol and 2,4,5-trimethylphenol were the predominant products produced from each of the phenolic foam samples, which was also the case for SW1 and, to a much lesser extent, the testing performed on GW in helium. The identified products of SW1 across all the py-GCMS testing conditions generally very closely resembled those of both PF1 and PF2. EW did not produce any identifiable volatiles under either environment.

5. DISCUSSION AND CONCLUSIONS

5.1 Pyrolysis GCMS optimisation method

Styrene is the predominant product from the pyrolysis of polystyrene and this was reflected in the py-GCMS optimisation results. The methods were individually evaluated and a summary of their evaluation is shown in Table 29.

Method	Chromatogram quality	Range of elutants	Efficiency
A	Good separation	Some expected products did not occur	Ran for a suitable amount of time
B	Good separation	Relatively few products identified	Too long, 15+ minutes longer than last significant peak
C	Separation issues	Relatively few products identified	Suitable length
D	Separation issues	Relatively few products identified	Too long
E	Separation issues	Difficult to identify some peaks due to separation issues, expected elutants not found	Too long
F	Separation issues	Relatively few elutants	Suitable length
G	Good separation	Relatively few elutants	Suitable length
H	Good separation	Some expected products did not occur	Too long, ran for over 20 minutes after last significant peak
I	Excellent separation	Acceptable range of elutants	Too long
J	Poor separation	Some peaks could not be identified accurately due to the poor separation but otherwise good range of volatiles identified	Slightly longer than needed but in the acceptable range
K	Poor separation	Good range of volatiles identified	Too short, run potentially ended before all products eluted
L	Good separation	Good range of volatiles identified	Slightly longer than needed but in the acceptable range
M	Excellent separation	Good range of volatiles identified	Suitable length

Table 29: GCMS method comparison

5.2 Summary of thermal analysis from insulation materials

The results from the TGA testing indicated that, for the materials that degrade, the decomposition process typically starts around 50°C earlier than in nitrogen. Of the materials tested, five did not show any significant decomposition in either environment: SW1, SW2, SW3, EW and GW. In air, the decomposition was more marked than in nitrogen, with eight materials losing more than 80% of their mass (EPS, PF1, PF2, PIR1, PIR2, PIR3, PUR1 and PUR2) compared to three in nitrogen (EPS, PUR1 and PIR2). This shows that while the decomposition of the materials was broadly similar in nitrogen and air and occurred in the same temperature region, the environmental composition does have an effect.

Compared to literature, the PIR foams tested decomposed at similar temperatures. Liggat et al[35] found that the decomposition of the isocyanate group specifically occurred at around 300°C and all of the tested PIR foams showed significant mass loss within this temperature range, as did the PUR foams which also contain isocyanate groups. Hu *et al* had found that phenolic foam decomposition occurs in three temperature regions, between 100-200°C initially then two decompositions between 200-900°C.[95] Although testing was only carried out until 700°C in this study, the regions were very similar to those described in the literature for untreated phenolic foam.

Similarly to the TGA data, the results of the MCC testing showed that decomposition starts around 50°C earlier in air compared to nitrogen. However, the point of peak heat release in air actually occurred later in air for a significant percentage of the materials tested.

5.3 Summary of volatile analysis from insulation materials

The conclusions reached from the testing on expanded polystyrene largely supported the literature results, with styrene being by far the most predominant product both via FTIR and py-GCMS as shown in Table 22, Table 23 and Table 28. There was no real evidence found that the EPS sample contained a fire retardant although it almost certainly would have contained hexabromododecane (HBDD). Other products included methylstyrene, benzene, toluene and other PAH, which again reflects the results found in literature, in particular the analysis of styrene by Westblad *et al*.

The results for the three polyisocyanurate foams tested and the two polyurethane foams tested were broadly similar, which reflects the similarity of monomers used to form these. Additionally, four out of the five foams were identified as containing phosphorus, PIR2, PIR3, PUR and PUR2, with all of these foams showing the presence of chlorine which suggests that they contain a chlorophosphate fire retardant, a result which is backed up by the py-GCMS results which identified tris(2-chloro-1-methylethyl)ester phosphoric acid and bis(2-chloro-1-methylethyl)-3-chloropropylphosphate as present in all five foams. Additionally, as expected from the literature, hydrocarbons, cyclic compounds and nitrogen products were all identified as products from the py-GCMS testing. One difference between the PIR and PUR foams was that ammonia appeared to be consistently released under nitrogen conditions in the TGA for PUR, possibly due to the greater relative stability of the PIR bonding. Cyclopentane, which is used as a blowing agent, was consistently identified for all of these foams across both air and inert analysis, both via FTIR and py-GCMS. In the FTIR analysis for all materials, HCN was identified more commonly in air, while methane and ammonia were identified exclusively in nitrogen. 1,4-dioxane was also identified during the FTIR testing, for PIR3 in both environments and for PUR in air.

Across both nitrogen and air, as identified in the tables for each material it is possible to see the break-up of the polymer backbone in all of the PIR and PUR samples. Though it has not been possible for the specific polyurethane and polyol to be identified, the general mechanism and very similar degradation patterns can be found in a study by Jiao *et al*.[33] In addition, the temperature ranges at which this begins to occur (before 350°C) supports the findings from Liggat *et al* who found that the isocyanate group traditionally used in the foams started to decompose at around 300°C.

For the two phenolic foams the results were supportive of the literature, with the main products identified as various stereoisomers of di- and tri-methylphenol. Additionally chlorine was identified in the first phenolic foam sample both via EDAX and in the py-GCMS analysis as 2-chloropropane which could suggest that the foam contained a fire retardant. In the FTIR analysis a large amount of sulphur dioxide was released, reflecting the presence of sulphur from the elemental analysis. As in the py-GCMS results, 1,4-dioxane was identified as a product from PF in air and nitrogen from the FTIR data, whereas ammonia, methane and phenol products only identified in nitrogen from the FTIR. Under FTIR, carbon dioxide and carbon monoxide were also released as expected from the results collated in literature study of phenolics described in Table 5

Contrary to expectations, the first fibre sample released a relatively large amount of pyrolysis products when tested via py-GCMS. The volatiles released were almost identical to those of phenolic foam: toluene, xylene isomers, phenol and di- and tri-methylphenols. This suggests that a phenolic resin based binder has been used during the manufacturing process.

Due to the limitations of the FTIR in distinguishing between methyl isocyanate, carbon dioxide and isocyanic acid at 2200cm^{-1}, for most materials it was not possible to make a definite analysis of these peaks.

For SW, methyl isocyanate was discovered as a pyrolysis product, suggesting that the unidentified 2200cm^{-1} peak in the FTIR analysis could be due to methyl isocyanate. The third fibre sample, SW3, also showed the release of volatiles that are suggestive of binder usage, such as toluene and phthalic acid. As expected, the second fibre sample, SW2, showed only very minor degradation via TGA and released no identifiable volatiles during pyrolysis.

As expected the fourth fibre sample, EW, did not show any noticeable degradation via TGA or release any identifiable volatiles via py-GCMS.

The final fibre sample, GW, released a small amount of volatiles via py-GCMS: toluene, phenol and di- and tri-methylphenol isomers, which appear to reflect the use of a phenolic filler. Ammonia and isocyanic acid were both positively identified during the FTIR analysis. As mentioned in Section 3.2.1 this was the only place where isocyanic acid could be positively identified.

6. FUTURE WORK

To investigate these materials further, more analysis is needed of the insulation materials via py-GCMS at each stage of decomposition, using the temperatures determined by TGA analysis. In addition, ways to distinguish the differences between carbon dioxide, methyl isocyanate and isocyanic acid on the FTIR should be further investigated. A possible solution could be to use the more sensitive MCT detector on the FTIR or to spike materials with isocyanate standards and run alongside py-GCMS. In addition, testing these materials in fire conditions could provide further insight into the released volatiles and fire behaviour.

7. REFERENCES

[1] A. A. Stec and T. R. Hull, “Assessment of the fire toxicity of building insulation materials,” *Energy Build.*, vol. 43, no. 2–3, pp. 498–506, 2011.

[2] S. K. Durlak, P. Biswas, J. Shi, and M. J. Bernhard, “Characterization of Polycyclic Aromatic Hydrocarbon Particulate and Gaseous Emissions from Polystyrene Combustion,” *Env. Sci Technol*, vol. 32, no. 15, pp. 2301–2307, 1998.

[3] EPFA, “Phenolic Foam Properties,” [Online]. Available: http://www.epfa.org.uk/Pdfs/eng.pdf. [Accessed: 09-Mar-2016].

[4] G. Rein, “Smouldering Combustion Phenomena in Science and Technology,” *Int. Rev. Chem. Eng.*, vol. 1, pp. 3–18, 2009.

[5] International Organisation for Standardization, “Guidelines for assessing the adverse environmental impact of fire effluents,” *ISO 26367-1:2011 Guidelines for assessing the adverse environmental impact of fire effluents*. 2011.

[6] D. Purser, “Fire retardant materials Toxicity of fire retardants in relation to life safety and environmental hazards,” in *Fire retardant materials*, 2001, pp. 69–127.

[7] D.A. Purser, “Lung Irritance and Inflammation During and After Exposure to Thermal Decomposition Products from Polymeric Materials,” *Med. Sci. Law*, vol. 23, pp. 142–150, 1983.

[8] D.A. Purser, “Biological Studies of Combustion Atmospheres,” *J. Fire Sci.*, vol. 1, p. 118–145, 1983.

[9] EPA, “Polystyrene fact sheet.” [Online]. Available: http://www.epa.gov/ttnchie1/ap42/ch06/final/c06s06-3.pdf. [Accessed: 09-Mar-2016].

[10] D. M. S. Al-Homoud, “Performance characteristics and practical applications of common building thermal insulation materials,” *Build. Environ.*, vol. 40, no. 3, pp. 353–366, Mar. 2005.

[11] C. Westblad, Y. A. Levendis, H. Richter, J. B. Howard, and J. Carlson, “A study on toxic organic emissions from batch combustion of styrene,” *Chemosphere*, vol. 49, no. 4, pp. 395–412, 2002.

[12] L. Jiao and J. Sun, “A Thermal Degradation Study of Insulation Materials Extruded Polystyrene,” *Procedia Eng.*, vol. 71, pp. 622–628, 2014.

[13] I. C. McNeill, M. Zulfiqar, and T. Kousar, “A detailed investigation of the products of the

thermal degradation of polystyrene," *Polym. Degrad. Stab.*, vol. 28, no. 2, pp. 131–151, Jan. 1990.

[14] H. Takigami, M. Watanabe, and N. Kajiwara, "Destruction behavior of hexabromocyclododecanes during incineration of solid waste containing expanded and extruded polystyrene insulation foams.," *Chemosphere*, vol. 116, pp. 24–33, Dec. 2014.

[15] T. R. H. A. A. Stec, "Assessment of the fire toxicity of building insulation materials," *Energy Build.*, vol. 43, no. 2–3, pp. 498–506, 2011.

[16] G. Grause, D. Karakita, J. Ishibashi, T. Kameda, T. Bhaskar, and T. Yoshioka, "TG-MS investigation of brominated products from the degradation of brominated flame retardants in high-impact polystyrene.," *Chemosphere*, vol. 85, no. 3, pp. 368–73, Oct. 2011.

[17] G. Grause, D. Karakita, J. Ishibashi, T. Kameda, T. Bhaskar, and T. Yoshioka, "Impact of brominated flame retardants on the thermal degradation of high-impact polystyrene," *Polym. Degrad. Stab.*, vol. 98, no. 1, pp. 306–315, Jan. 2013.

[18] J. L. Gurman, L. Baier, and B. C. Levin, *Polystyrenes : a review of the literature on the products of thermal decomposition and toxicity*. Gaithersburg, Md.: National Bureau of Standards, 1986.

[19] P. Kannan, J. J. Biernacki, D. P. Visco, and W. Lambert, "Kinetics of thermal decomposition of expandable polystyrene in different gaseous environments," *J. Anal. Appl. Pyrolysis*, vol. 84, no. 2, pp. 139–144, Mar. 2009.

[20] C. Bouster, P. Vermande, and J. Veron, "Study of the pyrolysis of polystyrenes: I. Kinetics of thermal decomposition," *J. Anal. Appl. Pyrolysis*, vol. 1, no. 4, pp. 297–313, 1980.

[21] J. D. Peterson, S. Vyazovkin, and C. A. Wight, "Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene)," *Macromol. Chem. Phys.*, vol. 202, no. 6, pp. 775–784, Mar. 2001.

[22] H. H. G. Jellinek, "The combustion of organic polymers, C. F. Cullis and M. M. Hirschler, Eds., Oxford university press, London, 1981.," *J. Polym. Sci. Polym. Lett. Ed.*, vol. 20, no. 11, p. 606, 1982.

[23] H. Kaya and J. Hacaloglu, "Thermal degradation of polystyrene composites. Part I. The effect of brominated polyepoxy and antimony oxide," *J. Anal. Appl. Pyrolysis*, vol. 105, pp. 301–308, Jan. 2014.

[24] S. Hu and F. You, "The Effects of Oxygen Contents and Heating Rates on Characteristics of

Pyrolysis Prior to Smoldering of Flexible Polyurethane Foam," *Procedia Eng.*, vol. 52, pp. 145–151, 2013.

[25] M. Zieleniewska, M. K. Leszczyński, M. Kurańska, A. Prociak, L. Szczepkowski, M. Krzyżowska, and J. Ryszkowska, "Preparation and characterisation of rigid polyurethane foams using a rapeseed oil-based polyol," *Ind. Crops Prod.*, vol. 74, pp. 887–897, Nov. 2015.

[26] M. A. Garrido and R. Font, "Pyrolysis and combustion study of flexible polyurethane foam," *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 202–215, May 2015.

[27] D. C. W. D. K.Chattopadhyay, "Thermal stability and flame retardancy of polyurethanes," *Prog. Polym. Sci.*, vol. 34, no. 10, pp. 1068–1133, 2009.

[28] E. D. Weil and S. V. Levchik, *Flame Retardants for Plastics and Textiles*. München: Carl Hanser Verlag GmbH & Co. KG, 2015.

[29] A. Marklund, B. Andersson, and P. Haglund, "Screening of organophosphorus compounds and their distribution in various indoor environments.," *Chemosphere*, vol. 53, no. 9, pp. 1137–46, Dec. 2003.

[30] G.-L. Wei, D.-Q. Li, M.-N. Zhuo, Y.-S. Liao, Z.-Y. Xie, T.-L. Guo, J.-J. Li, S.-Y. Zhang, and Z.-Q. Liang, "Organophosphorus flame retardants and plasticizers: sources, occurrence, toxicity and human exposure.," *Environ. Pollut.*, vol. 196, pp. 29–46, Jan. 2015.

[31] M. Zhang, Z. Luo, J. Zhang, S. Chen, and Y. Zhou, "Effects of a Novel Phosphorus-Nitrogen Flame Retardant on Rosin-based Rigid Polyurethane Foams," *Polym. Degrad. Stab.*, Aug. 2015.

[32] M. Herrera, M. Wilhelm, G. Matuschek, and A. Kettrup, "Thermoanalytical and pyrolysis studies of nitrogen containing polymers," *J. Anal. Appl. Pyrolysis*, vol. 58–59, pp. 173–188, Apr. 2001.

[33] L. Jiao, H. Xiao, Q. Wang, and J. Sun, "Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS," *Polym. Degrad. Stab.*, vol. 98, no. 12, pp. 2687–2696, Dec. 2013.

[34] O. Terakado, H. Yanase, and M. Hirasawa, "Pyrolysis treatment of waste polyurethane foam in the presence of metallic compounds," *J. Anal. Appl. Pyrolysis*, vol. 108, pp. 130–135, Jul. 2014.

[35] Z. X. Y. Zhang H. Huang, "A degradation study of waterborne polyurethane based on TDI," *Polym. Test.*, vol. 28, no. 3, pp. 264–269, 2009.

[36] Y. Zhang, Z. Xia, H. Huang, and H. Chen, “Thermal degradation of polyurethane based on IPDI,” *J. Anal. Appl. Pyrolysis*, vol. 84, no. 1, pp. 89–94, 2009.

[37] E. Dominguez-Rosado, J. J. Liggat, C. E. Snape, B. Eling, and J. Pichtel, “Thermal degradation of urethane modified polyisocyanurate foams based on aliphatic and aromatic polyester polyol,” *Polym. Degrad. Stab.*, vol. 78, no. 1, pp. 1–5, 2002.

[38] M. Modesti, A. Lorenzetti, F. Simioni, and M. Checchin, “Influence of different flame retardants on fire behaviour of modified PIR/PUR polymers,” *Polym. Degrad. Stab.*, vol. 74, no. 3, pp. 475–479, Jan. 2001.

[39] J. P.-S. Bogusław Czupryński and Joanna Liszkowska, “Modyfication of the Rigid Polyurethane-Polyisocyanurate Foams,” *J. Chem.*, vol. 2014, no. 130823, p. 12, 2014.

[40] S. A. Song, Y. S. Chung, and S. S. Kim, “The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles,” *Compos. Sci. Technol.*, vol. 103, pp. 85–93, Oct. 2014.

[41] A. Desai, S. R. Nutt, and M. V Alonso, “Modeling of Fiber-reinforced Phenolic Foam,” *J. Cell. Plast.* , vol. 44 , no. 5 , pp. 391–413, Sep. 2008.

[42] P. K. Johnston, E. Doyle, and R. A. Orzel, “Phenolics: A Literature Review of Thermal Decomposition Products and Toxicity,” *Int. J. Toxicol.* , vol. 7 , no. 2 , pp. 201–220, Mar. 1988.

[43] “EPRA -Mineral wool resins.” [Online]. Available: http://epra.eu/22.html. [Accessed: 09-Mar-2016].

[44] S. Kowatsch, “Mineral Wool Insulation Binders,” in *Phenolic Resins: A Century of Progress SE - 10*, L. Pilato, Ed. Springer Berlin Heidelberg, 2010, pp. 209–242 LA – English.

[45] H. Jiang, J. Wang, S. Wu, Z. Yuan, Z. Hu, R. Wu, and Q. Liu, “The pyrolysis mechanism of phenol formaldehyde resin,” *Polym. Degrad. Stab.*, vol. 97, no. 8, pp. 1527–1533, Aug. 2012.

[46] D. M. Price and S. P. Church, “FTIR evolved gas analysis of the decomposition products of cellulose diacetate,” *Thermochim. Acta*, vol. 294, no. 1, pp. 107–112, Jun. 1997.

[47] C. A. Wilkie, “TGA/FTIR: an extremely useful technique for studying polymer degradation,” *Polym. Degrad. Stab.*, vol. 66, no. 3, pp. 301–306, Dec. 1999.

[48] R. G. Davidson, “Enhancement of evolution profiles in pyrolysis-evolved gas-infrared spectroscopy of polymers,” *J. Anal. Appl. Pyrolysis*, vol. 16, no. 2, pp. 143–152, Jun. 1989.

[49] A. A. Stec, “Fire Toxicity and its measurement,” University of Bolton, 2007.

[50] Mettler Toledo, “Thermal Analysis Excellence Unrivalled TGA Performance with Balances from the Market Leader.” [Online]. Available: http://uk.mt.com/dam/Analytical/ThermalAnalysi/TA-PDF/30064774_V10.12_TGA1_Brochure_en.pdf. [Accessed: 09-Mar-2016].

[51] A. Witkowski, “The Use of Numerical Methods to Interpret Polymer Decomposition Data,” University of Central Lancashire, 2012.

[52] A. Witkowski, “The Use of Numerical Methods to Interpret Polymer Decomposition Data,” University of Central Lancashire, 2012.

[53] R. E. Lyon, R. N. Walters, S. I. Stoliarov, and N. Safronava, “Principles and Practices of Microscale Combustion Calorimetry,” 2013.

[54] R. E. Lyon, R. N. Walters, S. I. Stoliarov, and N. Safronava, “Principles and Practices of Microscale Combustion Calorimetry,” 2013.

[55] A. Chauhan, “GC-MS Technique and its Analytical Applications in Science and Technology,” *J. Anal. Bioanal. Tech.*, vol. 5, no. 6, Dec. 2014.

[56] L. C. Speitel, “Fourier Transform Infrared Analysis of Combustion Gases,” *J. Fire Sci.* , vol. 20 , no. 5 , pp. 349–371, Sep. 2002.

[57] ThermoScientific, “XRF Technology,” 2015. [Online]. Available: https://www.thermoscientific.com/en/about-us/general-landing-page/xrf-technology.html. [Accessed: 09-Mar-2016].

[58] Bruker, “How does XRF work?,” 2015. [Online]. Available: https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/how-xrf-works.html.

[59] Intertek, “Energy Dispersive X-Ray Spectroscopy,” 2015. [Online]. Available: http://www.intertek.com/analysis/microscopy/edx/. [Accessed: 09-Mar-2016].

[60] Royal Society of Chemistry, “CHNS analysers - A technical brief,” 2008.

[61] O. US EPA, “EPA Method 8270D (SW-846): Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC-MS).” .

[62] O. US EPA, “EPA Method 8260C (SW-846): Volatile Organic Compounds by Gas Chromatography-Mass Spectrometry (GC/MS).” .

[63] J. M. Delgado-Saborit, N. Aquilina, S. Baker, S. Harrad, C. Meddings, and R. M. Harrison,

“Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples,” *Anal. Methods*, vol. 2, no. 3, pp. 231–242, 2010.

[64] M. Camacho, L. D. Boada, J. Oros, P. Calabuig, M. Zumbado, and O. P. Luzardo, “Comparative study of polycyclic aromatic hydrocarbons (PAHs) in plasma of Eastern Atlantic juvenile and adult nesting loggerhead sea turtles (Caretta caretta).,” *Mar. Pollut. Bull.*, vol. 64, no. 9, pp. 1974–1980, Sep. 2012.

[65] J. M. Norbeck, M. R. Smith, J. Arey, N. Kado, and B. Okamoto, “Evaluation of factors that affect diesel exhaust toxicity. Final report,” Jul. 1998.

[66] Sigma Aldrich, “Benzene,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=443603&brand=SIAL&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/sial/443603?lang=en. [Accessed: 09-Mar-2016].

[67] Sigma Aldrich, “Styrene MSDS,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=45993&brand=FLUKA&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=Styrene&lang=en&region=GB&focus=product&N=0+220003048+219853121+219. [Accessed: 09-Mar-2016].

[68] Sigma Aldrich, “Alphamethylstyrene MSDS,” [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=M80903&brand=ALDRICH&PageToG [Accessed: 09-Mar-2016]

[69] “Naphthalene MSDS.” [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=84679&brand=FLUKA&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3DNaphthalene%26interface%3DProduct%2520Name%26N%3D0%2B%26mode%3Dmode. [Accessed: 09-Mar-2016].

[70] Sigma Aldrich, “Toluene,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=244511&brand=SIAL&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=Toluene&lang=en&region=GB&focus=product&N=0+220003048+219853121+219. [Accessed: 09-Mar-2016].

[71] Sigma Aldrich, “P-xylene,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&la

nguage=en&productNumber=95680&brand=FLUKA&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=p-xylene&lang=en&region=GB&focus=product&N=0+220003048+219853121+21. [Accessed: 09-Mar-2016].

[72] "Aniline IARC." [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=242284&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F242284%3Flang%3Den. [Accessed: 09-Mar-2016].

[73] "ATSDR - Aniline MSDS." [Online]. Available: http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=449&tid=79. [Accessed: 09-Mar-2016].

[74] Sigma Aldrich, "Sulphur Dioxide," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=295698&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/295698?lang=en. [Accessed: 09-Mar-2016].

[75] Sigma Aldrich "Phenol." [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=W322318&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2Fw322318%3Flang%3Den. [Accessed: 09-Mar-2016].

[76] Sigma Aldrich, "1,4-diphenyl-1,3-butadiene," *MSDS*, 2015. [Online]. Available: https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=D206008&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D1%252C4-diphenyl-1%252C3-butadiene%26interface%3DAll%26N%3D0%. [Accessed: 01-Aug-2015].

[77] Sigma Aldrich, "1,3,5-trimethylbenzene," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=M7200&brand=SIAL&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/sial/m7200?lang=en. [Accessed: 09-Mar-2016].

[78] Sigma Aldrich, "2-methylphenol," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&la

nguage=en&productNumber=442361&brand=SUPELCO&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/supelco/442361?lang=en. [Accessed: 09-Mar-2016].

[79] Sigma Aldrich, “2,4-dimethylphenol,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=D174203&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/d174203?lang=en. [Accessed: 09-Mar-2016].

[80] Sigma Aldrich, “2,3,6-Trimethyl Phenol MSDS,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=W396303&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/w396303?lang=en. [Accessed: 09-Mar-2016].

[81] Sigma Aldrich, “Z-Stilbene MSDS,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=S4808&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/s4808?lang=en. [Accessed: 09-Mar-2016].

[82] Sigma Aldrich, “2-pentene,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=143774&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=2-pentene&N=0&mode=match partialmax&focus=product&lang=en&region. [Accessed: 09-Mar-2016].

[83] “EPA Indene Factsheet.” [Online]. Available: http://epa.ohio.gov/portals/27/regs/3745-114/3745-114ToxicsI-Z.pdf. [Accessed: 09-Mar-2016].

[84] “Indene MSDS.” [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=168769&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F168769%3Flang%3Den. [Accessed: 09-Mar-2016].

[85] Sigma Aldrich, “2,3-dimethylphenol IARC,” *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=D174009&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/d174009?lang=en. [Accessed: 09-Mar-2016].

[86] Sigma Aldrich, “2,3-dimethylphenol msds,” *MSDS*, 2015. [Online]. Available: http://hazmap.nlm.nih.gov/category-details?table=copytblagents&id=2972.

[Accessed: 09-Mar-2016].

[87] Sigma Aldrich, "1,2,3-trimethylbenzene." [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=T73202&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2Ft73202%3Flang%3Den. [Accessed: 09-Mar-2016].

[88] Sigma Aldrich, "O-cyanobenzoic acid," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=C89803&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/c89803?lang=en. [Accessed: 09-Mar-2016].

[89] Sigma Aldrich, "Ethyl Benzene MSDS," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=03079&brand=FLUKA&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=Ethylbenzene&N=0&mode=match partialmax&focus=product&lang=en&region. [Accessed: 09-Mar-2016].

[90] Sigma Aldrich, "P-aminotoluene," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=236314&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=p-aminotoluene&lang=en&region=GB&focus=product&N=0+220003048+219. [Accessed: 09-Mar-2016].

[91] Sigma Aldrich, "Bibenzyl MSDS," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=B33706&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?interface=All&term=Bibenzyl&lang=en&region=GB&focus=product&N=0+220003048+219853121. [Accessed: 09-Mar-2016].

[92] Sigma Aldrich, "1,2-diphenylpropane," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=43181&brand=FLUKA&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/fluka/43181?lang=en. [Accessed: 09-Mar-2016].

[93] Sigma Aldrich, "diphenylmethane," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&la

nguage=en&productNumber=D209317&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3DDiphenylmethane%26interface%3DProduct%2520Name%26N%3D0%2B%26mod. [Accessed: 09-Mar-2016].

[94] Clearsynth "2-phenylnapthalene." [Online]. Available: http://www.clearsynth.com/docs/MSD-CS-G-32100.pdf. [Accessed: 09-Mar-2016].

[95] Sigma Aldrich, "4-vinylbiphenyl," *MSDS*, 2015. [Online]. Available: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=V1805&brand=ALDRICH&PageToGoToURL=http://www.sigmaaldrich.com/catalog/search?term=4-Vinylbiphenyl&interface=Product Name&N=0+&mode%. [Accessed: 01-Aug-2015].

[96] CDC, "Isocyanatomethane," *http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=629&tid=116*, 2015. [Online]. Available: http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=629&tid=116. [Accessed: 09-Mar-2016].