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Waste tyre pyrolysis: Sustainable recovery and reuse of a valuable resource

by

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ABSTRACT

End-of-life car passenger tyres represent a major waste management problem, with more than 450,000 tonnes of used tyres being generated each year in the UK alone (approximately 55,000,000 tyres). Recent legislation has made 100% material or value recovery from waste tyres an imperative.

There are many different waste tyre management options available. The most commonly used processes include: retreading, use as fuel in incinerators and cement kilns and reprocessing to produce rubber crumb which has further applications in asphalt mixtures, carpet underlay and playgrounds.

The theme of the research presented is a fundamental study and development of tyre pyrolysis. Pyrolysis is an attractive method to sustainably recover valuable components of the tyre rubber through the generated carbonaceous solid, oil and gas. Both conventional and microwave-induced pyrolysis have been investigated. Microwave pyrolysis offers an exciting alternative to traditional pyrolysis because of the potentially significant energy efficiency advantage offered.

In the first instance an investigation of the optimisation of the pyrolysis conditions by statistical design using conventional means to produce a carbonaceous solid char has been undertaken. This was followed by the investigation of microwave-induced pyrolysis using modified commercially available microwave equipment as well as a bespoke and novel 2450 MHz, 2 kW rotary microwave furnace developed for the purposes of this project by *Cobham Microwave Ltd*. Carbonaceous solids produced by varying different experimental parameters, such as power levels and pyrolysis duration are reported and analysed. In addition, the main constituents of the oils generated have been identified and comparisons made with traditional thermal pyrolysis oil.

Reuse of the solid residue is an important activity which has been researched. This char is often described as carbon black, but given that it contains all the solid, inorganic components present in the tyre, as well as carbon black, it is better described as “char filler”. The suitability of this waste tyre-derived char for reuse in the rubber industry as a filler substitute has been evaluated and is presented. The results show that the char has similar properties to a semi-reinforcing filler with potential for improvement.

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To my mum, R.I.P

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List of abbreviations

AMAT	Advance Molecular Agitation Technology
ANOVA	ANalysis Of Variance
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BS	British Standard
CHNS	Carbon Hydrogen Nitrogen Sulfur
DEFRA	Department for Environment, Food and Rural Affairs
df	degrees of freedom
DMA	Dynamic Mechanical Analysis
DSA	Double Strain Amplitude
DTG	Derivative ThermoGravimetry
DUKES	Digest of UK Energy Statistics
E _b	Elongation at break
EDX	Energy Dispersive X-ray
ETRMA	European Tyre and Rubber Manufacturers Association
EU	European Union
FTIR	Fourier Transform Infrared
GC/MS	Gas Chromatography/Mass Spectroscopy
ICBA	International Carbon Black Association
ICES	International Committee on Electromagnetic Safety
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
IR	InfraRed
ISM	Industrial, Scientific and Medical
ISO	International Organisation for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LOF	Lack of Fit
M100	Modulus at 100% elongation
M300	Modulus at 300% elongation
MATLAB	MATrix LABoratory
MDR	Moving Die Rheometer

MS	Mean Square
NMR	Nuclear Magnetic Resonance
NR	natural rubber
OAN	Oil Absorption Number
PAH	Polycyclic Aromatic Hydrocarbons
PBR	polybutadiene rubber
PE	Pure Error
phr	parts per hundred rubber
PTFE	polytetrafluoroethylene
R^2	Coefficient of determination
RMA	Rubber Manufacturers Association
rpm	revolutions per minute
RSM	Response Surface Methodology
R μ PERT	Rubber Product Enhanced Recovery Technology
SBR	styrene butadiene rubber
SEM	Scanning Electron Microscopy
SS	Sum of squares
SS _E	Sum of squares of errors
SS _R	Sum of squares of regression
SS _T	Total sum of squares
stdev	standard deviation
TEM	Transmission Electron Microscopy
TG	ThermoGravimetry
TGA	ThermoGravimetry Analysis
TPD	Temperature-programmed desorption
TS	Tensile Strength
UHPW	Ultra High Pressure Water
UNECE	United Nations Economic Commission for Europe
WRAP	Waste and Resources Action Programme

1 Introduction and Literature Review

1.1 General Overview

The work presented in this thesis is part of a project supported by the Technology Strategy Board (TSB): an agency established by the UK government to stimulate innovation. The major objective of the project was the development of an integrated tyre recycling system and involved the participation of six partners: ARTIS, ABB Robotics, Cobham Microwave, Hughes Pumps, Symphony Energy and Imperial College London. This project was titled the RμPERT (Rμbber Product Enhanced Recovery Technology) project.

The project was divided into two parts: (i) the disassembly of tyres by Ultra High Pressure Water (UHPW) to produce crumb, steel and fibres and (ii) the pyrolysis of the tyre crumb i.e. the thermal degradation of the material in the absence of oxygen. The UHPW aspect of the work does not form part of this Thesis. Pyrolysis is an attractive method to sustainably recover valuable components of the tyre rubber through the generated carbonaceous solid, oil and gas. This research has investigated both traditional and microwave induced pyrolysis.

This chapter presents a brief literature review on tyres, the current methods for handling end-of-life tyres which have been discarded and the relevant controlling legislation. In addition, the theory behind microwaves and rubber fillers is introduced.

1.2 Introduction to tyres

Tyres are known as one of the best engineered products, and their manufacture is a well established process which involves tight quality controls. They are designed to perform a number of functions, such as providing mobility, safety and comfort to the passengers of a vehicle even under extreme conditions.

Tyres consist of a complex mixture of more than 200 component parts. The specific composition of a tyre will depend on a number of factors including but not limited to the following:

- The tyre manufacturer

- The vehicle category (passenger car, trucks, van and light utility vehicles, airplanes etc.)
- The type of car (family, sports etc.)
- The weather conditions (cold, wet, summer conditions etc.)
- The intended use (driving) terrain: on-road, off-road or both

All tyres, however, contain the same groups of materials (Shulman, 2004; Feraldi et al., 2012) in varying design percentages, rubber being the main component. A typical composition of a passenger car tyre is given in Table 1.1 below.

Rubber, the main ingredient of tyres, is an elastic hydrocarbon polymer. The most frequently employed rubbers in tyre manufacture are natural rubber (NR), polybutadiene rubber (PBR) and styrene butadiene rubber (SBR). Their structures are presented in Figure 1.1.

Table 1.1. Typical composition of a car passenger tyre (Adapted from Shulman, 2004)

Material	wt. %
Rubber (Natural and/or synthetic)	43
Fillers (Carbon black, silica)	27
Reinforcing Materials	16
• <i>Metals</i>	11
• <i>Textiles</i>	5
Chemicals additives ¹	14
• <i>Vulcanisation aids</i>	3
• <i>Other additives</i>	3
• <i>Aromatic oils</i>	8

¹ Chemical additives include stearic acid, zinc oxide, sulfur etc.

Different types of rubbers are used in the various components of the tyre depending on their function within the tyre. For example, SBR is extensively used in tyre treads, as it provides wet skid and traction properties, as well as good abrasion resistance; PBR is used in treads and sidewalls as it can provide good abrasion resistance, tread wear performance and enhanced cut propagation resistance (Rodgers & Waddell, 2005).

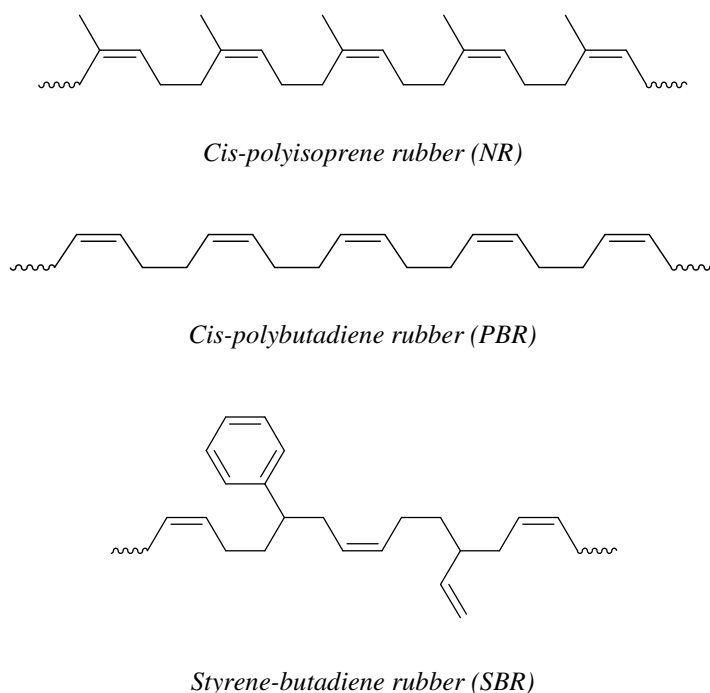


Figure 1.1. Chemical structures of the most widely used rubbers in tyre manufacturing

Accordingly, the rubbers are mixed with fillers (material used to provide reinforcement in the rubber compound, for example different grades of carbon blacks and/or silica), as well as with various chemical additives. Fillers are described in detail in Section 1.2.1. The chemical additives used in rubber mixes can be classified into different categories such as: antidegradants, vulcanisation aids, plasticizers, accelerators etc. The antidegradants like p-phenylene diamines, substituted phenols and quinolines are used to retard the degradation of the tyre from oxygen, ozone and heat. Vulcanisation agents are used in the vulcanisation process. This is a curing process whereby the addition of chemicals and heat results in the cross linking of the polymers, as shown in Figure 1.2. In addition, bonds are created between the copper in the brass coating of the steel and the rubber. This results in a durable and integrated material. The most widely used vulcanising agent is sulfur. Vulcanisation is discussed again in Chapter 6. Accelerators are added to reduce the vulcanisation time and include organic chemicals such as sulfenamides, thiazoles and guanidines. Furthermore, activators are added to activate the accelerators – zinc oxide and stearic acid are the chemicals most commonly used for this purpose. Plasticisers – mainly esters – refer to a group of compounds used to enhance the flexibility of the rubber (British Standard ISO 1382:2008; Dick, 2001).

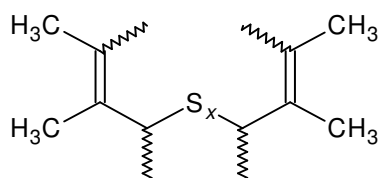


Figure 1.2. Representation of the crosslinking during vulcanisation

The ingredients are mixed beforehand and shaped into rubber sheet layers. The specific formulations are chosen from each manufacturer after a series of tests. These tests are conducted to find the optimum balance of the ingredients' properties. For example, use of an increased amount of carbon black leads to a higher modulus compound. However, the hysteresis and heat build up from deformational cycling also increases, thus compromises are required to achieve the best compounding (Dick, 2001). Furthermore, cost plays a major role in choosing the formulation materials. Figure 1.3 illustrates a constructional cross-section of a modern passenger car tyre.

The first layer is the *inner liner* which consists of an airtight material, usually butyl rubber or its halogenated derivatives. This layer is impermeable to gases, ensuring that the air between the tyre and the rim does not escape. The *casing ply*, also known as the carcass, consists of fine textiles arranged in straight lines and sandwiched in rubber. It extends from bead to bead and constitutes the main framework of the tyre. The casing ply provides the primary reinforcement responsible for supporting the air pressure, vertical load and absorption of shocks. In fact, in each ply of a tyre, there are around 1,400 cords, each one of which can resist a weight of 15 kg (Michelin, 2009).

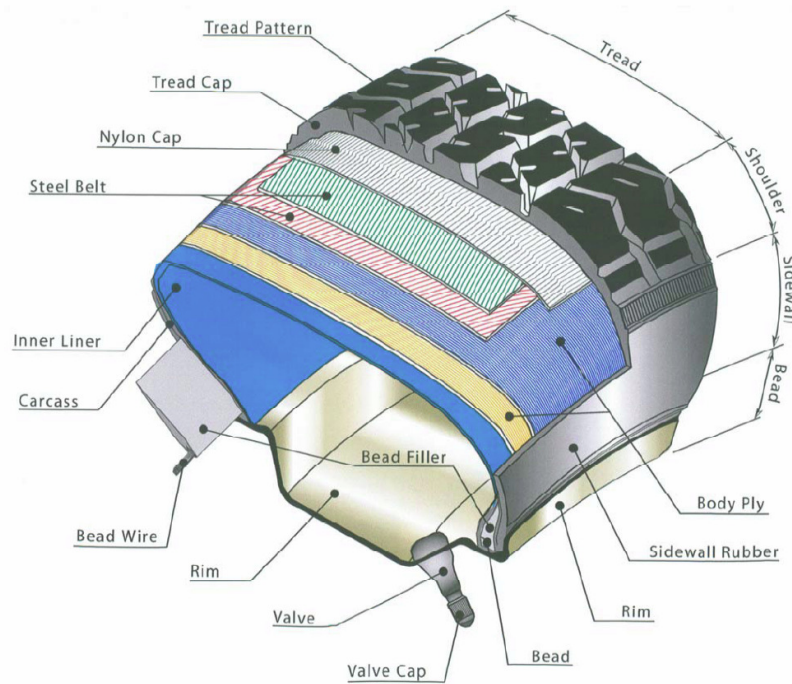


Figure 1.3. Cross-section of a modern car passenger tyre (WRAP, 2006)

The *bead area* which consists of the bead filler and wires ensures that the tyre remains securely attached to the rim. The wires are made of steel coated with zinc or brass and each can sustain a weight of 1,800 kg (Michelin, 2009). The *sidewalls* of the tyre have to be flexible to handle road irregularities and hard enough to resist impacts from pavements and protect the casing. Compounds used for the sidewalls include antidegradants, since they are exposed to wear abrasion and UV degradation (Shulman, 2004). *Belts* are placed between the carcass and the tread. These are made of layers of steel and textiles bonded with rubber and are used to protect the casing ply. The steel belts cross at 60° angles to each other. After the tyre is cured, these belts will cross the casing cords to form triangles, which make the top part of the tyre rigid. The textile cords, usually made of nylon, help to maintain the shape of the tyre and to reduce the effect of heating. In addition, the *shoulder* placed between the tread and the sidewall is quite thick to allow heat dissipation. Finally, the *tread* is the part of the tyre that comes in contact with the road surface. The specific characteristics such as its pattern will vary depending on the tyre's category and the requirements for local conditions (Kovac & Rodgers, 1994; Michelin, 2009).

Overall, it can be seen that a tyre is a complex engineered product the design of which reflects its purpose; an object which must operate under extreme conditions whilst not displaying signs of weakness.

The following sub-section is an introduction to fillers, the focus of the experimental investigation presented in the later part of this thesis (Chapter 6).

1.2.1 Fillers

Carbon black is the most commonly used reinforcement filler in rubber. It is usually manufactured by the incomplete combustion of heavy hydrocarbons, which has a considerable carbon footprint; 2.4 tonnes of CO₂ are estimated to be emitted per tonne of carbon black – this compares to 0.8 tonnes of CO₂ per tonne of cement for cement manufacture (Cabot Corporation, 2010; IEA, 2007). Current global production of carbon black is estimated to be 8.1 million tonnes per year (ICBA, 2006), of which 70% is used in the tyre rubber industry, 20% in other rubber applications while the rest is used for other purposes such as a pigment for printing inks, coatings and plastics (Kühner & Voll, 1993; ICBA, 2006).

Over 95% of carbon black is manufactured by the incomplete combustion of hydrocarbons, in a well-defined and controlled process that ensures the production of carbon black with specific and consistent properties. Carbon black should not be confused with soot which is an impure by-product of thermal decomposition of hydrocarbons, full of inorganic contaminants and extractable organic residues (Wang et al., 2000).

The raw materials primarily used for its manufacture include natural gas or oils that are preferentially rich in 3- or 4-membered aromatic rings but can be vaporised under the reaction conditions, since carbon blacks are formed in the gas phase (Kühner & Voll, 1993). Fuel such as natural gas is burned with preheated process air at the first part of the reactor. The feedstock is then added and under turbulent flow the oxidative decomposition occurs. Frequently, alkali metal salt additives are used to control the structure of carbon black. Water is used to quench the reaction and cool the carbon black formed in the gas phase and the off-gases. These undergo further processing to achieve separation, purification, pelletisation, densification and packaging of the carbon black as a finished product. Carbon black can also

be formed by thermal decomposition in the absence of oxygen (Kühner & Voll, 1993; Medalia & Kraus, 1994).

Carbon black is composed of aggregates which consist of spheres fused together, known as “nodules”. These nodules are in turn composed of many tiny graphite-like stacks or crystallites. Figure 1.4 below from *Carbon Black* by Wang et al. in *Kirk-Othmer Encyclopaedia of Chemical Technology* (2000) provides a good representation of carbon black structure. Specifically “... carbon black consists of well-developed graphite platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers...” (Wang et al., 2000). Just like graphite, carbon black forms large sheets of condensed aromatic ring systems with the same interatomic spacing within the sheet as in the graphite structure. However, the interplanar distances are larger (0.350 – 0.365 nm) than the ones found in graphite (0.335 nm) (Wang et al., 2000).

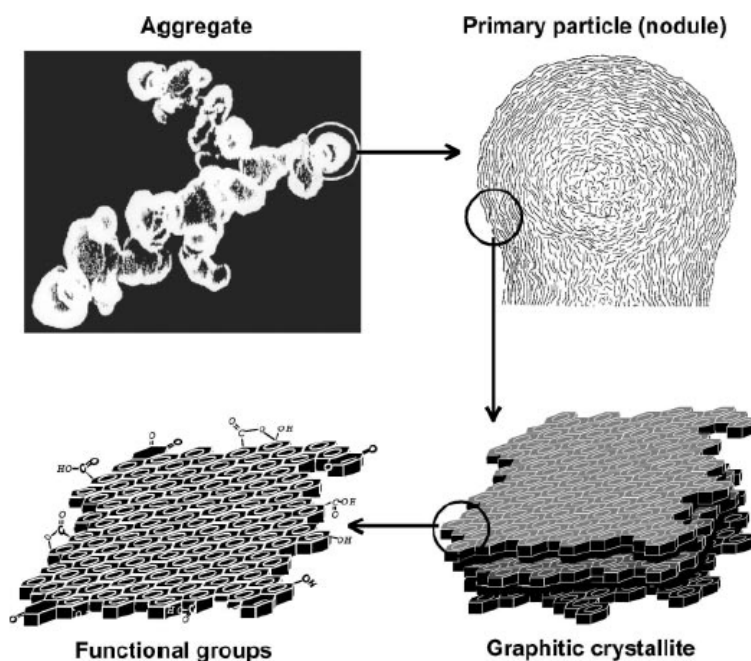


Figure 1.4. Carbon black structure (Wang et al., 2000)

Carbon blacks consist of more than 97% elemental carbon. Other elements present include hydrogen, oxygen, sulfur, and nitrogen, which are incorporated in the carbon structure depending on the feedstock and manufacturing process (Wampler et al., 2004).

Various grades of carbon black exist, and there is a classification system consisting of 4 characters made up of one letter followed by 3 digits. The letter denotes the curing rate of a

typical compound containing the carbon black, which is either a normal curing rate (N-) or a slow curing rate (S-) (Wampler et al., 2004). The first digit, immediately following the letter, denotes the range of average specific surface area grouped from 0 to 9, while the other two digits are arbitrary numbers. N300 series for example denote fillers which result in normal curing rate of the host rubber compound and specific surface area between 70 and 99 m²/g. The complete classification of carbon blacks is presented in Appendix I (Table A).

Their aggregate dimensions can range from tens to a few hundreds of nanometres (Wang et al., 2000). Larger particles are used in the inner part of the tyre, whereas smaller particles are employed in the casing and tread. The addition of carbon black to tyres reinforces the rubber by increasing its tear and tensile strength, abrasion resistance as well as the modulus of elasticity (Medalia & Kraus, 1994).

Another filler used increasingly in the rubber industry and, in particular, for the manufacture of “green tyres” is silica, as it helps reduce the rolling resistance (Michelin, 2009). Silica has been used in rubber compounds as a simple filler for years – it did not qualify as a reinforcing filler due to its poor dispersion in rubber. It was not until the introduction of specific precipitated silica and coupling agents that resulted in homogeneously and finely dispersed silica particles, a prerequisite for high reinforcement, that silica became a serious candidate for tyre filler (Meon et al., 2004).

Precipitated silicas, most commonly used in the rubber industry, are formed by the alkaline fusion of pure sand and an alkaline salt to form a silica glass, which is then solubilised in water at high temperature and acid precipitated. During this process primary particles are formed which link together via siloxane bonds to form aggregates. The aggregates are held together by hydrogen bonding or van der Waals interactions to form agglomerates (Meon et al., 2004). The silica suspension is sequentially filtered, washed and dried (Donnet & Custodero, 2005).

Precipitated silica is hydrophilic by nature, due to the presence of silanols, Si–OH on its surface (Donnet & Custodero, 2005). Mixing silica with rubber, which is a hydrophobic material, was not ideal until bifunctional organosilanes were added in conjunction with the silica, that act as coupling agents by reacting with both silica’s surface and rubber (Meon et al., 2004).

Currently, most of the European-made tyres incorporate more silica than carbon black as filler material.

1.3 The management of waste tyres

This section discusses the management of waste tyres, and begins with an introduction to waste management and relevant legislation in waste tyre management as a suitable backdrop to a review of current practices and issues in the management of this significant and problematic waste stream.

1.3.1 Introduction to waste management

Waste, as defined by the latest European Union (EU) Directive 2008/98/EC on waste, (2008) is “... *any substance or object which the holder discards or intends or is required to discard*”.

The waste strategy conveyed in the various UK Regulations and European Directives has, as its primary objective, the prevention of waste. Prevention of waste is the best option according to the waste hierarchy which has been adopted in all the recent waste strategies and reiterated in the Directive 2008/98/EC on waste. The waste hierarchy is illustrated in Figure 1.5 and can be summarised as follows (The Waste (England and Wales) Regulations 2011; Directive 2008/98/EC on waste):



Figure 1.5. Waste hierarchy

- *Prevention*: Taking the necessary measures before a product becomes waste that will reduce the amount of waste generated, prolong its life, reduce the negative environmental effects and risks to human health and limit the use of harmful substances in the products.
- *Preparing for re-use*: Any operation that enables the reuse of materials for the original purpose they were intended.

- *Recycling*: Any recovery operation that involves the reprocessing of waste to form materials that will be useful either by restoring them to their original form or as a replacement of other raw materials. This does not include energy recovery.
- *Other recovery*: Energy recovery including gasification and pyrolysis.
- *Disposal*: Any operation which is not recovery, such as landfill.

Deviations from this hierarchy can be accepted if justified by life-cycle thinking on the overall impacts of the generation and management of specific wastes (Directive 2008/98/EC). Life cycle approach involves the investigation of the environmental impacts of a material or system over its whole life cycle (that is raw material acquisition, manufacture, use and end of life (which includes its final disposal or recycle/reuse), as well as transport during all these stages). This is collectively known as cradle-to-grave (ISO 14040:2006). All the energy consumed during the above processes and generally all the emissions generated into all environmental compartments (air, water and soil) are taken into consideration.

1.3.2 Relevant legislation

Used tyres can be considered a high-volume waste. Worldwide, used tyre generation is estimated to be 1 billion units per year; the UK alone produces more than 55 million waste tyres a year (Environment Agency, 2012; Shulman, 2004). The European Commission identified waste tyres as one of the ‘priority waste streams’ from the mid-1990s below (DEFRA, 2007) and has since introduced legislation regulating their disposal.

1.3.2.1 Council Directive 1999/31/EC on the landfill of waste

The Council Directive 1999/31/EC on the landfill of waste (1999) was composed with the objective of setting operational and technical requirements to ensure the prevention or reduction of the negative environmental effects caused by the disposal of waste in landfills.

Three categories of landfills were defined by this Directive, according to the type of waste each can accept: (i) hazardous, (ii) non-hazardous, and (iii) inert. Targets were also set for reducing the quantity of wastes disposed in landfills. As conveyed in England’s waste strategy 2007, this required a reduction in the amount of biodegradable municipal waste going to landfill. Using the 1995 data on the total amount of the biodegradable municipal waste produced, this would reduce to 75% by 2010, 50% by 2013 and 35% by 2020.

In addition, the Directive listed the conditions necessary to obtain a permit to operate a landfill site, defined waste acceptance procedures and described measures for the control and monitoring of the landfill during its operation as well as during the after-closure phase.

Of significance to the current work, the Directive banned certain wastes, particularly tyres, from landfill disposal. Specifically, the disposal of whole tyres in landfills from 2003 and shredded tyres from 2006 was outlawed. Bicycle tyres and tyres with an outside diameter above 1400 mm are excluded from this restriction. Tyres will only be allowed in landfills if they are used for engineering purposes, such as their employment as leachate drainage layer.

1.3.2.2 Directive 2000/53/EC on end-of-life vehicles

The 2000/53/EC Directive on end-of-life vehicles (2000) aims primarily to prevent waste arising from vehicle disposal and at the reuse, recycling and recovery of the vehicles and their components. Thus, it encourages manufacturers of vehicles and their components to develop new designs which would take into consideration the need for prevention of waste, facilitate reuse and recovery and limit the amount of hazardous substances used.

The Directive set up the following targets for all the end-of-life vehicles:

- The reuse and recovery will be increased to at least 85%, while the reuse and recycling will be increased to a minimum of 80% by an average weight per vehicle and year, from 1 January 2006. Lower targets of 75% and 70% respectively, will apply to vehicles produced before 1 January 1980.
- The reuse and recovery will be increased to at least 95%, while the reuse and recycling will be increased to a minimum of 85% by an average weight per vehicle and year, no later than 1 January 2015.

The reuse and recovery of waste tyres can make a significant contribution to the achievement of these targets as the relevant infrastructure already exists.

1.3.2.3 Directive 2000/76/EC on the incineration of waste

The Directive 2000/76/EC on the incineration of waste (2000) aims to prevent or limit the negative environmental effects and the resulting risks to human health from the incineration and the co-incineration of waste.

The Directive describes the necessary requirements to obtain a permit to operate an incineration plant, defines the operating conditions and sets up various parameters and emission limit values for the control and monitoring of the process.

The Directive defines incineration plants as plants that thermally treat waste by oxidizing it, with or without the recovery of the combustion heat generated. It also includes other thermal treatment processes such as pyrolysis, gasification or plasma processes as long as the substances obtained by these treatments are subsequently incinerated.

Co-incineration plants include plants intended for the generation of energy or to produce material products such as cement kiln plants, but additionally use a waste stream as fuel or with the intention of its disposal.

The importance of this Directive will be further discussed in Section 1.3.4.5.2.

1.3.2.4 Directive 2008/98/EC on waste and repealing certain Directives

Article 6 of the Directive 2008/98/EC on waste sets up conditions where waste ceases to be a waste when it has undergone a recovery operation and fulfils the following criteria:

- “the substance or object is commonly used for specific purposes
- a market or demand exists for such a substance or object
- the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation, and
- the use of the substance or object will not lead to overall adverse environmental or human health impacts”

The article dictates specific waste streams that the end-of-waste criteria should be applied to, among which are tyres.

1.3.3 Problematic waste

End-of-life tyres are considered a problematic waste, and the reasons for this are summarised as follows:

- Large quantities of tyres are generated every year
- Tyres, by design, are not easily degradable

- Harmful gases are generated when tyres are burnt
- Tyres have been banned from landfill disposal by Directive 1999/31/EC
- Tyres are subject to fly-tipping – requiring unnecessary and costly clean up operations by local authorities
- There are problems associated with collection of data and inaccuracies on the handling of tyres when they enter the waste stream
- Tyres do not have a consistent formulation – they are composed of so many different ingredients and proportions that it is difficult to produce something that will give a consistent output. New developments are ongoing and drastic changes are expected as a result of the recent directives which require the limitation of harmful substances and encourage the manufacturers to design new ‘greener’ products

1.3.4 End-of-life tyre management methods

There are currently various methods employed in the management of waste tyres. The favoured method is to retread the tyre; however there is a limit to the number of times this can be done. Another approach is to utilise crumb produced from waste tyres. These crumbs are used for various purposes including road applications, carpet underlays, playgrounds etc. Furthermore, the high calorific value of waste tyres makes them an attractive substitute solid fuel in incineration plants and cements kilns for energy recovery. However, the implementation of the 2000/76/EC Waste Incineration Directive (2000) has imposed stricter emission limits, which affect the number of waste tyres that can be used in these plants. Figure 1.6 presents the 2010 UK statistics of used tyres allocation (Environment Agency, 2012). As shown in the Figure, the most popular waste tyre management route in the UK was the generation of crumbs. The management of waste tyres within the context of waste hierarchy is described in the following subsections.

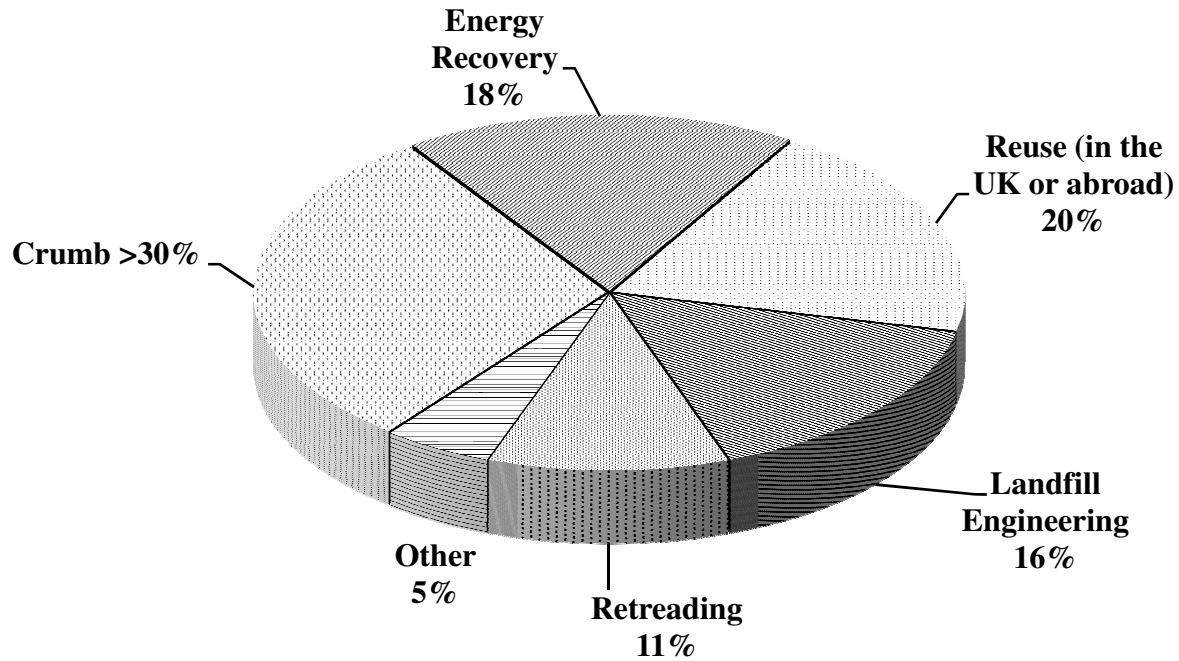


Figure 1.6. Used Tyre Statistics of 2010 (Environment Agency, 2012)

1.3.4.1 Prevention

There is ongoing development by all major tyre manufacturing companies to provide a material with extended lifetime. Also, the amount of tyres requiring disposal every year can be minimised by simple good driving practices and maintenance of the tyres by vehicles owners.

1.3.4.2 Reuse and Recycling (of whole tyres)

Part worn tyres are reused for their original purpose usually by exporting them to countries with fewer restrictions on the thickness of the tread (Environment Agency, 2004). Also, whole tyres can be used directly for civil engineering applications such as for noise barriers. They provide low cost structures and help in the implementation of the 2002/49/EC Directive on environmental noise (2002). Furthermore, whole tyres find applications in the marine sector. For example, their use as artificial reefs offer habitat to corals and algae. They are also popular in marine barriers and embankments (Fenner & Clarke, 2003). Their arrangement into bales provides a lightweight and long-life alternative to cement and gravel for use in construction (Dufton, 2001; Shulman, 2004). Published research also report material, environmental and financial benefits from the reuse of waste tyres. Curry et al. (2011), for

example, reported raw material savings of 1.53 – 4.42 tonnes and CO₂ emissions savings of 0.19 – 0.55 tonnes per bale when aggregate gabions are replaced by car tyre bales, as well as cost savings of between £10 and £57.

1.3.4.3 Retreading for Reuse

Retreading involves the removal of the worn tread from the tyre casing and its replacement with a new one. This process is performed under strict regulations to ensure that the performance and safety of the retreaded tyre is comparable to or even better than the performance and the safety of many new tyres. This strict regulation implies that not all tyres will qualify for retreading. Statistical evidence of this is presented in a report by Dufton (2001) stating that only 15% of car tyres and 50 – 70% of truck tyres qualified for retreading in 2001. Of this figure, only 9% of the used passenger car tyres and 24% of the truck tyres were actually retreaded. This was attributed to the severe competition the retreading industry faces from low budget tyres and the reduced profitability from selling these tyres compared to others. In addition, retreading suffers from unfavourable public perception. This is completely unjustified given that all processes used in the retreading industry are governed by stringent legislation (Lawton, 2001). Specifically, they must comply with the United Nations European Commission for Europe (UNECE) Regulations 108 and 109 for retreaded tyres (UNECE, 1998a, b). Accordingly, passenger car tyres that have been retreaded previously or that have a casing more than 7 years old are rejected even before the initial inspection. Then each of them is thoroughly examined both internally and externally to ensure that the tyre does not have any damage that will compromise its performance, such as extensive cracking extending through to the carcass, appreciable oil or chemical attack, non-repairable deterioration or damage to the inner liner etc.

After the worn tread is removed (buffing), the tyre is re-examined before the attachment of new material through the application of heat, pressure and time. The integrity of the final product is inspected and is subject to the same standards applied for new tyres. Curry et al. (2011) report that life cycle analysis of retreading car tyres in comparison to the manufacture of new car tyres results in raw materials savings of between 0.01 and 0.09 tonnes per tyre, CO₂ emissions savings of between 0.02 and 0.04 tonnes per tyre and cost savings of between £33 and £88 per tyre.

1.3.4.4 Material Recovery (Recycling)

Whole tyres or pre-treated tyres can be reduced to rubber crumb by mechanical or cryogenic means. Pre-treatment involves bead removal, tread/sidewall removal, bailing and/or compression. Mechanical means involve the use of knives to produce rubber crumb. Shredding of tyres produces a material of particle size 50 – 300 mm. Chipping of tyres further reduces the material to a size of 10 – 50 mm. Shreds and chips are ground and metals are magnetically separated. The rest of the material passes through the granulators and screens for further processing. Textiles are removed using air separators (Shulman, 2004). Cryogenic grinding involves the cooling of the shredded material using liquid nitrogen to temperatures of -80 to -120°C. At these temperatures the material becomes brittle and is easily reduced in size by use of a hammer mill (Rouse, 2005; Shulman, 2004).

In general, ambient tyre rubber granulate (1 – 10 mm) and powder (less than 1 mm) produce irregularly shaped surfaces in contrast to cryogenic grinding that generates crumb with smooth regular surfaces. Crumb production is an energy intensive process, especially when finer particles are produced (Feraldi et al., 2012). Heat is generated during the procedure that can alter the properties of the crumb; for example it may initiate a chain of radical reactions or damage equipment (Jones, 2001).

Another technology for the production of crumb has been developed at Imperial College London in association with ABB Robotics, ARTIS, Hughes Pumps and Symphony Energy. Crumb generated from this technology was employed in the current work, which uses an ultra high pressure water cutting system to separate the tyre into its constituents (Section 3.1).

Shreds are employed in landfill engineering for construction cells, daily covers and as drainage layers. In fact, in 2005 almost 60,000 tonnes of tyres were used for this application and usage has grown strongly through 2006 (DEFRA, 2007). Curry et al. (2011) compared the use of tyre shreds in landfill engineering in place of primary aggregates and found that 2.67 tonnes of raw materials per tonne and 159 tonnes of CO₂ emissions per tonne are saved by this replacement. The analysis, however, also indicated a per tonne cost increase of £17. Nevertheless, as the 1999/31/EC Directive targets for waste diversion from landfills are fulfilled, the number of landfills will reduce and thus the market for this application for reusing tyres will decline.

Rubber crumb finds use in civil engineering applications, in asphalt and in carpet underlays. It is also used to provide drainage in layers below road surfaces, helping the water percolate through the soil (Shulman, 2004). Other applications include its use as a material for thermal and vibration insulation and as a lightweight fill in road constructions, sports surfaces and playgrounds. Granulate rubber in sports surfaces acts as a shock absorbing material.

Powder from tyres can be used as a feedstock for rubber reclaim. This process involves the partial devulcanisation of the rubber, which is usually achieved with the addition of various chemicals and the application of heat and pressure to form a material in plastic state (Rouse, 2005). This material can ultimately be incorporated with new rubber compounds and revulcanised for the production of new tyres, although the high quality control and complex nature of tyre compounding reduces this potential use (Jones, 2001).

Material recovery from waste tyres through crumb production has shown an increasing trend according to the latest statistics published by both the Rubber Manufacturers Association (RMA) of the United States and the European Tyre and Rubber Manufacturers Association (ETRMA). The RMA (2011) reported a 9% increase based on a comparison of 2007 and 2009 figures for the USA and the ETRMA (2012) reported a similar increase of 10% based on a comparison of 2009 and 2010 figures for Europe. The ETRMA further identifies material recovery as the main recovery route in Europe. In the UK, the Environment Agency (2012) reports that over 30% of the waste tyre arisings are managed through this route (see Figure 1.6).

1.3.4.5 Other recovery

1.3.4.5.1 Pyrolysis of tyres

Pyrolysis refers to the thermal decomposition of a material in the absence of oxygen. Pyrolysis of tyre rubber results in the production of char, oil and gases, all of which have the potential to be reused. Various types of reactors have been employed for the pyrolysis of tyres including rotary kilns, fluidised bed reactors, conical spout reactors and static batch reactors. The process is governed by various parameters including temperature, retention time, pressure, composition of atmosphere and type of reactor. Table 1.2 highlights the product yields in relation to the different pyrolysis conditions as reported by various authors.

Table 1.2. Tyre pyrolysis product yields under different conditions

Reference	Type of reactor	Experimental Conditions							Yields (wt. %)					Notes
		Particle size (mm)	Temp (°C)	Dwell Time (hr)	Heating rate (°C/min)	Atmosphere	Flow rate (mL/min)	Pressure (kPa)	Solid Residue	Oil	Gas	Steel	Water	
Roy & Unsworth, 1989	Bench scale	6.35 - 12.70	250	–	N/A	Vacuum	–	< 3	91.1	7.2	Traces	–	1.7	Fibres included
			310						79.4	17.7	0.3		2.6	
			335						68.8	27.2	1.7		2.3	
			363						45.6	48.3	2.9		3.2	
			415						36.6	56.6	2.2		4.6	
			500						35.5	56.2	4.3		4.0	
		150-400	420						34.8	58.4	2.1		4.7	
Cunliffe & Williams, 1998b	Static bed batch	30 x 15 x [500-1500]	450	1.5	5	Nitrogen	N/A	–	37.4	58.1	4.5	–		Steel and fibres included
			475						37.3	58.2	4.5			
			500						38.3	56.2	5.5			
			525						37.8	56.9	5.2			
			560						38.1	55.4	6.5			
			600						38.0	53.1	8.9			
San Miguel et al., 1998	Rotary kiln reactor	< 0.42	500	–	5	Nitrogen	500	–	42.0	53.0	5.0	–		
Roy et al., 1999	Continuous	20 x 30	550	–	–	Vacuum	–	10	33	56	10	–	1	Car tyre
	Batch	100 x 120	520	until no more	10			7	36	45	6	10	3	Car tyre

Reference	Type of reactor	Experimental Conditions							Yields (wt. %)				Notes				
		Particle size (mm)	Temp (°C)	Dwell Time (hr)	Heating rate (°C/min)	Atmosphere	Flow rate (mL/min)	Pressure (kPa)	Solid Residue	Oil	Gas	Steel	Water				
Gonzalez et al., 2001	Batch	Whole tyre	500	gaseous products	10	Nitrogen	75	–	37	47	5	10	1	Car tyre with silica filler			
	Batch	100 x 120	520		10				39	43	5	10	3	Truck tyre			
		0.20-1.6	400	0.5	–				81.5	18.1	0.4		Metal included				
			350						55.1	42.9	2						
			450						40.3	55.2	4.5						
			500						38.6	55.4	6						
			550						37.6	55.6	6.8						
			575						37.4	54.6	8.1						
			600						37	52.2	10.8						
			700						36.7	36.6	26.7						
			600		5				40.9	55	4.1						
					10				40.3	55.2	4.5						
					15				39.1	55.4	5.6						
					20				38.7	54.7	6.6						
Williams & Brindle, 2003	Fixed Bed	1-1.4	570	1	5	Nitrogen	1500	–	38.7	57.1	4.3						
Barbooti et al., 2004	Fixed Bed batch	10	430	N/A	–	Nitrogen	5833	–	32.6	51.2	16.2						
Laresgoiti et al., 2004		20 x 30	300	0.5	15	Nitrogen	1000	–	87.6 ± 7.8	4.8 ± 3.9	7.6 ± 3.9						
			400						55.9 ± 5.5	24.8 ± 6.0	19.3 ± 2.2						
			500						44.8 ± 0.6	38 ± 1.8	17.2 ± 1.8						
			600						44.2 ± 0.6	38.2 ± 0.5	17.6 ± 0.8						
			700						43.7 ± 0.4	38.5 ± 1.2	17.8 ± 1.2						

Reference	Type of reactor	Experimental Conditions							Yields (wt. %)				Notes	
		Particle size (mm)	Temp (°C)	Dwell Time (hr)	Heating rate (°C/min)	Atmosphere	Flow rate (mL/min)	Pressure (kPa)	Solid Residue	Oil	Gas	Steel	Water	
Li et al., 2004	Continuous rotary kiln	13 - 15	450	N/A	–	Nitrogen	–	At kiln outlet - 10 to -20 Pa	43.9	43	13.1			
			500						41.3	45.1	13.6			
			550						39.9	44.6	15.5			
			650						39.3	42.7	18			
			600						38.8	42.9	18.3			
Berrueco et al., 2005	Static bed	20 x 20	400	4	12	Nitrogen	400	–	64	30	2.4			Metal and textiles included
			500						52.7	39.9	3.6			
			550						52.5	39.1	3.6			
			700						51.3	42.8	4.4			
Diez et al., 2005	Laboratory scale fixed bed	0.42	550	–	Not constant	Helium	200	–	33	38	29			
	Pilot Plant rotary bed reactor	10-50	500-600	0.5	–	Oxygen-free	–		33.4	–	66.5			
Kyari et al., 2005	Fixed bed reactor	25-30	500	1	10	Nitrogen	200	–	37.7-35.5	55.4-57.8	2.7-5.7			Same tyre type, steel included Different tyre type, steel included
									37.1-41.7	56.6-60.1	1.9-3.7			

Reference	Type of reactor	Experimental Conditions							Yields (wt. %)				Notes
		Particle size (mm)	Temp (°C)	Dwell Time (hr)	Heating rate (°C/min)	Atmosphere	Flow rate (mL/min)	Pressure (kPa)	Solid Residue	Oil	Gas	Steel	Water
Ucar et al., 2005	Fixed bed reactor	1.5-2	550	1	7	Nitrogen	25		42.0 ± 2.5	47.4 ± 1.8	7.4 ± 2.5		3.2 ± 0.9
			650						41.7 ± 2.7	48.4 ± 1.9	7.6 ± 2.7		2.3 ± 0.5
			800						41.5 ± 2.3	47.2 ± 1.9	7.8 ± 2.3		3.5 ± 0.4
Aylon et al., 2007	Fixed bed	2	600	–	50	Nitrogen	10	–	37.9	54.6	7.5		
Arabiourrutia et al., 2007	Conical Spouted Bed Reactor	1	500	–	–	Nitrogen	6500	–	33.7	63.2	3.1		
Mui et al., 2010	Muffle Furnace	1-2	500			Nitrogen	500		37.15				
			600						35.43				
			700						34.93				
			800						33.71				
			900						32.34				

Pyrolysis conditions can be varied depending on the desired output. For example, if the formation of oils is the primary aim of the experiment, high heating rates and rapid removal of the products from the reaction zone are required. The latter minimises the extent of secondary reactions that result in carbonaceous residue formation and increases in char yield (Williams et al., 1993).

The gas generated from tyre pyrolysis consists mainly of hydrogen, CO, CO₂ and light hydrocarbons (Roy & Unsworth, 1989). Its calorific value is approximately 32 MJ/kg (Laresgoiti et al., 2000). The gas can be used to power the pyrolysis plant and, if there is an excess, for electricity or heat generation (Environment Agency, 2004).

The oil generated from tyre pyrolysis has a high content of valuable hydrocarbons such as limonene, toluene, xylene and styrene (Cunliffe & Williams, 1998a). Limonene has significant applications as it is widely used as a constituent in cleaning agents, resins and adhesives (Pakdel et al., 1991). It has been suggested that pyrolytic oil can be used as number 4 ASTM bunker oil, light petroleum oil and feedstock. Its calorific value ranges between 40 – 43 MJ/kg (Roy & Unsworth, 1989; Cunliffe & Williams, 1998a).

The pyrolytic char consists mainly of carbon black, carbonised rubber polymer and ash from the inorganic ingredients of rubber. The char, depending on the experimental conditions which influence its qualities, can be reused in tyres, bitumen, dye works wastewater decolourization and as smokeless fuel (Gross Calorific Value ~ 28 – 30 MJ/kg) (Roy & Unsworth, 1989; Cunliffe & Williams, 1998b). Studies have investigated the potential use of chars as activated carbon after physical activation; even though the surface area can be comparable to activated carbons, their use in water treatment plants is prohibited due to leaching of metals (San Miguel, 1999). Suggestions for the use of char as carbon black substitute are restrained by the high ash content. To enable its use as carbon black upgrading is required (Cypres & Bettens, 1989). Nevertheless, the technology is yet to be proven on a commercial scale. This is attributed to the low value of the end products compared to the costs of operating the plant (Roy & Unsworth, 1989).

In a review of the management of waste tyres, Sienkiewicz et al. (2012) stated that industrial-scale pyrolysis of tyres is rarely used due to high capital costs (installation and servicing costs) and uncompetitive product prices. Nevertheless, according to Sienkiewicz et al., considerable potential of this management method is evidenced by ongoing research in this field along with increasing costs of energy and petroleum products.

Microwave-driven pyrolysis has been identified as an energy-efficient alternative to the current heating technologies employed for the treatment of problematic waste such as used tyres (Appleton et al., 2005). A number of patents exist on proposed equipment (Pringle, 2006; Kim, 2005; Holland, 1992); however there is limited information on actual experiments performed using microwave technology to pyrolyse tyres.

A study conducted by Pang (2007) proved the feasibility of tyre microwave pyrolysis. A domestic microwave oven was used to generate 45% char, 21% gas and 33% oil by mass. Pyrolysis was completed after 5 minutes using 40% of the power level and 4 minutes using 60% of the power level. In addition, it was shown that devulcanisation of the rubber was completed after one minute of microwave radiation exposure.

Industrially, Advance Molecular Agitation Technology (AMAT) used microwave technology to pyrolyse whole tyres. It was reported that the oil generated had similar calorific value to commercial diesel (Environment Agency, 2004). A comparison of the oil produced from the process with kerosene is shown in Table 1.3. The char was claimed to be of a higher quality than that produced by conventional thermal pyrolysis with a wider variety of higher-value applications. However, the AMAT tyre processing facility ceased to operate due to insufficient funding.

Table 1.3. Properties of the oil derived from the AMAT process compared to kerosene (Environment Agency, 2004)

Property	Kerosene	Tyre-derived Oil
Carbon (%)	86.40	83.60
Hydrogen (%)	13.48	12.30
Oxygen (%)	0.00	3.68
Sulfur (%)	0.09	0.40
PAH	0.03	0.02
Specific gravity	0.7245	0.74
Calorific Value (MJ/kg)	42	40.68
Average Mol Weight	106.51	108.78

The limited information regarding the behaviour of rubber under microwave-induced pyrolysis is a driver for this research project. Microwave theory is introduced in detail in Section 1.4.

1.3.4.5.2 Energy recovery

Tyres have a high calorific value in the range of 31 – 33 MJ/kg (Sharma et al., 2000; Laresgoiti et al., 2000). This enables them to be used as an alternative to fossil fuel in energy generation (steam and electricity). They are commonly used in incinerators, cement kilns and pulp and paper mills either as whole or shredded tyres (Feraldi et al., 2012). According to recent statistics, energy recovery accounts for 38% (based on 2010 statistics) of end-of-life tyres in Europe (ETRMA, 2012) and 40.3% (based on 2009 statistics) in USA (RMA, 2011). However, both ETRMA and RMA reported a decrease of the trend from previous years (-3% and -12.5% respectively). In the UK, energy recovery consumes only approximately 18% of waste tyres based on 2010 statistics (Figure 1.6) (Environment Agency, 2012).

Tyres used in incineration plants provide for the generation of steam for the production of electricity; for example 32,000 tonnes of tyres would generate 10 MW of electricity (Shulman, 2004).

Cement manufacture is an energy intensive process; energy accounts for 30 – 40% of the total cost (Davies & Worthington, 2001). The presence of iron in the whole tyre is beneficial, though care must be taken not to create blockage in the feeding system (Kääntec et al., 2001). The presence of sulfur in tyres also provides an advantage by altering the melting behaviour of the mixture.

The implementation, however, of recent directives such as the 2000/76/EC Incineration Directive (2000), which sets stringent regulations on the gas emissions released in the atmosphere, requires extended and costly procedures to obtain a permit to use tyres for energy recovery. External testing is necessary to measure the presence of substances such as Polycyclic Aromatic Hydrocarbons (PAH), benzene, styrene, chloromethane and HBr with high associated costs (Davies & Worthington, 2001). In addition, this application of tyres faces competition from other waste streams.

1.3.5 Concluding remarks

A brief overview of the current management options for handling end-of-life tyres has been presented in the above section. Even though the management options are typically considered according to the waste hierarchy, it must be emphasised again that deviations are accepted if justified by life-cycle thinking. In fact recent life cycle assessment of nine recovery methods

for end-of-life tyres (four destructive and five non-destructive) reported that the environmental assessment showed that material recycling methods were not systematically better than the energy recovery methods (Clauzade et al., 2010).

Significant efforts are being made to optimise the management of waste tyres in Europe, in line with the relevant European Council Directives. Consequently, there are three main systems applied within the European Union (EU) as summarised by ETRMA (2012):

- i) **Producer responsibility:** Under this system the law confers the responsibility for the organisation of the management chain of end-of-life tyres to the producers (tyre manufacturers and importers). This system seems to be the most suitable for achieving the goal of 100% recovery rate in a sustainable and economic way and was adopted by 15 countries within the EU in 2011 with more countries expected to follow. This is the preferred system by the tyre manufacturers.
- ii) **Tax system:** Under this system, funding for the organisation of the recovery and recycling of tyres is provided by the government, using taxes levied on the manufacturer. By implication, the true cost is borne by the consumer. Only two countries in the EU practise this system.
- iii) **Free market system:** Under this system, the legislation dictates the targets that need to be fulfilled without assigning responsibility to any party. In 2011, 6 EU members operated this system. The UK follows a similar system, known as managed free-market system, where even though the free market system is used, collectors and treatment operators are obliged to report to the national authorities.

Beyond the application of these systems and the existing end-of-life tyre management methods, is the requirement to develop and optimise suitable and sustainable value recovery means for the management of waste tyres, such as microwave-driven pyrolysis; and this is the background of the work presented in this Thesis.

In the following section, microwave theory is introduced.

1.4 Microwaves

1.4.1 Introduction to microwaves

Electromagnetic radiation is energy carried in the form of electromagnetic waves. Electromagnetic waves are transverse waves travelling with the speed of light in vacuum, and consist of electric and magnetic fields oscillating in phases perpendicular to each other.

Their wavelength and frequency are related by:

$$c = \lambda \cdot f \quad (\text{Eq. 1.1})$$

Where: c = the speed of light (2.998×10^8 m/s in vacuum)

λ = the wavelength (m)

f = the frequency (Hz)

Microwaves are electromagnetic waves that range in frequencies from 300 MHz to 300 GHz. These frequencies correspond to wavelengths between 1 mm and 1 m and are mainly used for communication services. In addition, some frequencies are designated for non-communication purposes which include '*industrial, scientific and medical*' (ISM) applications such as heating. Microwave heating is achieved primarily at either 915 MHz (896 MHz in the UK) or 2450 MHz (Meredith, 1998; Chan & Reader, 2000). The former frequency is used predominantly in industry whereas all domestic microwave ovens operate at 2450 MHz ($\lambda = 12.2$ cm) (Will et al., 2004).

1.4.2 Microwave interactions with materials

Materials respond to microwave energy differently depending on their properties. Some are transparent to the microwave radiation, thus the electromagnetic waves pass through the material without causing any effect. Such materials include quartz and polytetrafluoroethylene (PTFE). Other materials reflect the electromagnetic waves. This category includes conductors such as stainless steel. Conductors have electric charges that move freely through the material. On the other hand, a group of materials known as insulators or dielectrics, absorb microwaves. Dielectrics have charges that are attached to specific atoms or molecules and can only move a bit within the atoms or molecules (Griffiths, 1998).

Microwave heating is achieved from the interaction of the electric field component of the electromagnetic wave with charged particles in the material via two mechanisms; the dipolar polarization mechanism and the conduction mechanism.

1.4.2.1 Dielectrics and polarisation

When a dielectric is placed in an electric field the material will become polarised. Polarization involves the short-range displacement of charge through the formation and rotation of electric dipoles (or magnetic dipoles if present) (Clark & Sutton, 1996). An electric dipole is illustrated in Figure 1.7 and it refers to a positive and a negative charge separated by a certain distance. A dipole in a molecule can be permanent, due to uneven distribution of charge, or it can be induced when a material is under the influence of an electric field (Bolton, 1992). Regardless of the dipole's origin, on application of an electric field these tend to align with the field direction.



Figure 1.7. Electric Dipole

Total polarization is the sum of a number of components depending on their mechanisms: electronic polarization, ionic polarization, dipolar polarization and interfacial polarization.

Electronic polarization is caused by the displacement of electron charges in relation to their nuclei, resulting in the distortion of the distribution of the electron cloud. *Atomic polarisation* results from the relative displacement of atomic nuclei due to unequal distribution of charge in molecule formation. *Molecular or dipole polarisation* occurs in molecules with permanent dipoles. In the presence of an electromagnetic field these dipoles align themselves with the electric field. *Interfacial polarization*, also known as the Maxwell-Wagner effect, occurs due to imperfect arrangements of the atoms, ions or molecules in a material, inhomogeneity and presence of impurities or a few free electrons. On the application of an external electric field, these can move through a material to its surface (Bolton, 1992; Metaxas & Meredith, 1983; Von Hippel, 1954).

When the dielectric is placed in an electric field, the induced dipoles try to align themselves with the changing electric field. At very low frequencies, the dipoles follow precisely the

electric field alternations. Even though the molecules will gain some energy by doing so, the overall heating effect is small. At very high frequencies, the dipoles cannot follow the oscillating electric field so they do not rotate. If no motion occurs, no energy transfer takes place and consequently heat is not generated (Lidström et al., 2001). At the microwave radiation frequencies a situation between the two extremes occurs. The dipoles will rotate, as they have enough time to respond to the alternating field. However, they are not able to keep up with the oscillating field. This creates a phase lag, known as relaxation time, between the orientation of the field and the dipole. Energy is lost by molecular friction and collision and is dissipated as heat within the material (Lidström et al., 2001; Thostenson & Chou, 1999). The dipolar polarisation mechanism is illustrated in Figure 1.8.

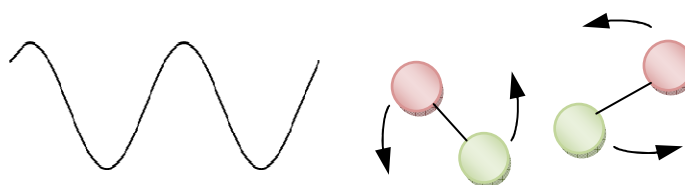


Figure 1.8. Dipolar polarisation mechanism (Adapted from Lidström et al., 2001)

Dipolar polarisation operates at these frequencies and is the main contributor to the heating effects associated with microwave radiation (Caddick, 1995). The interfacial polarisation can also contribute to the heating effect when the conducting particles are in contact with a non-conducting medium, e.g. in heterogeneous reactions.

Dielectrics are described by the following equations:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

Where: ε^* = the complex dielectric constant

ε' = the relative dielectric constant

$$j = \sqrt{-1}$$

ε'' = the relative dielectric loss factor

The relative dielectric constant is a measure of the microwave energy density in a material i.e. the ability of a dielectric to be polarised by an electric field. The relative dielectric loss factor is an imaginary part that considers the internal loss mechanisms, thus it measures the efficiency with which the absorbed energy can be converted to heat.

The ratio of the relative dielectric constant and the dielectric loss factor is given by Equation 1.3.

$$\tan\delta = \varepsilon'' / \varepsilon' \quad (\text{Eq. 1.3})$$

Where: $\tan\delta$ = the loss tangent.

The loss tangent, also known as the dissipation factor, is a measure of the penetration of the electric field in a material and the ability of the material to convert electromagnetic energy into heat energy, at a given frequency and temperature (Caddick, 1995; Lidström et al., 2001). Both ε' and $\tan\delta$ depend on frequency and sample temperature (Chen et al., 1993). Higher values of $\tan\delta$ indicate better coupling with microwave radiation.

Microwave heating originates from dielectric power absorption as described by Equation 1.4.

$$P = 2\pi f \varepsilon'' E^2 \quad (\text{Eq. 1.4})$$

Where: P = the power dissipation (W/m^3)

f = the applied frequency (Hz)

E = the electric field strength (V/m)

The electric field is assumed to be uniform throughout the volume of the material. However, as energy is absorbed within the material, the electric field decreases as a function of the distance from the surface of the material; so that Equation 1.4 is valid only for thin materials (Thostenson & Chou, 1999). An important parameter is the penetration depth, which is defined as the distance from the sample surface where the absorbed power is $1/e$ of the absorbed power at the surface. Beyond this depth, volumetric heating due to microwave energy is negligible (Thostenson & Chou, 1999). Penetration depth, d , is given by Equation 1.5.

$$d = c\varepsilon^0 / 2\pi f \quad (\text{Eq. 1.5})$$

Where: ε^0 = dielectric constant of free space

If the penetration depth of the microwave is much less than the thickness of the material, non-uniformities in the temperature occur and only the surface is heated. The rest of the sample is heated through heat transfer (Metaxas & Meredith, 1983; Thostenson & Chou, 1999).

1.4.2.2 Conduction mechanism

The conduction mechanism involves the long range (compared to rotation) transport of charge (Clark & Sutton, 1996). It occurs when charge carriers move in the presence of an electric field, as illustrated in Figure 1.9, inducing currents which will cause heating in the sample due to any electrical resistance; expenditure of energy due to an increased collision rate results in the conversion of kinetic energy to heat. This mechanism is characterised by an equivalent dielectric conductivity term σ .



Figure 1.9. Conduction mechanism (Adapted from Lidström et al., 2001)

This mechanism is much stronger than the dipolar mechanism regarding heat generation. Poor electrical conductors are susceptible to this mechanism. Materials that are good conductors such as metals will reflect the electromagnetic waves.

1.4.3 Microwave equipment components

A microwave equipment comprises three major components: the source, the transmission line and the applicator. The *source* is responsible for the generation of electromagnetic radiation. Magnetrons are most commonly used for this purpose, and are cheap due to mass production. In a magnetron a cathode is surrounded by a hollow circular metal anode (Figure 1.10). High potential difference between them generates an electric field. The electrons are removed from the cathode and accelerate spirally towards the anode, due to magnetic fields applied axially. Inside the anode there are a number of cavities that are designed to resonate in the chosen frequency; in the case of the microwave oven at 2.45 GHz. As the electrons pass the cavities, these set up oscillations in the electron cloud created at the chosen frequency. Power is extracted via a loop from one of the resonant cavities to the *transmission lines*. Waveguides are usually employed for this purpose. The transmission lines couple the electromagnetic energy to the *applicator*, where the waves resonate and form standing waves. Thus, areas

with nodes and antinodes are created, i.e. areas where the electromagnetic field is at a minimum and areas where it is at a maximum.

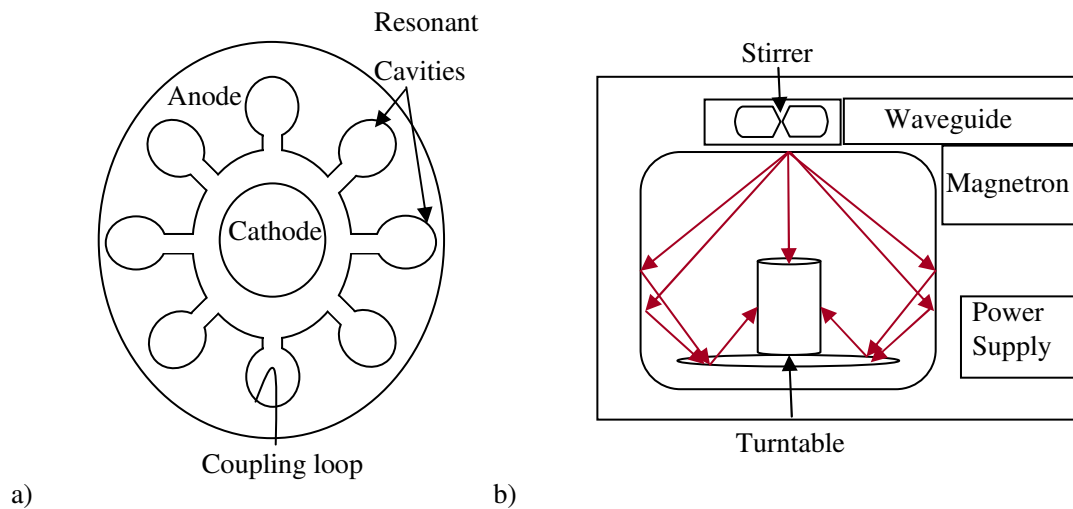


Figure 1.10. a) Illustration of magnetron and b) Typical microwave oven diagram

Applicators include single mode and multimode resonant cavities (Thostenson & Chou, 1999). A single mode cavity is one that can sustain one mode, so there is only one area where the electromagnetic field is at a maximum, whereas a multimode cavity has a number of nodes and antinodes.

An important aspect of a microwave equipment design is to make provisions for safety from exposure to microwave radiation. Usually this is achieved by cavity seals. There are emission limits of 1 and 5 mW/cm² for new and used ovens measured at a distance of 5 cm from the external surfaces of the oven, as defined by international organisations such as the International Electrotechnical Commission (IEC), the International Committee on Electromagnetic Safety (ICES) of the Institute of Electrical and Electronics Engineers (IEEE) and the European Committee for Electrotechnical Standardization (Chan & Reader, 2000; WHO, 2005). Also, a sealing system is required to ensure there is no interference from cellular phones and bluetooth operations.

If the microwaves are not absorbed by the material they may be reflected back down the waveguide and damage the magnetron; thus it is essential to have a microwave active “dummy load” which will absorb excess microwaves and avoid such damage (Caddick, 1995). For this purpose, a three-port circulator is often employed in microwave equipment. One of the ports is connected to the microwave source, the other to the applicator and the last to the dummy load. The generated microwaves are only transmitted in one direction, so that

any reflected power will be diverted and absorbed by the dummy load (Thostenson & Chou, 1999).

1.4.4 Advantages and disadvantages of using microwaves

Microwave energy is delivered directly through interaction with the electromagnetic field, which results in volumetric heating – unlike conventional heating where the energy is transferred through convection, conduction and radiation (Thostenson & Chou, 1999). In conventional pyrolysis the heat is transferred via conduction, thus the exterior of the sample is hotter than the interior. The volatiles released from the centre of the sample will pass through a high temperature surface region, where undesired secondary reactions can occur that will produce low molecular weight species which will deposit. In microwave heating the centre will probably be heated first (the exterior will act as an insulator). Volatile gases released will pass through low temperature regions and undesired secondary reactions are reduced, producing a cleaner structure (Miura et al., 2004).

Overall, the potential advantages of using microwaves are numerous and include (Jones et al., 2002): (i) efficient heating, (ii) rapid reaction times, (iii) energy savings, (iv) selective heating and material property dependence that ensures no energy is lost in bulk heating, and (vi) potentially better quality outputs.

There are, however, disadvantages to microwaves. One of the major disadvantages of microwave processing involves the difficulty of accurate temperature measurements and control of experimental conditions (Zong et al., 2003). Simple instruments such as thermocouples and thermistors cannot be used due to their interaction with microwaves.

In addition, hot spots can be created due to thermal runaway. This occurs when the power dissipation in an area of the sample exceeds the rate of heat transmission to its surroundings, thus it heats faster, with increasing temperature due to the abrupt increase of the dielectric constant. This effect is more pronounced in multimode cavities, where the sample experiences different intensities of electromagnetic field depending on its position in the cavity, which leads to its non-uniform heating.

The design of the furnace is crucial to achieve uniform electromagnetic field within the cavity, which will ensure uniform heating. In domestic microwave ovens this is solved by stirring the sample or using a stirring modem – a fan – that bounces the electromagnetic

waves to different directions within the cavity. In addition, further difficulties in the design of a microwave cavity arise from the change in dielectric properties of a sample during microwave processing – which makes it even harder to control and monitor.

The inability to accurately monitor, or at least give reasonable explanations to microwave-driven phenomena gave rise to the term “microwave effects”. Microwave effects have been a controversial issue amongst scientists, as there are different opinions whether unexpected results from microwave processing such as the enhancement in the rates of activated processes, differences in reaction pathways and reaction products are due to poor temperature measurements and localised temperature variations or effects due to different mechanisms occurring (Clark & Sutton, 1996).

1.5 Summary

The UK produces more than 450,000 tonnes of used tyres each year and combined with their otherwise desired property to resist degradation, their disposal presents a significant waste management problem. The 99/31/EC directive on the landfill of waste banned their disposal from landfill, effectively enforcing 100% recovery.

The most sustainable method for handling waste tyres is retreading. However, a car passenger tyre can only be retreaded once, thus limiting the options for tyre recycling. Reprocessing of tyres to produce rubber crumb for use in asphalt mixtures, carpet underlays, playgrounds and other applications are options currently employed. In addition, the use of tyres as fuel in incineration plants and cement kilns is heavily regulated. Furthermore, waste tyres are frequently subject to fly-tipping causing local authorities significant costs and waste of resources for the clean-up. Pyrolysis provides an alternative means for recovery of value from waste tyres, and this is investigated in the current work.

The following chapter presents the aim and objectives of this work.

2 Research Aim and Objectives

The aim of this research was to investigate end-of-life tyre pyrolysis using conventional and microwave heating with a view to recovering value from this high volume waste in the form of reusable products.

The objectives of this research were the following:

- i) To review the current practices in end-of-life tyre management, including value recovery from this waste and relevant legislation
- ii) To characterise samples of rubber crumb obtained from different sources using various techniques
- iii) To pyrolyse these crumb samples by both conventional and microwave heating, and to evaluate the characteristics of the char obtained
- iv) To investigate the potential of using this char as a alternative to current filler material in rubber compounds

Following the review presented in Chapter 1, the remainder of this Thesis contains the outcome of the work that was carried out as follows:

In Chapter 3, tyre crumb samples from various sources were characterised using selected analytical techniques and the results discussed. Chapters 4 and 5 describe the pyrolysis investigations while Chapter 6 presents the investigation of filler replacement in rubber formulations. The conclusions reached in this work and the recommendations for future work are summarized in Chapter 7.

3 Characterisation of tyre rubber crumb

3.1 Introduction

In the current work, samples of tyre rubber crumb were supplied by ARTIS and by Imperial College London in batches. The ARTIS supplied materials, obtained from external collaborators, ranged in particle size from over 5 mm to less than 420 μm (Table 3.1). The samples from Imperial College, on the other hand, were obtained as whole used tyres and converted into crumb using UHPW jet technology. This prototype equipment enabled the disassembly of the tyres using a robotic arm manufactured by ABB Ltd (Figure 3.1a) and water jets up to 2,750 bars provided by Hughes Pumps Ltd. The process can be controlled to obtain crumb from specific parts of the tyres, for example the tread or the sidewalls. This ensures a more uniform composition of the crumb as different formulations are used in the various sections of the tyres as discussed in Section 1.2.

Table 3.1. Tyre rubber crumb samples record

Sample ID	Supplier	Source	Features	Chapters used in
A	ARTIS	unknown	Particle size 1 – 2 mm, no fibres ¹	3, 5
B	ARTIS	Polymer Recyclers Limited	Particle size > 5 mm, no fibres, sticky crumb	3
C	Imperial College London (UHPW)	Waste tyre depot	Particle size < 4 mm, some fibres, car passenger tyre tread only	3, 4
D	ARTIS	Crumb Rubber UK	Particle size 180 – 420 μm , no fibres/textiles, whole passenger tyres, ambient ground	3, 4, 5
E	Imperial College London (UHPW)	Waste tyre depot	Particle size < 4 mm, some fibres, car passenger tyre tread only	3, 4
F	ARTIS	Crumb Rubber UK	Particle size < 420 μm , no fibres/textiles, whole passenger tyres, ambient ground	3, 5

¹: Fibres obtained from tyre textile component described in Section 1.2

Using the UHPW system, crumb mixed with fibres was obtained from the tread of the tyre, leaving “clean” steel as shown in Figure 3.1b. The mixture of crumb and fibres was collected,

dried (first in air and then in an oven at 70°C for 24 hours) and manually sieved to obtain crumb of less than 4 mm particle size (Figure 3.1c). Note that not all fibres were successfully removed by manual sieving.

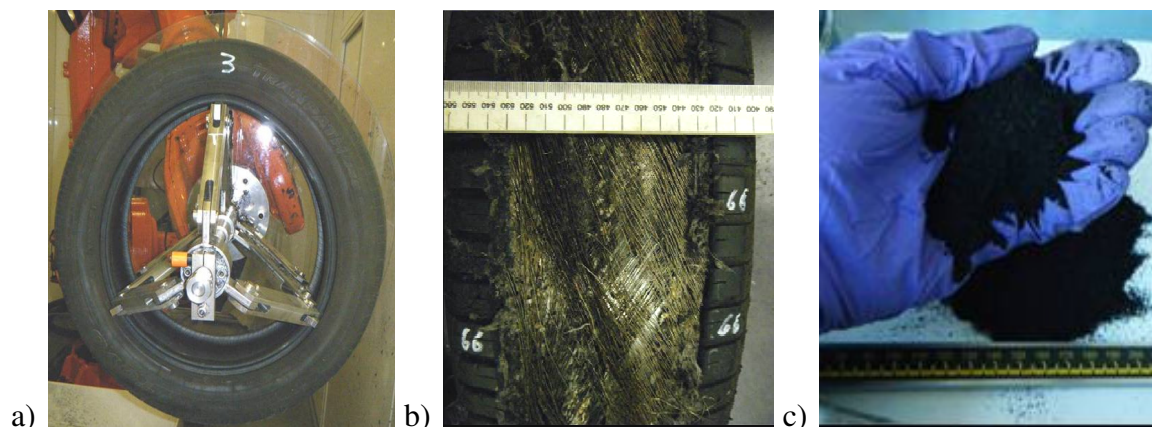


Figure 3.1. UHPW system at Imperial College: a) the placement of the whole passenger tyre onto a robotic arm, b) the steel remaining after the process, and c) the crumb generated

The samples of tyre crumb were characterised using the following analytical techniques, which are described in Section 3.2 below:

- Thermal analysis
- Carbon, hydrogen, nitrogen, sulfur analysis
- Bomb Calorimetry

These tests were selected because they provide key data necessary to design and understand the subsequent pyrolysis testing regime described and used later.

3.2 Characterisation

3.2.1 Thermal Analysis

Thermal analysis refers to a group of techniques whereby a property of a sample is monitored as a function of temperature or time, in a specified atmosphere, under controlled temperature conditions (Haines, 1995).

In the current work, a Rheometric Scientific STA 1500 simultaneous thermal analyser was used. The analyser enabled the measurement of the weight change in relation to temperature, known as thermogravimetric analysis (TGA). The instrument's software allowed the

calculation of the rate of mass loss using the TG data collected, providing derivative thermogravimetric (DTG) results.

For each analysis 12 ± 1 mg of sample were weighed in an alumina crucible and placed on the hang-down of the thermobalance. The samples were subjected to either a continuous flow of nitrogen or a combination of air and nitrogen all at 50 ml/min. One data point was recorded per 1°C temperature increase.

3.2.1.1 Under Nitrogen atmosphere

Thermal analyses of the samples listed in Table 3.1 were carried out using a 5°C/min heating rate and temperatures up to 800°C. Samples of natural rubber and SBR provided by ARTIS were also tested under the same conditions. Further, sample A was also heated under nitrogen atmosphere at the additional heating rates of 2.5°C/min, 10°C/min, 20°C/min and 40°C/min.

3.2.1.2 Under Nitrogen/Air atmosphere (Proximate analysis)

British Standard method BS ISO 9924-1:2000 for rubber and rubber products was employed to provide a proximate estimation of the composition of the different crumb samples. Accordingly, samples were heated to 300°C at a rate of 10°C/min and maintained at this temperature for 10 minutes. The temperature was then raised to 550°C, at a rate of 20°C/min, where the samples remained for 15 minutes. The temperature was further raised to 650°C at 40°C/min and maintained until the mass change remained negligible. The temperature was allowed to cool down to 300°C and the nitrogen atmosphere was switched to air. The gas flow was adjusted to correct for changes in buoyancy that would have an effect on the apparent weight of the sample. The furnace temperature was raised again to 650°C as rapidly as the instrument allows (40°C/min) and maintained for 15 minutes. Finally the heater was switched off, and the air stream was replaced with nitrogen while the samples cooled down.

3.2.2 Carbon Hydrogen Nitrogen Sulfur Analysis

Carbon hydrogen nitrogen and sulfur (CHNS) analysis was carried out by combustion analysis by MEDAC Ltd, Surrey, UK. Combustion analysis involves the burning of a sample in excess of oxygen in the presence of a catalyst. The products of this combustion are then separated by gas chromatography and the components measured. Carbon is oxidised to

carbon dioxide, hydrogen to water and sulfur to sulfur dioxide. The technique had accuracy of 0.30% and detection limit $< 0.1\%$.

3.2.3 Bomb Calorimetry

Calorific values, as measured by bomb calorimeters, represent the heat released by a sample when combusted with oxygen in an enclosure of constant volume (Parr Instrument Company, 2007). Calorific values were measured using a Parr 6100 Calorimeter.

When the sample, placed in a metal pressure vessel or bomb that is surrounded by water in a container located inside a calorimeter jacket is ignited, heat is liberated. The resulting temperature rise of the bomb and the surrounding water container is recorded. The calorific value of the sample per unit weight is then obtained by multiplying the temperature change with the heat capacity of the calorimeter and dividing by the sample's weight.

In this study, the equipment was first calibrated with benzoic acid to determine the heat capacity of the calorimeter. Then approximately 0.15 g of the crumb samples in Table 3.1 were tested in triplicate, taking into consideration their sulfur content as determined by the CHNS analysis. The sulfur under these experimental conditions oxidises to trioxide which reacts with the water present to form sulfuric acid.

3.3 Results and discussion

The TG and DTG plots obtained from thermal analysis of weighted portions of sample C from Table 3.1 (the first UHPW batch produced crumb) are presented in Figure 3.2.

Three regions are identified, as annotated in Figure 3.2:

- Region I, between approximately 150°C to 300°C, associated with volatilisation of the various chemical additives present in tyres such as processing oils and plasticisers (Brazier & Nickel, 1975)
- Region II, from approximately 300°C to 400°C with a peak in the DTG curve at 368°C, representing weight loss associated with rubber degradation, and
- Region III, between 400°C and 480°C with a peak at 427°C also representing weight loss associated with rubber degradation.

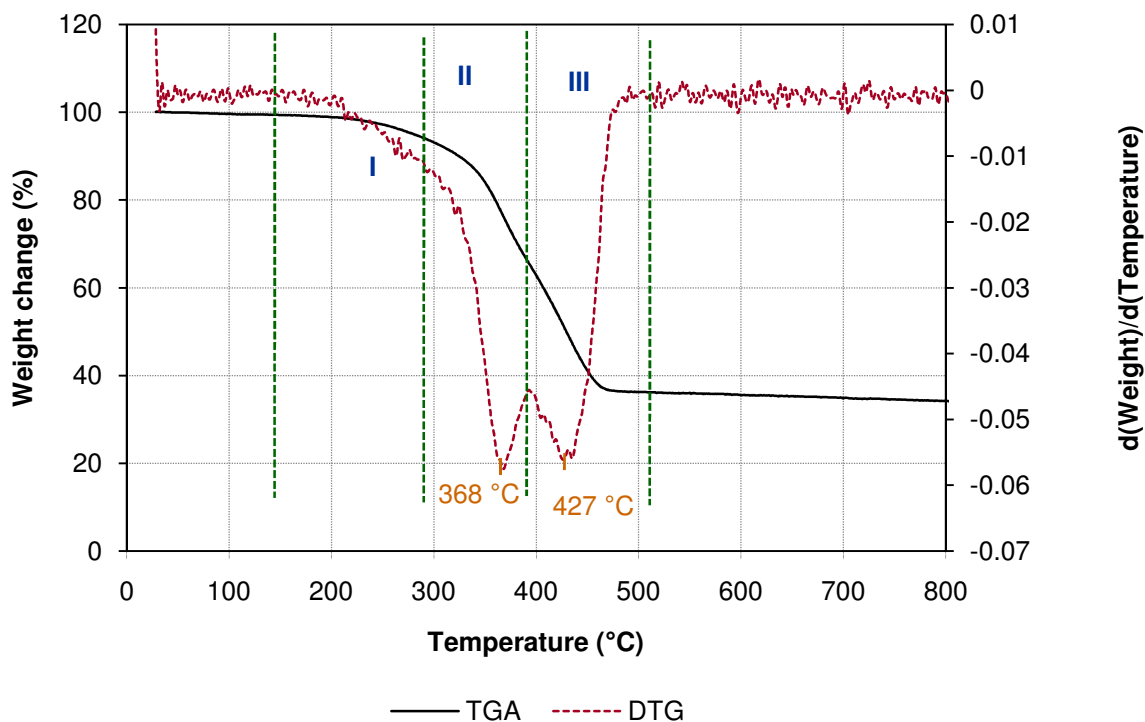


Figure 3.2. TG and DTG plots of sample C at 5°C/min heating rate in N₂

After 500°C, pyrolysis is essentially completed and further weight loss is attributed to char rearrangement and thermal cracking and volatilisation of large molecular hydrocarbons formed during the pyrolysis (San Miguel, 1999).

Williams & Besler (1995) stated that tyre rubber degradation could be related to the specific elastomers present in each tyre's formulation. As stated in Section 1.2, the main elastomers used in tyre production are natural rubber, SBR and PBR. In the current work, samples of natural rubber and SBR were also analysed and the TG and DTG plots obtained are presented in Figures 3.3 and 3.4 respectively.

From the results of the analysis, both natural rubber and SBR left minimal residue following decomposition, 0.08% and 0.82% at 800°C respectively (Figure 3.3), though natural rubber fully degraded at a lower temperature (~460°C) than SBR (~488°C).

The DTG plot for natural rubber presents a peak at ~372°C and a shoulder at higher temperatures. Using the same heating rate (5°C/min), Williams & Besler (1995) also observed a peak at 375°C and Seidelt et al. (2006) observed a peak at 378°C using a 10°C/min heating rate.

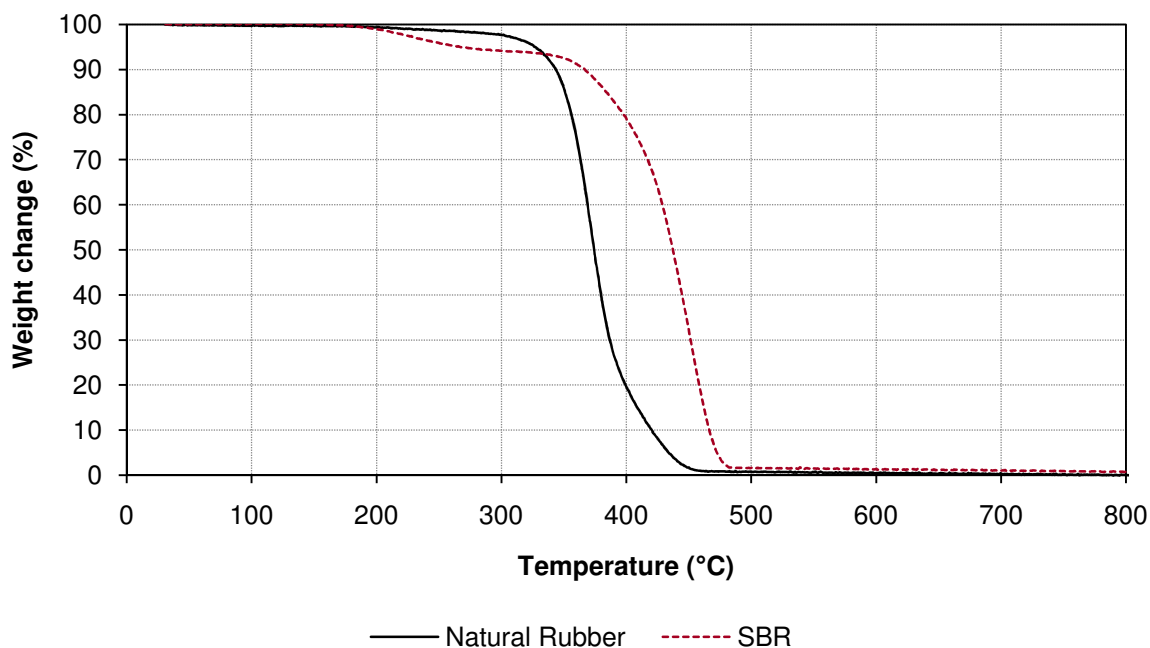


Figure 3.3. TG plot of natural rubber and SBR at 5°C/min heating rate in N₂

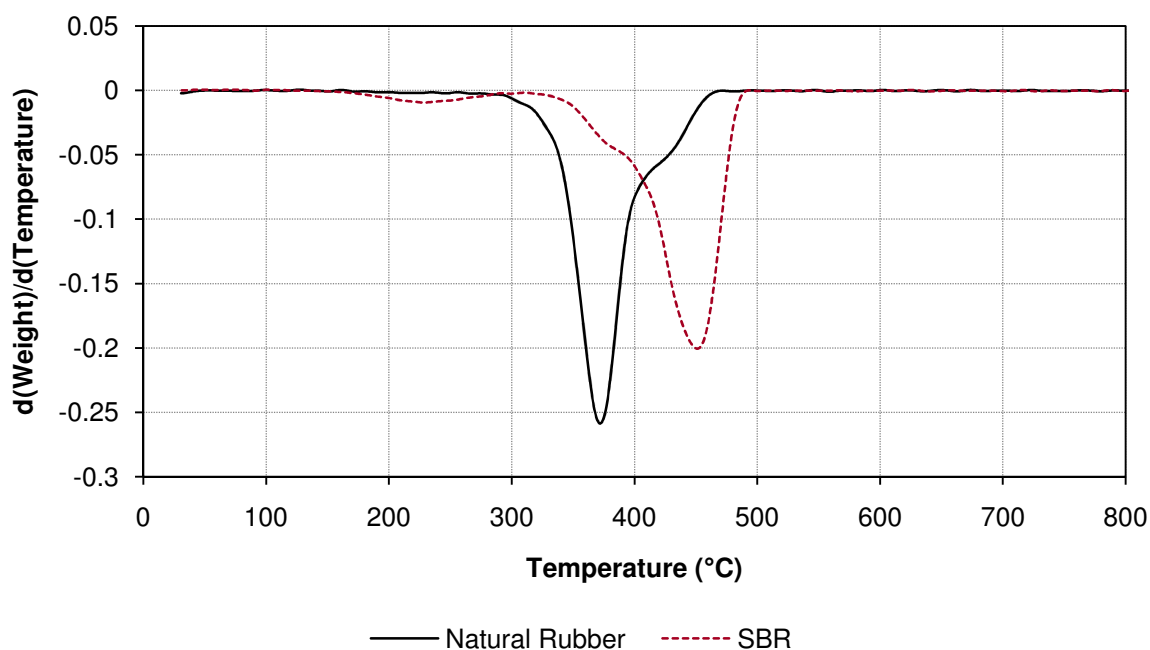


Figure 3.4. DTG plot of natural rubber and SBR at 5°C/min heating rate in N₂

In addition, as observed in Figure 3.4, SBR shows a two-step mass loss. The first step presented as a small broad peak at around 150 – 300°C is attributed to the volatilisation of processing oils required in the manufacture of synthetic rubber. The second step which presents a shoulder and then a major peak at 450°C is due to the thermal decomposition of the

rubber. Williams & Besler (1995) recorded a peak at 455°C using the same heating rate and Seidelt et al. (2006) at 458°C using 10°C/min rate of heating. The small differences of peak temperatures between authors may arise from different heating rates, sample masses and instrument calibration.

To illustrate the differences arising from changing heating rates, crumb sample A was analysed using various heating rates and the TG and DTG plots obtained are presented in Figures 3.5 and 3.6 respectively.

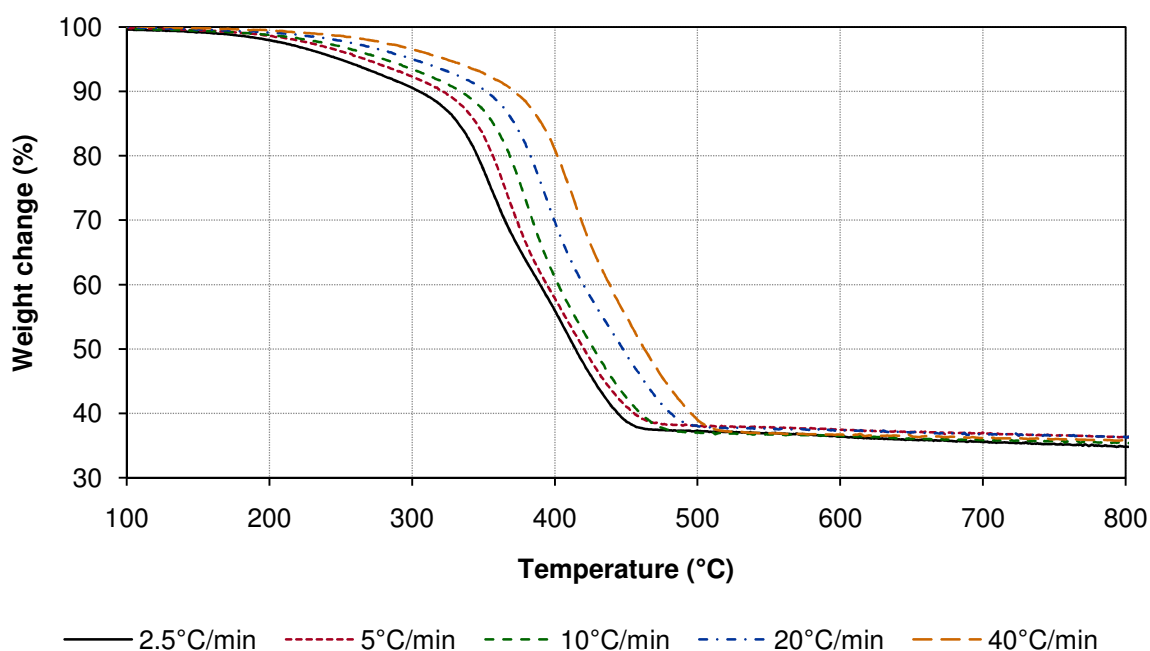


Figure 3.5. TG plots of sample A at different heating rates in N₂

The char yield at 550°C remained constant (37 – 38%) irrespective of the heating rate under these experimental conditions, with minor differences possibly due to the different formulations of the crumb within the sample. This was also observed by Williams & Besler (1995) and Senneca et al. (1999) etc.

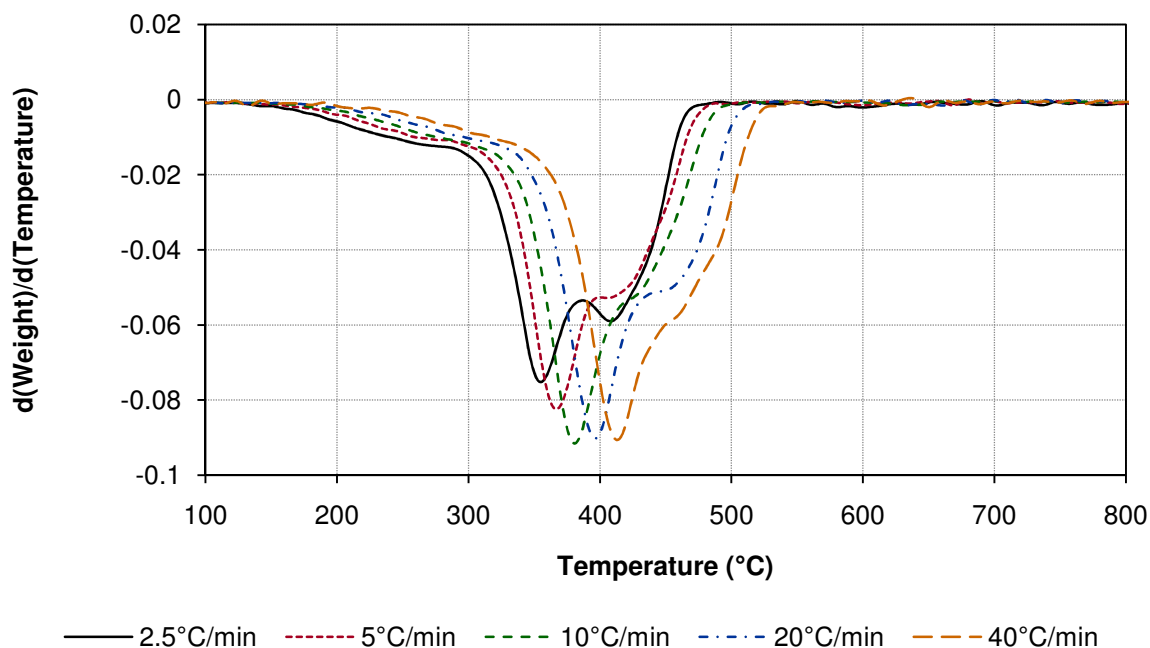


Figure 3.6. DTG plot of sample A at different heating rates in N_2

On increasing the heating rate a shift of the peaks to higher temperatures is observed. Williams & Besler (1995) attributes this to a combined effect of heat transfer and kinetics of decomposition. The former occurs because the transfer of heat from the furnace to the sample is not instantaneous but rather depends on the conduction, convection and radiation within the apparatus. A thermal lag is thus created between the different parts of the instrument. This effect is more pronounced when higher heating rates are used (Haines, 1995). In addition, at lower heating rates better resolution of changes occurring at close temperatures is achieved. Indeed, using 2.5°C/min heating rate, the two main peaks of the DTG are clearly identified. On increasing the rate, the two peaks merge and shift to higher temperatures, as observed by other authors (Williams & Besler, 1995; Gonz  les et al., 2001; Lah et al., 2013).

In the case of SBR, different peak temperatures reported can be due to different styrene ratios present in the samples. In fact, Seidelt et al. (2006) recorded DTG curves of SBR samples with differing oil content and styrene-butadiene ratio of the copolymer. Similar styrene ratio samples showed identical peaks in the rubber degradation region (between 360°C – 520°C using 10°C/min heating rate), whereas a higher styrene ratio sample had a more pronounced shoulder at the beginning of the rubber degradation. This is because the release of styrene starts at ~360°C while that of 4-ethenylcyclohexene, the main decomposition product of

butadiene, starts after $\sim 420^{\circ}\text{C}$. Increased content of processing oils increased the intensity of the minor peak at around $150 - 300^{\circ}\text{C}$.

The other possible main constituent of tyre rubber, polybutadiene rubber (which has not been examined in the present work) shows one major weight loss in its DTG plot, observed at 461°C by Brazier & Nickel (1975) and 468°C by Seidelt et al. (2006). In addition, a minor peak is observed at 385°C (Seidelt et al., 2006) and 372°C of height 4 – 10 % of that at 461°C (Brazier & Nickel, 1975), using $10^{\circ}\text{C}/\text{min}$ heating rate.

The two stage degradation of polybutadiene containing rubbers involves first a main scission of the polymer to generate radicals. These can undergo further depolymerisation or react to form cyclised and cross-linked products. Sanglar et al. (2010) investigated the thermal degradation of 1,4-PBR using ^{13}C Nuclear Magnetic Resonance (NMR) and identified two compounds possibly formed by crosslinking, according to the mechanism shown in Figure 3.7. In addition, Golub & Gargiulo (1972) attributed the infrared spectroscopy and NMR results of the thermally degraded cis 1,4-PBR to the formation of a polymeric residue which is nearly fully cyclised. It is to these cyclised and cross-linked products, which possibly require higher temperatures to degrade, that the observed second peak is attributed (Brazier & Schwartz, 1978). In the case of natural rubber, cyclised polyisoprene is not as thermally stable as polybutadiene and degrades just above the depolymerisation temperature; thus the one major peak observed in DTG curves (Brazier & Schwartz, 1978).

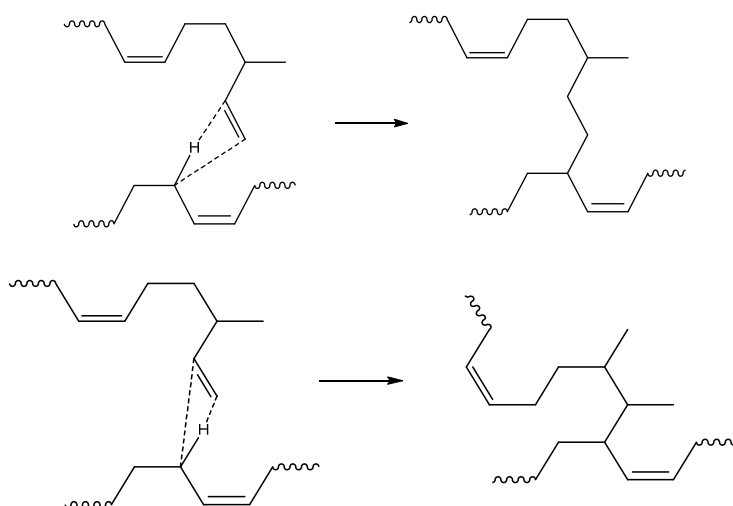


Figure 3.7. Sanglar et al.'s (2010) proposed cross-linked structures from 1,4-polybutadiene degradation

Williams & Besler (1995) suggested the use of TGA analysis to give a rough indication of the elastomers present in each tyre sample. Lower temperature decomposition is related to natural rubber, as its major weight loss peak temperature has $\sim 80 - 100^\circ\text{C}$ difference from SBR/PBR's main peak (Lee et al., 2007). The higher decomposition temperature is related to SBR/PBR and cannot be distinguished between the two by this method, as their major peak temperatures have less than 20°C difference.

Furthermore, Seidelt et al. (2006) showed that the three most commonly used tyre additives – zinc oxide, sulfur and carbon black – had no significant influence on the DTG curves of natural rubber and SBR, justifying further the use of DTG curves as an identification method for rubber mixtures due to their characteristic peak temperature.

The TG and DTG plots obtained from thermal analyses of the tyre rubber crumb samples in Table 3.1 are presented in Figures 3.8 and 3.9, respectively. All samples generated char yield between $34 - 37\%$, irrespective of their composition. The remaining residue is a mixture of the carbon black and the inorganic materials present in tyres, as well as carbonisation residue from the pyrolysis process (Kim et al., 1995).

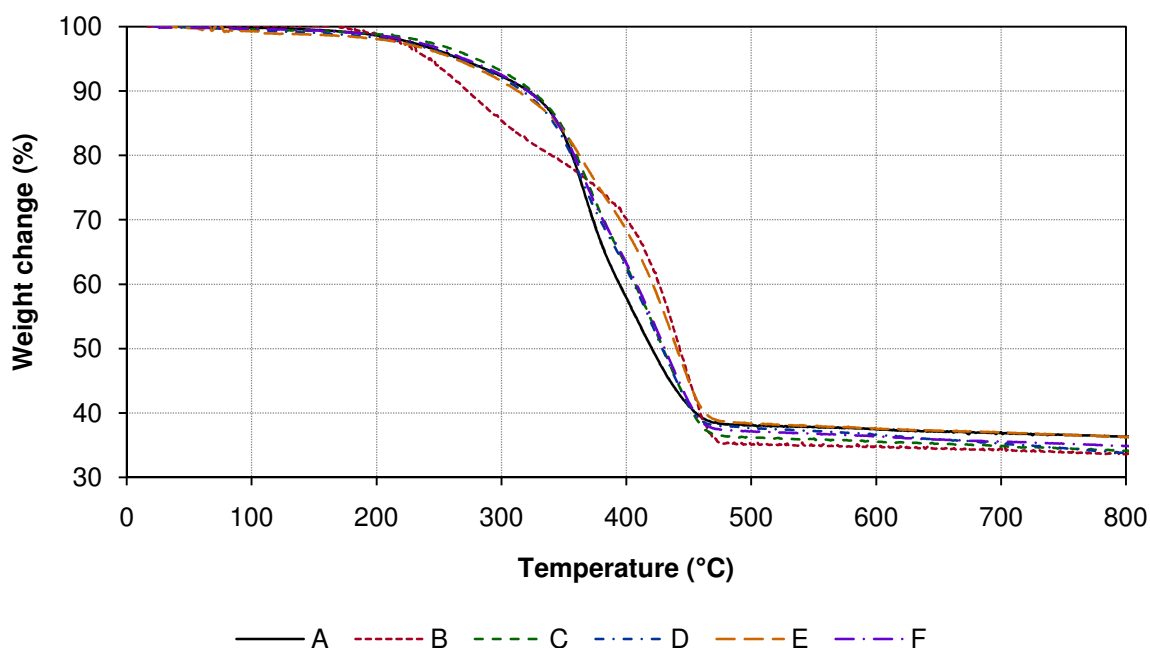


Figure 3.8. TG plot of different rubbers at $5^\circ\text{C}/\text{min}$ heating rate in N_2

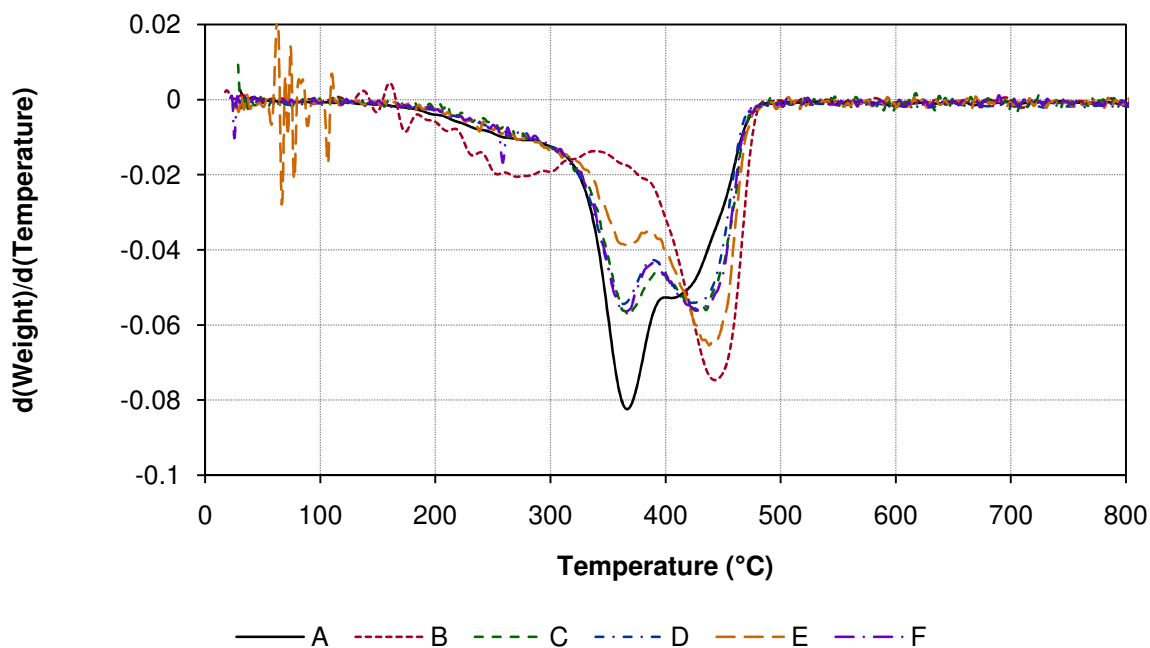


Figure 3.9. DTG plot of different rubbers at 5°C/min heating rate in N₂

The DTG plots obtained indicated comparable proportions of natural rubber and SBR/PBR in samples C (obtained from IC UHPW), and D and F (both from Crumb Rubber UK) with similar peak temperatures observed at 368°C, 363°C, 367°C and second peak temperature at 427°C, 423°C and 428°C respectively. Senneca et al. (1999) recorded similar peak temperatures of 360°C and 420°C when pyrolysing scrap tyre samples of 1 mm size at 5°C/min heating rate. A summary of all the peak temperatures is presented in Table 3.2.

Table 3.2. Peak temperatures of samples A – F

	A	B	C	D	E	F
Peak 1 Temp (°C)	367	270	368	363	366	367
Peak 2 Temp (°C)	405	443	427	423	438	428

Sample E, originating from a second batch from the UHPW jet system had SBR/PBR blend as the main constituent probably due to different types of tyres being used in the process. Whereas the first peak at 367°C is similar to the samples C, D and F, the second peak is higher at 438°C. Sample A showed a major peak at 367°C in the region where natural rubber degrades. This is usually expected from crumb originating from truck tyres, where natural rubber is the main rubber constituent used. There was a second peak presented at 405°C, a lower temperature than the ones recorded from the other samples examined.

As stated previously, cyclised products from natural rubber degradation are not stable and decompose just above the main degradation temperature, which would explain the consistency of the first peak in the DTG plots of samples A, C, D, E and F at around 367°C. The second peak is influenced by the specific formulations of the SBR/PBR blend that can promote secondary reactions and shift the second peak temperature. Nevertheless, tyre pyrolysis is a complex process associated with a number of reactions occurring both in parallel and in series. Peaks observed on the DTG plots are composites of one or more degrading components (Williams & Besler, 1995; Brazier & Nickel, 1975).

Sample B showed unusual behaviour, for tyre rubber. It presented a broad hump in the region between 125°C and 350°C with a maximum dip at 270°C and a major peak at 443°C. Using the proximate analysis (BS ISO 9924-1:2000) the compositions of the tyre crumb samples were estimated. Figure 3.10 presents typical results obtained from the analysis (in this example for sample C).

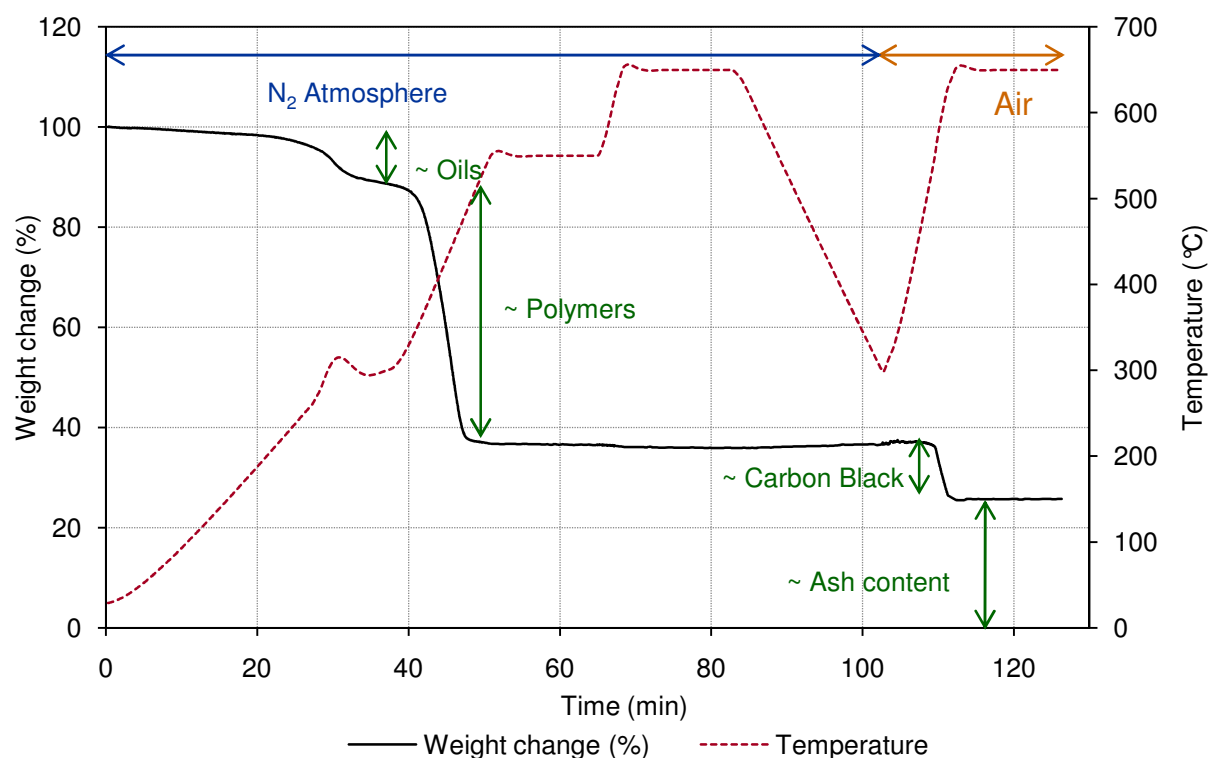


Figure 3.10. Proximate thermal analysis plot of sample C

The compositions shown in Table 3.3 were derived by assuming that the weight loss up to 300°C will give an approximation of the content of the oils. The weight loss from 300°C to 550°C is from the polymers. Changing the atmosphere to air means the weight loss from

550°C to 650°C is from the carbon black with remaining residue being the inorganic components (Silica, ZnO etc).

Table 3.3. Compositions of the rubbers using TGA

	Oils (%) ²	Polymers (%) ²	Carbon black (%) ²	Ash (%) ²	Pyrolysis char (%) ³
A	10.6	48.7	25	15.1	40.1
B	20.2	38.0	22	16.5 ¹	38.5
C	11.4	52.1	10.2	25.7	35.9
D	10.2	51.5	28.1	9.6	37.7
E	9.9	52.0	20.5	17.1	37.6
F	9.2	54.1	27.5	8.4	36.0

Note: ¹ Weight loss continued to occur beyond 650°C in air - Refer to Appendix II (Figure A)

² The minor deviation (<0.6%) of the sum of oils + polymers + carbon black + ash from 100% for samples A & C – F, is due to inevitable error introduced when manually adjusting the gas flow from nitrogen to air

³ Pyrolysis char = carbon black + ash

As can be seen in Table 3.3 sample B has a high amount of oils (20%) in comparison to the other samples which have around 10% (usual for tyres). The polymer content of sample B is also noticeably less (38%) than that of all the other samples (48 – 54%). Additional examination of sample B by ARTIS reported the presence of calcium carbonate, which confirms that this rubber crumb is unlikely to be of tyre origin.

It must be emphasised that this analysis is only approximate as it is often unclear when the volatile oils finish decomposing and the polymer degradation starts. To obtain more accurate results it is necessary to switch to lower heating rates or to use solvent extraction (usually with acetone) to remove the volatile oils before TGA analysis is performed.

Sample C obtained from the UHPW jet system has only 10% of carbon black, highlighting a decrease in the use of carbon black as filler by the tyre manufacturing industry. These samples also originated from the tread, an area where silica is typically included. The other batch of crumb from the UHPW, sample E, also has lower carbon black content (~20%) than that usually expected in car tyres (27 – 28%, see Table 1.1) which was observed in samples D and F, both received from Rubber Crumb, UK. The proximate analysis results for both D and F are comparable to those presented in Table 1.1 for a typical car passenger tyre composition. These samples were obtained from whole tyres (not just the tread).

The results obtained from CHNS analysis are presented in Table 3.4 along with data from Li et al. (2004) for comparison. Carbon values obtained confirm the lower percentage of carbon

black in sample C, and E to a lesser extent, as the carbon values reflect the carbon black levels – the polymer content is approximately the same. Hydrogen levels are between 6.60 and 6.99% for all the samples with the exception of sample B. Nitrogen is present in all samples at less than 1% and originates from chemicals such as p-phenylamine used as antidegradant in tyre formulations. All samples also contain sulfur, the most commonly used vulcanising agent in rubber industry, as observed by Kaminsky & Mennerich, 2001 (1.4%), Senneca et al., 1999 (1.9%) and so on.

Table 3.4. CHNS analysis and calorific values of tyre rubber samples

	C (%)	H (%)	N (%)	S (%)	Calorific Values (MJ/kg)
A	85.65	6.76	0.80	1.15	36.4
B	83.63	7.44	0.25	0.60	36.3
C	60.59	6.74	0.45	2.13	32.1
D	80.20	6.69	0.56	1.79	36.5
E	69.50	6.79	0.44	2.25	32.6
F	78.96	6.99	0.58	1.73	36.4
Li et al., 2004	84.08	6.71	0.49	1.51	34.9

Table 3.4 also presents the calorific values of the samples which are similar to those observed by other authors (36.8 MJ/kg by Roy & Unsworth (1989), 31.8 MJ/kg by Senneca et al. (1999) and so on). The high calorific value, which is comparable to that of anthracite and dry steam coal (34.6 MJ/kg), confirms why tyres are considered a valuable candidate for fuel recovery from waste (Digest of UK energy statistics (DUKES, 2013)). The calorific value of tyres is significantly higher than that observed from other renewable sources such as municipal solid waste (9.5 MJ/kg), wood pellets (17.2 MJ/kg), meat and bone (20.0 MJ/kg) etc, with the exception of that of biodiesel (38.7 MJ/kg) (DUKES, 2013).

3.4 Conclusions

The various tyre rubber crumb samples from different sources were characterised using CHNS analysis, calorific value measurements and thermal analysis.

The results obtained indicated that samples C and E, both from the UHPW jet system, had lower carbon content (60.6 – 69.5%) in comparison to the other crumb samples (79.0 – 85.7%). This is attributed to the increasing usage of silica as filler material in the tread in tyre manufacture. All samples had high calorific value (32.1 – 36.4 MJ/kg).

TG analysis showed that the main rubber degradation occurred at temperatures between 300°C and 480°C using 5°C/min heating rate. The DTG plots presented two peaks associated with the degradation of natural and synthetic rubber. Sample B showed different thermal degradation patterns than the rest of the samples. On this basis, samples A, C, D, E and F were chosen for further examination as presented in the following chapters of this thesis.

4 Conventional Thermal Pyrolysis

4.1 Introduction

As discussed in Section 1.3.4.5.1, the process of tyre pyrolysis is influenced by various parameters including temperature, retention time, pressure, type of reactor etc. The relationship of these parameters with the outcomes of pyrolysis experiments such as the surface area of the char generated are of great interest, especially if the process is to be optimised to achieve high-value end-products.

There are various ways to investigate how the different parameters of a process relate to the outcome. The most extensively used methodology is the ‘one-factor-at-a-time’ approach, whereby each factor under investigation is varied over a range, while the others are kept constant at a predefined baseline (Montgomery, 2005). This approach, however, does not take into consideration the possibility of interactions between the different parameters. The effect of one parameter using a certain baseline for the rest of the parameters kept constant, might not be the same at a different baseline. To overcome this, it is best to employ statistical designed experiments where factors are varied together (Montgomery, 2005). The “*collection of statistical and mathematical techniques useful for developing, improving and optimizing processes*” (Myers et al., 2009) is known as Response Surface Methodology (RSM).

In RSM, the relationship between the measured outcome of an experiment, known as the *response*, and the independent variables is modelled and examined using multiple linear regression as described below.

In this chapter the statistical background of RSM is first introduced and then used to investigate the influence of seven parameters on the characteristics of char generated from tyre pyrolysis (Part I). By elimination these parameters are reduced to three and investigated further (Part II). The experimental procedure and characterization techniques are described, followed by a discussion of the results.

4.2 Statistical Background

4.2.1 Multiple linear regression

Consider, for example, an experiment where the response is the surface area, denoted as y , and the independent variables are temperature and heating rate and so on, denoted as x_1 and x_2 up to x_k respectively. A multiple linear regression model describing the relationship can be defined as shown in Equation 4.1 below.

$$y = E(y) + \varepsilon = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_k x_k + \varepsilon \quad (\text{Eq. 4.1})$$

Where: $E(y)$ = mean value of y

β_j = regression coefficients for $j = 0, 1, \dots, k$

ε = random error

The model described in this equation assumes that y , for any given value of x , produces a straight line and any deviation from this line is due to a random error component, ε (Mendenhall & Sincich, 1995). The regression coefficient β_j expresses the expected change in response y per unit change in x_j when the rest of the independent variables x_i ($i \neq j$) are held constant (Myers et al., 2009).

This equation can be used to express the relationship between the response and the independent variables in the presence of interaction and second-order terms, as detailed by Myers et al. (2009).

In order to fit the linear regression model as described in Equation 4.1 to a set of data, the regression coefficients have to be estimated. This is achieved using the method of least squares. Assuming that the error component follows a normal probability distribution with the mean of error $E(\varepsilon) = 0$ and the variance equal to a constant, say σ^2 , and that the errors associated with different observations ε_i are uncorrelated random variables (Mendenhall & Sincich, 1995 and Myers et al., 2009); the least squares method minimises the sum of the squares of the errors, SSE , with respect to each of the individual regression coefficients by

setting the derivatives $\left. \frac{\partial SSE}{\partial \beta_0} \right|_{b_0, b_1, \dots, b_k}$ and $\left. \frac{\partial SSE}{\partial \beta_j} \right|_{b_0, b_1, \dots, b_k}$ to zero, where $b_0, b_1, \dots, b_k$ are the corresponding least square estimators.

This creates a set of $k + 1$, simultaneous equations, called least squares normal equations which are easier to be solved when rearranged into a matrix notation, described in Equation 4.2.

$$y = X\beta + \varepsilon \quad (\text{Eq. 4.2})$$

$$\text{Where: } y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}, X = \begin{bmatrix} 1 & x_{11} & x_{12} & \dots & x_{1k} \\ 1 & x_{21} & x_{22} & \dots & x_{2k} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & x_{n1} & x_{n2} & \dots & x_{nk} \end{bmatrix}, \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_k \end{bmatrix}, \text{ and } \varepsilon = \begin{bmatrix} \varepsilon_0 \\ \varepsilon \\ \vdots \\ \varepsilon_k \end{bmatrix}$$

The least square estimator b is then calculated using Equation 4.3:

$$b = (X'X)^{-1}X'y \quad (\text{Eq. 4.3})$$

MATLAB[®], which is a numerical programming language (MATrix LABoratory), can be used to provide a solution. To avoid errors occurring from rounding off numbers during the matrix solution of the equations, coding of the independent variables is recommended (Mendenhall & Sincich, 1995). There are various ways to do this, one of which is by setting the maximum value to 1 and the minimum to -1.

The fitted regression model generated is presented in Equation 4.4.

$$\hat{y}_i = b_0 + \sum_{j=1}^k b_j x_{ij} \quad (\text{Eq. 4.4})$$

Where $\hat{y}_i$ is the estimate of the response y_i

The difference between y_i and $\hat{y}_i$ is defined as residual $e_i = y_i - \hat{y}_i$, and is one of the parameters used to test the fitted model's accuracy in tests described in Section 4.2.2 below.

4.2.2 Testing model significance

There are certain statistical hypothesis tests that have to be performed to evaluate the fitted regression model, either to assess its significance in giving a good approximation of the responses or to verify the validity of the assumptions used in developing the model. The tests and parameters considered in this thesis to evaluate the model adequacy are: ANalysis Of Variance (ANOVA), coefficient of multiple determination R^2 and R_{adj}^2 , individual regression coefficients testing, and residual analysis. These are discussed below.

4.2.2.1 Analysis of variance

Analysing the variance of the least squares fit provides information on the usefulness of the overall model. The appropriate test examines the null hypothesis which considers that all regression coefficients are equal to each other and equal to zero ($H_0: \beta_1 = \beta_2 = \dots = \beta_k = 0$) against the alternative hypothesis that at least one of the regression coefficients is not equal to zero ($H_a: \text{at least one of } \beta_1, \beta_2, \dots, \beta_k \neq 0$). If at least one of the regression coefficients β is non-zero, then there is evidence of a linear relationship between the response and one or more of the independent variables, thus the constructed regression model is considered to be useful.

If the null hypothesis is rejected, when in fact it is true, it gives rise to what is known in statistics as a Type I error. The probability of making a Type I error is known as the significance level α , and hypothesis testing is usually conducted at a predefined significance level α .

To test this hypothesis the ANOVA table is constructed as shown in Table 4.1. The total sum of squares (SS_T) is the sum of squares of the difference between the response y_{ij} and the overall mean $\bar{y}$, calculated over all the distinct levels of the variables, $i = 1, 2, \dots, m$, and replicates at the same level, $j = 1, 2, \dots, n_i$. The total sum of squares is divided into two components: the sum of squares due to the regression (SS_R) and the sum of squares due to the residual or error (SS_E). The former (SS_R) is the sum of squares of the differences between the predicted values $\hat{y}_i$ and the average of the response variable $\bar{y}_i$, and the latter (SS_E) is the sum of squares of residuals between the experimental responses y_{ij} and the predicted values $\hat{y}_i$ from the model.

Table 4.1. ANOVA

Source of variation	Sum of Squares	Degrees of Freedom (df)	Mean Square	F ₀	p-value
Regression	$SS_R = \sum_{i=1}^m \sum_{j=1}^{n_i} (\hat{y} - \bar{y})^2$	k	MS_R	MS_R/MS_E	Model significant <α
Error of residual	$SS_E = \sum_{i=1}^m \sum_{j=1}^{n_i} (y_{ij} - \hat{y})^2$	$n-k-1$	MS_E		
<i>Lack of Fit</i>	$SS_{LOF} = \sum_{i=1}^m \sum_{j=1}^{n_i} (\bar{y}_i - \hat{y}_i)^2$	$m-k-1$	MS_{LOF}	MS_{LOF}/MS_{PE}	Model significant >α
<i>Pure Error</i>	$SS_{PE} = \sum_{i=1}^m \sum_{j=1}^{n_i} (y_{ij} - \bar{y}_i)^2$	$n-m$	MS_{PE}		
Total	$SS_T = \sum_{i=1}^m \sum_{j=1}^{n_i} (y_{ij} - \bar{y})^2$	$n-1$			

* n = number of observations, k = number of regression coefficients, m = number of distinct levels of the variable x ,

$n = \sum_{i=1}^m n_i$ and *Mean Square* = $\frac{\text{Sum of squares}}{\text{Degrees of Freedom}}$

If $F = \frac{MS_R}{MS_E} > F_{\alpha, \nu_R, \nu_E}$, then the null hypothesis is rejected. Every F-value has a corresponding observed significance level, known as a *p-value*. For a significant model, the observed *p-value* must be less than the predefined α . Reporting *p-values* allows individual readers to decide the maximum level of α they would tolerate and draw their own conclusions (Mendenhall & Sincich, 1995).

From Table 4.1 we note that the Error of residual has two components, Lack of Fit (LOF) and Pure Error (PE). Testing for lack of fit is essential for the determination of the models appropriateness. This involves having more than one observation at the same setting of variables, to check on the variability of the process. For the overall model to be significant, it has to be proved that the variation of the predicted values is large with respect to the relative error, otherwise the model has been fitted to the errors only (Myers et al., 2009).

If $F = \frac{MS_{LOF}}{MS_{PE}} > F_{\alpha, \nu_{LOF}, \nu_{PE}}$ and the corresponding p-value is low, then the null hypothesis that the model is adequate is rejected; there is evidence of lack of fit and thus the model is not suitable.

Further, the ratio of $\frac{SS_R}{SS_T}$ from the ANOVA table is known as the coefficient of determination R^2 . This provides a measure of the amount of reduction in the variability of y gained by the use of the regression variables $x_1, x_2, \dots, x_k$ in the model (Myers et al., 2009) i.e. gives an indication of how well the least squares equation fits the data.

For example, if a model has $R^2 = 0.95$, this means that the least squares line relating y with the x_j can explain 95% of the variation present in the sample of y values (Mendenhall & Sincich, 1995).

Care must be taken when interpreting the value of R^2 , as it increases with increasing number of variables, irrespective of whether the added variables are significant or not. In fact, it is better, if used in conjunction with R_{adj}^2 , which is an adjusted version of R^2 , that takes into consideration the sample size and number of variables in the model (Eq. 4.5).

$$R_{adj}^2 = 1 - \frac{SS_E(n-p)}{SS_T(n-1)} = 1 - \frac{n-1}{n-p} (1 - R^2) \quad (\text{Eq. 4.5})$$

A noticeable difference between R^2 and R_{adj}^2 highlights the presence of non-significant terms in the model.

4.2.2.2 Individual regression coefficients

Testing individual regression coefficients is important, even if the overall model has been found significant. This can give information on which of the $x_1, x_2, \dots, x_k$ variables are the most important, or whether insignificant parameters are included in the model.

The appropriate test statistic to investigate the null Hypothesis $H_0: \beta_j = 0$ against the alternative $H_a: \beta_j \neq 0$ is given below (Eq. 4.6):

$$t_0 = \frac{b_j}{\sqrt{\hat{\sigma}^2 c_{jj}}} \quad (\text{Eq. 4.6})$$

Where C_{jj} is the diagonal element of $(X'X)^{-1}$ corresponding to b_j

H_0 is rejected if $|t_0| > t_{\alpha/2, n-k-1}$. If the null Hypothesis is rejected, there is evidence that $\beta_j \neq 0$, so x_j contributes information for the prediction of y .

4.2.2.3 Residual analysis

One of the assumptions in creating the least square model is that the error component is described by a normal distribution. This can be checked graphically by plotting the residuals $e_i = y_i - \hat{y}_i$ on a normal probability graph in which the ordinate (y-axis) is scaled using the cumulative normal distribution (Magrab et al., 2005). If the data are normal, this would give a linear plot. A typical graph, as produced using MATLAB[®], is illustrated in Figure 4.1.

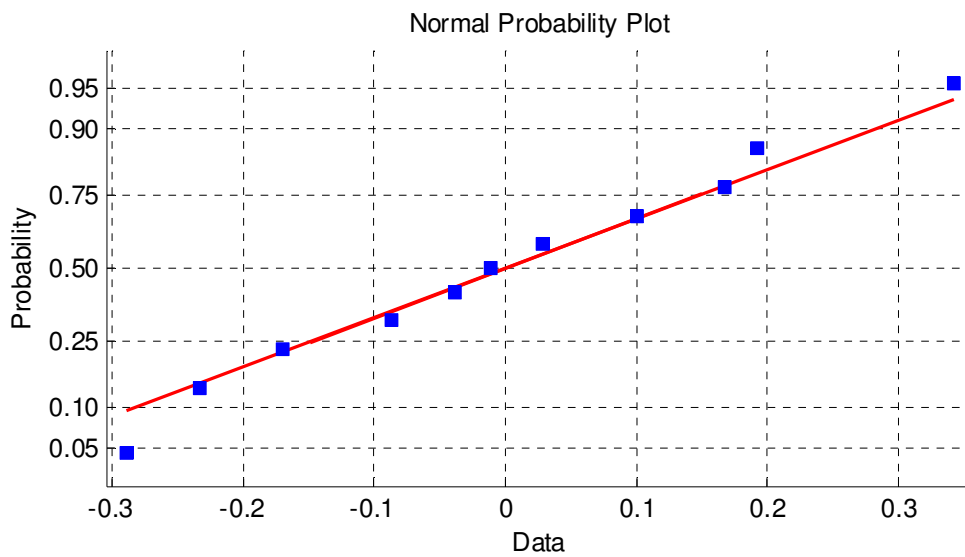


Figure 4.1. Normal probability plot of the residuals

4.3 Part I – Screening test

4.3.1 Experimental procedure

4.3.1.1 Plackett and Burman design

In order to identify the more influential parameters in the current study a screening test was used based on the Plackett and Burman design. Plackett-Burman designs are two-level fractional factorial designs for $k = N - 1$, where N is a multiple of 4 (Montgomery, 2005). They are constructed using the appropriate plus and minus signs depending on N from Table 4.2.

Table 4.2. Plus and minus signs used for the Plackett-Burman Designs

$k = 11, N = 12$	+ + - + + + - - - + -
$k = 19, N = 20$	+ + - - + + + + - - + - - - - + + -
$k = 23, N = 24$	+ + + + + - + - + + - - + + - - + - - - -
$k = 35, N = 36$	- + - + + + - - - + + + + + - + + + - + - - - - + - + - + + - - +

This is written as the first row or column of the design as shown in Table 4.3 for $N = 12$, $k = 11$. The second row or column is obtained by moving the elements of the column (or row) down (or to the right) one position and transferring the last element in the first position. This process continues until column (or row) k is produced. The design is completed by adding a row of minus signs (Plackett & Burman, 1946).

Table 4.3. Plackett-Burman Design for N=12

Run	A	B	C	D	E	F	G	H	I	J	K
1	+	-	+	-	-	-	+	+	+	-	+
2	+	+	-	+	-	-	-	+	+	+	-
3	-	+	+	-	+	-	-	-	+	+	+
4	+	-	+	+	-	+	-	-	-	+	+
5	+	+	-	+	+	-	+	-	-	-	+
6	+	+	+	-	+	+	-	+	-	-	-
7	-	+	+	+	-	+	+	-	+	-	-
8	-	-	+	+	+	-	+	+	-	+	-
9	-	-	-	+	+	+	-	+	+	-	+
10	+	-	-	-	+	+	+	-	+	+	-
11	-	+	-	-	-	+	+	+	-	+	+
12	-	-	-	-	-	-	-	-	-	-	-

In the current study seven parameters were chosen to be tested. These are the temperature, the dwell time, the heating rate, the nitrogen flow, the rotation of the vessel, the particle size and the sample load. Therefore an adjusted Plackett-Burman 11 factor design was used, by removing columns from the right.

4.3.1.2 Experimental set-up

The experimental set-up was as follows:

Rubber crumb sample C (Table 3.1) was pyrolysed by conventional means using a Carbolite HTR 11/150 (Hope Valley, UK) laboratory scale rotary furnace (Figure 4.2). This furnace consists of a quartz reaction vessel that has up to 1 kg capacity, suspended by air-tight rotary

fixtures inside an electrically heated box-furnace. The temperature is controlled by a thermal programmer which is connected to a thermocouple located inside the box-furnace. Nitrogen gas is introduced to the reaction vessel via gas inlet ports at a controlled flow rate (San Miguel, 1999). The reaction vessel is connected to a glass trap where the condensed oils are collected. Volatile gases are vented to the fume cupboard.



Figure 4.2. Carbolite HTR/ 11/150 rotary furnace

For each experiment, the char and oil yields were recorded by weighing the reactor and the oil trap before and after pyrolysis, while the gas yields were calculated by difference.

4.3.1.3 Experimental conditions

For each parameter a specific range was chosen.

- The temperature range under investigation was between 500 and 700°C. The lower limit of 500°C is based on tyre pyrolysis investigations by San Miguel (1999) using the same furnace, in which he concluded that pyrolysis was complete at 500°C, using a heating rate of 5°C/min and 200 g sample weight and is in agreement with the TGA results presented in Chapter 3 (Figures 3.8 & 3.9).
- The furnace was heated at a constant rate at values between 2 and 10°C/min. The lower limit of 2°C/min was selected as a compromise of having a slow rate while being able to run an experiment over a reasonable duration. Furthermore, a higher heating rate than 10°C/min would have been preferred, but that exceeded the capabilities of the furnace.

- When the desired end temperature was reached, a dwell time between 0 – 90 minutes was used to ensure complete pyrolysis.
- Particle sizes of less than 0.5 mm and between 2 – 4 mm were obtained by manual sieving of the crumb produced by UHPW. These were the lower and upper limits of the particle size parameter.
- Both the nitrogen flow and the rotation ranges were chosen according to the furnace capabilities, 100 – 500 ml/min and 6 – 15 revolutions per minute (rpm) respectively.
- The weight range was 150 g to 400 g, where 150 g is the minimum amount that would result in enough char for the subsequent analysis given an approximate weight reduction of 60% following tyre pyrolysis. The maximum of 400 g was enough to fill just under half of the vessel.

The upper and lower limits of these parameters as listed above, were assigned to the positive and negative positions respectively, as shown in Table 4.3. The experimental conditions are summarised in Table 4.4, where CP_{I,C} stands for Conventional Pyrolysis, Part I, using crumb sample C.

Table 4.4. Experimental conditions for Part I pyrolysis by conventional means

Std Order ¹	Run Order	ID	Temp. (°C)	Heating rate (°C/min)	Dwell time (hr)	Particle size (mm)	N ₂ flow (ml/min)	Rotation (rpm)	Weight (g)
1	4	CP _{I,C} 4	700	2	1.5	< 0.5	100	6	400
2	7	CP _{I,C} 7	700	10	0	2 - 4	100	6	150
3	3	CP _{I,C} 3	500	10	1.5	< 0.5	500	6	150
4	10	CP _{I,C} 10	700	2	1.5	2 - 4	100	15	150
5	2	CP _{I,C} 2	700	10	0	2 - 4	500	6	400
6	12	CP _{I,C} 12	700	10	1.5	< 0.5	500	15	150
7	5	CP _{I,C} 5	500	10	1.5	2 - 4	100	15	400
8	1	CP _{I,C} 1	500	2	1.5	2 - 4	500	6	400
9	8	CP _{I,C} 8	500	2	0	2 - 4	500	15	150
10	11	CP _{I,C} 11	700	2	0	< 0.5	500	15	400
11	6	CP _{I,C} 6	500	10	0	< 0.5	100	15	400
12	9	CP _{I,C} 9	500	2	0	< 0.5	100	6	150

¹: Std order = Standard Order

The experiments were performed randomly as noted in the Run Order column and the identities of the generated outcomes were assigned using this random order i.e. CP_{I,C}1

identifies the experiment with the conditions listed in standard order 8. The parameters were assigned a coding name as shown in Table 4.5 to facilitate the modelling in MATLAB[®].

Table 4.5. Assigned coding of parameters

Parameter	Code in MATLAB[®]
Temperature (°C)	x1
Heating rate (°C/min)	x2
Dwell time (hr)	x3
Particle size (mm)	x4
N ₂ flow (ml/min)	x5
Rotation (rpm)	x6
Weight of sample (g)	x7

The modelling involved a sequential process, where all seven parameters were tested in the model and, depending on the individual regression coefficients, some parameters were eliminated until a significant model ($p < \alpha$) was achieved. The significance level α was chosen to be 0.05. All normal probability plots of the residuals are shown in Appendix II (Figure B).

4.3.2 Characterisation

The chars generated were powdered in a Tema[®] mill until a maximum particle size of < 150 μm was obtained prior to analysis, unless otherwise stated. For this operation approximately 25 grams was milled each time for a period of 1 minute and then passed through a 150 μm wire mesh screen. Any oversized material was re-milled.

The chars were then tested for the following properties:

- pH-value
- CHN analysis
- Ash content
- Transmittance of toluene extract
- Infrared Spectroscopy
- Scanning Electron Microscope-Energy Dispersive X-ray Analysis
- Surface Area

The methodology of the above tests is described below.

4.3.2.1 *pH-value*

The pH of the char produced was determined using a modified method derived from Bagreev et al. (2001). After drying for 1 hour at 125°C, 0.4 g of the sample was added to 20 ml of deionised water. The mixture was mechanically agitated for 24 hrs (at 150 rpm) and after the removal of the char by filtration with a Whatman No.1 filter paper, the pH of the recovered solution was measured. The equipment (Fisherbrand HYDRUS 300 pH-meter with a VWR 662-1761 electrode) was calibrated prior to use at pH = 4, 7 and 10 and measurements were done in duplicate. This is not a standard method, but the measurements were carried out simply for comparison between the samples under investigation.

4.3.2.2 *CHN Analysis*

The method for CHN analysis was described previously in Section 3.2.2. Samples of chars obtained were sent to MEDAC, UK for this analysis.

4.3.2.3 *Ash Content*

Ash tests were conducted according to American Society for Testing and Materials (ASTM) method 1506 – 99. The chars were first dried in the oven at a temperature of 125°C for 1 hour and allowed to cool to room temperature. Two grams of each of the dried samples were then placed in a porcelain crucible, and heated at 550°C $\pm$ 25°C for 16 hours. The change in weight was recorded. Experiments were performed in duplicate.

4.3.2.4 *Transmittance of toluene extract*

This test was performed to investigate the presence of organic (toluene soluble) residuals in the char. This test, adopted from the ASTM D1618 – 99, measured the transmittance at 425 nm (using a spectrophotometer) of the filtrate obtained from the toluene mixed with the char produced (2 g $\pm$ 0.01 g), in comparison to the transmittance of pure toluene. Duplicate measurements were performed.

4.3.2.5 *Infrared Spectroscopy*

In infrared spectroscopy the absorption of electromagnetic radiation in the infrared region by a sample is measured. The absorption in mid-infrared region (4000 cm⁻¹ – 400 cm⁻¹) is related

to the vibration of specific sets of chemical bonds from within a molecule (Coates, 2000) and therefore this method enables deductions to be made on the likely functional groups within the sample under observation.

In this study, a Nicolet Magna-IR 560 spectrometer using Fourier Transform (FT) was employed. To perform the analysis the sample (dried at 125°C for an hour) was mixed with potassium bromide in a 1 to 200 ratio and pressed at 10 tonne load to form a disc. This disc is then mounted in the light path of the machine and infrared radiation passing through the sample detected and an absorption spectra generated.

4.3.2.6 Scanning Electron Microscope-Energy Dispersive X-ray Analysis

Scanning Electron Microscopy (SEM) is a technique for studying the microstructural characteristics of materials. In SEM, a beam of high energy electron scans the surface of a sample. From this interaction secondary electrons are emitted and the signal generated is collected and processed to generate a high resolution image of the surface's features (Brandon & Kaplan, 2008).

Certain electron energy losses from the interaction of the electron beam and the sample lead to the emission of characteristic X-rays (Brandon & Kaplan, 2008). When SEM is used in conjunction with an energy dispersive X-ray (EDX) analyser, information on the composition of the sample can be determined.

SEM-EDX analysis of a selected char was carried out by ARTIS, UK using a JEOL T100 SEM with Princeton Gamma Tech 'Imagemaster' and Princeton Gamma Tech 'Spirit' EDX analyser.

4.3.2.7 Surface area

Nitrogen gas adsorption at 77 K was carried out using a Coulter Omnisorp[®] 100 automatic adsorption analyser to measure the char's total surface and external surface area. The sample (approximately 0.25 g) was weighed accurately in an analysis tube to be degassed at 75°C until the pressure in the tube dropped to less than 10^{-5} Torr. This ensured that any physisorbed material present in the char was removed.

The degassed sample was then transferred under vacuum to the analysis side of the instrument, where it was immersed in liquid nitrogen. The sample in the tube was exposed to

a continuous flow of nitrogen gas using a slow flow rate to establish equilibrium conditions between the adsorbed nitrogen and the nitrogen remaining in the atmosphere around the sample. The instrument is fully automated so once the parameters are entered and the experiment is completed, full adsorption/desorption data are obtained.

Adsorption refers to *the enrichment of one or more components in an interfacial layer of a solid* (IUPAC, 1985). Adsorption can be either physical (physisorption) or chemical (chemisorption). In physical adsorption, the substance attached to the surface (adsorbate) is held to the surface of the adsorbent by relatively weak Van der Waals forces. In chemisorption, on the other hand, a bond is formed between the adsorbent and the adsorbate by exchange or sharing of electrons (Bansal & Goyal, 2005). The adsorptive capabilities are provided by the porous structure of the adsorbents. There are three classes of pores in physisorption (i) micropores – pores of less than 2 nm width (ii) mesopores – pores between 2 nm and 50 nm and (iii) macropores – widths exceeding 50 nm (IUPAC, 1985).

Adsorption isotherm is a graphical representation of the amount of gas adsorbed by a solid at different gas pressure, p , at constant temperature. The amount of gas adsorbed is usually plotted preferentially against the relative pressure, $\frac{p}{p_0}$, instead of p itself, where p_0 is the saturation pressure of the gas (Bansal & Goyal, 2005). Adsorption isotherms give an indication of the porosity of a material. Thus, different materials with different porosities give different types of isotherms. The possible isotherms can be grouped in 5 types and are shown in Figure 4.3 (Bansal & Goyal, 2005). The most common ones are (i) Type I isotherms, obtained by microporous solids with small external surfaces, (ii) Type II, obtained by non-porous or macroporous adsorbents, and (iii) Type IV, obtained by mesoporous adsorbents.

All isotherms, irrespective of their type, tend to be linear at low pressures, in accordance with Henry's Law (IUPAC, 1985).

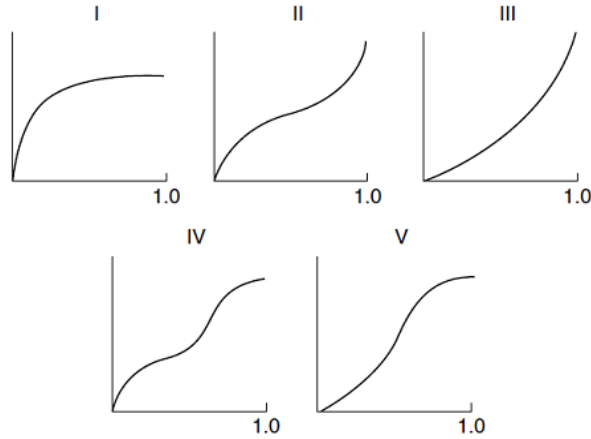


Figure 4.3. Types of physisorption isotherms (Bansal & Goyal, 2005)

The surface areas are obtained using the Brunauer-Emmett-Teller (BET) equation shown below (Eq. 4.7).

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{(C-1)p}{V_m C p_0} \quad (\text{Eq. 4.7})$$

Where: p = pressure of the gas or vapour

p_0 = saturation pressure of the gas

V = volume of the gas adsorbed at pressure p

V_m = volume of gas adsorbed in the monolayer

C = constant related to the enthalpy of adsorption

Plotting $\frac{p}{V(p_0 - p)}$ against $\frac{p}{p_0}$ results in a straight line from which V_m and C can be calculated.

The BET surface area is then calculated using the following equation (Eq. 4.8) (Coulter Corporation, 1991).

$$SA = V_m \times N \times A_m \quad (\text{Eq. 4.8})$$

Where: SA = Surface area of the sample

N = Avogadro's number

A_m = cross-sectional area of the adsorbate molecule

BET surface area calculates the total surface area. To obtain the external surface area, which includes the area provided from the meso and macropores, but not the micropores, t-plot analysis was used. T-plot analysis involves plotting the adsorption isotherm in terms of the volume of the gas adsorbed versus the statistical film thickness. The latter is the thickness of the adsorbed gas on the walls of the pores and is calculated using the following equation (Coulter, 1991).

$$t = \frac{V_{ads}}{V_m} \times \sigma \quad (\text{Eq. 4.9})$$

Where: t = average thickness of adsorbate layer

σ = average thickness of a single layer of nitrogen molecules (3.54 Å)

V_{ads} = volume of nitrogen gas adsorbed by the sample

V_m = volume of gas adsorbed in the monolayer

The slope of the plot of the volume of the gas adsorbed against the statistical thickness gives the external surface area.

4.3.3 Results and discussion

4.3.3.1 General overview

To obtain the yields, the weight of the vessel was recorded before and after the experiment. A second weight reading was also obtained following the cleaning of the arms to remove the oil residues. As this oil inevitably contains some of the char, both weights were considered to represent the weight range for the oil and char yields. The yields recorded are presented in Table 4.6. The char yields from the pyrolysis experiments range between 38.2 – 43.1 wt.% which is comparable to the yields observed by other authors (Table 1.2) apart from CP_{I,C}6 which had a yield of 47.6 – 49.1 wt.%. The char from CP_{I,C}6 was produced at a combination of low nominal end temperature (500°C), high heating rate (10°C/min), large sample size (400 g) and no dwell time, which resulted in incomplete pyrolysis of the tyre. This incomplete pyrolysis is evident in the other results as will be discussed below. The char yield range is slightly higher than the thermal analysis results for the same rubber (36 wt.%, Table 3.3). This is because unlike the conditions of the thermal analysis, the conditions of the

laboratory scale experiments will promote secondary reactions and some carbonization of the volatiles generated.

Table 4.6. Yield results of Part I experiments (conventional pyrolysis)

	Char Yield (wt. %)	Oil Yield (wt. %)	Gas Yield (wt. %)
CP _{I,C} 1	39.3 – 39.6	53.2 – 53.5	7.1
CP _{I,C} 2	38.2 – 38.7	51.9 – 52.4	9.4
CP _{I,C} 3	40.3	51.4	8.3
CP _{I,C} 4	42.2 – 42.7	50.1 – 50.6	7.2
CP _{I,C} 5	39.9 – 40.2	52.4 – 52.7	7.4
CP _{I,C} 6	47.6 – 49.1	44.1 – 46.0	6.4
CP _{I,C} 7	38.4 – 39.3	51.9 – 52.9	8.7
CP _{I,C} 8	39.1 – 41	51.2 – 53.1	7.8
CP _{I,C} 9	41.8 – 43.1	50.0 – 53.1	6.9
CP _{I,C} 10	40.6	51.5	7.9
CP _{I,C} 11	39.7 – 39.8	52.3 – 52.4	7.9
CP _{I,C} 12	39.3 – 40.1	50.5 – 51.3	9.3

The oil yields are also comparable with yields reported in various other published findings (Table 1.2) though higher yields have been observed, for example 58.1 wt.% by Cunliffe & Williams (1998a) and 56.6 – 60.1 wt.% by Kyari et al. (2005). Oil yields are dependent on the overall conditions as well as the efficiency of the condensation system. In the current research no cold traps were used, and therefore some oil would have escaped from the oil trap vent before condensing, especially at high heating rates. Also, during the experiments there was a problem of the oil condensing in the opposite direction, i.e towards the nitrogen flow (see Figure 4.4) especially when the gas flow was at a pressure insufficient to drive the generated gases towards the oil trap.

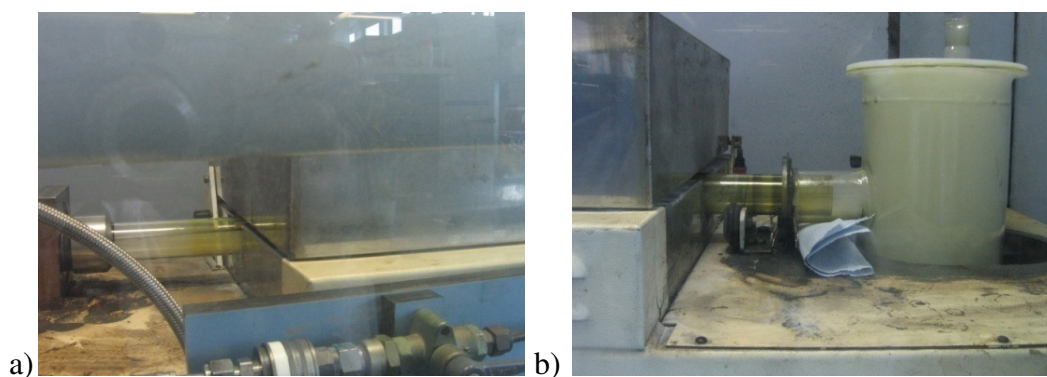


Figure 4.4. Illustration of oil condensation on the a) front arm and b) backend of the vessel

This flow anomaly introduced an error on the yields as the oil had to be cleaned before the char came out of the vessel. The furnace was tilted towards the oil trap to counteract this flow anomaly and the resulting error, but this proved to be ineffective. Further, losses (char or oil) were more pronounced for lower sample weights, while a lower weight in combination with smaller particle size, high nitrogen flow and possibly increased rotation speed increased the chances of generated char to gravitate towards the oil trap due to greater likelihood of the fine particles generated to be swept into the arm of the vessel.

The results obtained from the characterisation of the chars are shown in Table 4.7.

Table 4.7. Char characterisation results of Part I experiments (conventional pyrolysis)

	Ash Content (%)	Transmittance of Toluene Extracts (%)	C (%)	H (%)	N (%)	Surface Area (m ² /g)		pH-value
						BET	Meso & Macropore	
CP _{I,C} 1	56.0	98.7	40.1	1.0	0.1	124.6	100.03	7.75
CP _{I,C} 2	57.4	95.8	39.1	0.1	0.1	116.3	98.72	7.90
CP _{I,C} 3	53.6	97.8	42.4	0.9	0.1	128.6	111.13	7.75
CP _{I,C} 4	52.6	99.1	44.3	1.0	0.2	101.1	85.20	8.64
CP _{I,C} 5	58.9	93.4	36.7	1.0	0.1	122.0	103.14	7.81
CP _{I,C} 6	45.6	0.0	49.6	1.9	0.1	43.4	42.01	7.64
CP _{I,C} 7	57.8	99.5	40.2	1.0	0.1	112.9	96.12	7.99
CP _{I,C} 8	57.0	78.7	39.5	1.0	0.1	119.0	108.58	7.71
CP _{I,C} 9	52.6	31.8	45.0	1.2	0.2	107.4	97.90	7.67
CP _{I,C} 10	56.9	98.9	40.9	0.1	0.1	106.0	89.96	9.15
CP _{I,C} 11	54.7	99.9	42.6	0.1	0.1	115.0	94.79	8.39
CP _{I,C} 12	57.5	98.6	42.1	0.1	0.1	110.9	99.52	8.68

The percentage of transmittance of toluene extracts for most chars was above 90%, indicating that most of the organic residues had been removed from the char. The exception was CP_{I,C}6; the 0% transmission of the toluene extracts along with the low ash content and high carbon and hydrogen content indicate that part of the rubber had not been completely pyrolysed. CP_{I,C}8 and CP_{I,C}9 chars which also presented low toluene transmittance percentage at 78.7% and 31.8% respectively, were produced at 500°C and no dwell time. This prompted an investigation of the thermal lag of the thermocouple temperature inside the furnace box and the actual temperature inside the vessel (Section 4.4.2.2).

The ash results were very high compared to other studies on tyre pyrolysis such as 6.82 – 12.96% by Mui et al. (2010), 11.78 – 15.33% by Galvagno et al., (2002), 10.2 – 10.6% by San Miguel (1999) and 14.3 – 16.3% by González et al. (2001). However, like the current work, Ucar et al. (2005) had observed a relatively high amount of ash (40.3 – 40.8%) from passenger car tyres. Sample C, as stated in Chapter 3 was produced using the in-house UHPW equipment; most of the tyres disassembled in this batch were Michelin, known for using a high amount of silica as filler, which would explain the high ash content. Commercial carbon black grades have very low ash content that range from about <0.1 to 2% (Hess & Herd, 1993).

In the current work, further examination of the ash content of one of the samples, CP_{I,C}4, using SEM-EDX confirmed the presence in high quantities of SiO₂ (over 90%) as well as ZnO. The coloured areas of the images below (Figure 4.5) highlight the dense distribution of Si, the sparse to moderate distribution of Zn and the sparse distribution of Fe.

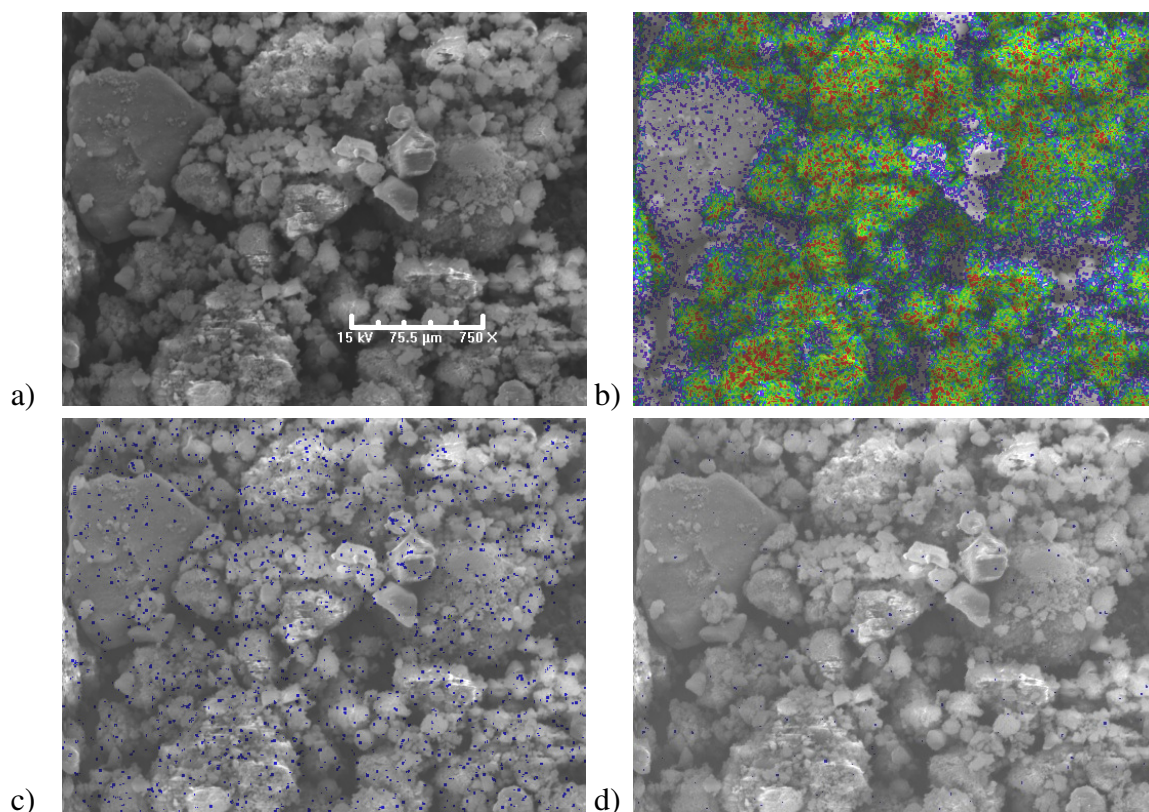


Figure 4.5. SEM Images of CP_{I,C}4 a) without distribution b) showing Si distribution c) showing Zn distribution and d) showing Fe distribution.

The presence of SiO₂ was also verified by the FTIR spectroscopy. Figure 4.6 presents the FTIR spectrum of CP_{I,C}4. Even though the transmittance was low due to the dominance of the

carbon (which permitted low amount of light to go through the sample disk), a main band with peak at $\sim 1110\text{ cm}^{-1}$ was identified and can be attributed to the asymmetrical stretching vibrations of silicon-oxygen covalent bonds Si–O–Si and Si–O–R (Al-Oweini & El-Rassy, 2009; Gendron-Badou et al., 2003). The peak at $\sim 470\text{ cm}^{-1}$ can be due to the bending modes of silicon-oxygen covalent bonds. The small peak at around 810 cm^{-1} is possibly due to Si–O–Si symmetric stretching vibration. There is no strong band in the range of $910 - 830\text{ cm}^{-1}$, expected from the Si–O stretching for Si–OH (Stuart, 1996) or it is overlapped by the main band at 1100 cm^{-1} . The weak band at around 1620 cm^{-1} could be due to H–OH bending vibration of H_2O molecules adsorbed on KBr or on the char if there are available surface silanol groups (Al-Oweini & El-Rassy, 2009; Gendron-Badou et al., 2003). The very minor broad band that peaks at 3450 cm^{-1} can be due to the presence of an –OH group either of hydrogen-bonded water molecules or surface silanols hydrogen-bonded to molecular water (Al-Oweini & El-Rassy, 2009). Most silanol groups in silica materials are removed when they are exposed to temperatures above $400 - 450^\circ\text{C}$; above 750°C only free, unpaired SiOH groups are present in minor concentrations and are nearly all removed at around 1000°C (Iler, 1979).

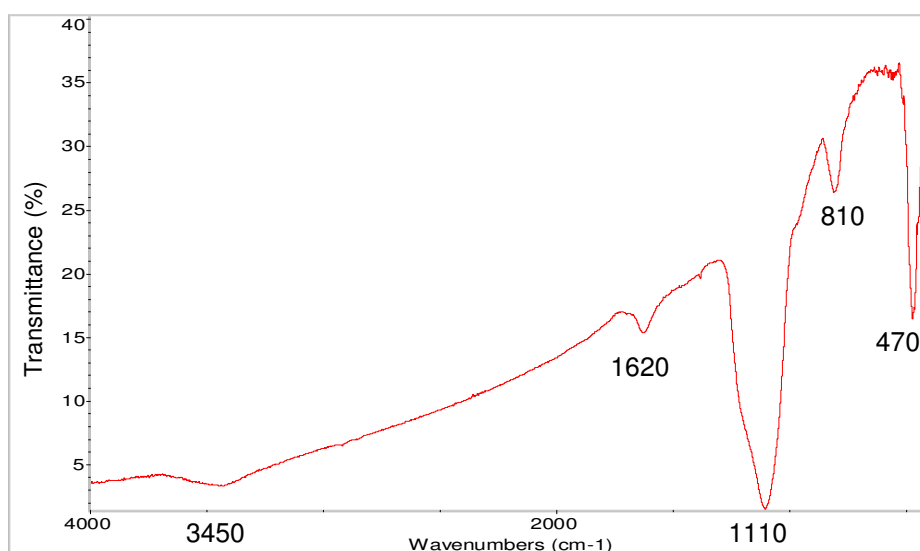


Figure 4.6. FTIR spectrum of CP_{1,c4}

The presence of a large amount of inorganic material in the char is expected considering the low carbon content of sample C (60.1%, Table 3.4). Carbon content is inversely proportional to ash content (Correlation = -0.94). Hydrogen content has been reduced to less than 1% (apart from CP_{1,c6} and CP_{1,c9}) signifying the increase in aromaticity of the carbon as the crumb is pyrolysed. Nitrogen is present in less than 0.2%.

pH-values of carbon blacks are usually recorded by measuring the pH of the slurry of carbon black and water. A different method was employed in this research as described in Section 4.3.2.1. Fabish & Schleifer (1984) measured the pH values of the slurries and their clear supernatant liquid obtained after centrifuging the slurry and found their values equal. The pH-value was recorded immediately after filtration as the readings are expected to drift over a long interval due to dissolution of atmospheric carbon dioxide.

The pH-values of the chars ranged between 7.71 and 9.15. Alkaline pH values are also observed for furnace carbon black grades with low concentration of oxygen complexes and very small amount of water soluble salts (Cabot Corporation, 2012).

The pH-values give an indication of the chemical activity of the carbons. The chemical activity of carbons is mainly a consequence of the heteroatoms present in the surface of the carbons, the most important being oxygen (Boehm, 1994). Several different types of surface oxides can be present in carbons, giving them acidic or basic properties. These include carboxyls, carboxylic anhydrides, carboxylic acids, lactones, phenols, hydroquinones, quinines, and neutral groups containing one or two oxygens (acidic properties) and γ -pyrone-like structures (basic properties) (Wang et al., 2000; Boehm, 1994; Leon y Leon et al., 1992).

In the case of the chars generated in this study the pH is also likely to be affected by the high ash presence.

The BET surface areas of the chars ranged between 101.1 – 128.6 m²/g apart from CP_{I,C}6 whose surface area was only 43.4 m²/g. These results were obtained by applying the BET equation in the region $p/p_0 = 0.05 - 0.24$ where linear sections with $r^2 = 1$ were obtained.

The isotherm plots of CP_{I,C}3 (128.6 m²/g), CP_{I,C}4 (101.1 m²/g) and CP_{I,C}6 are presented in Figure 4.7.

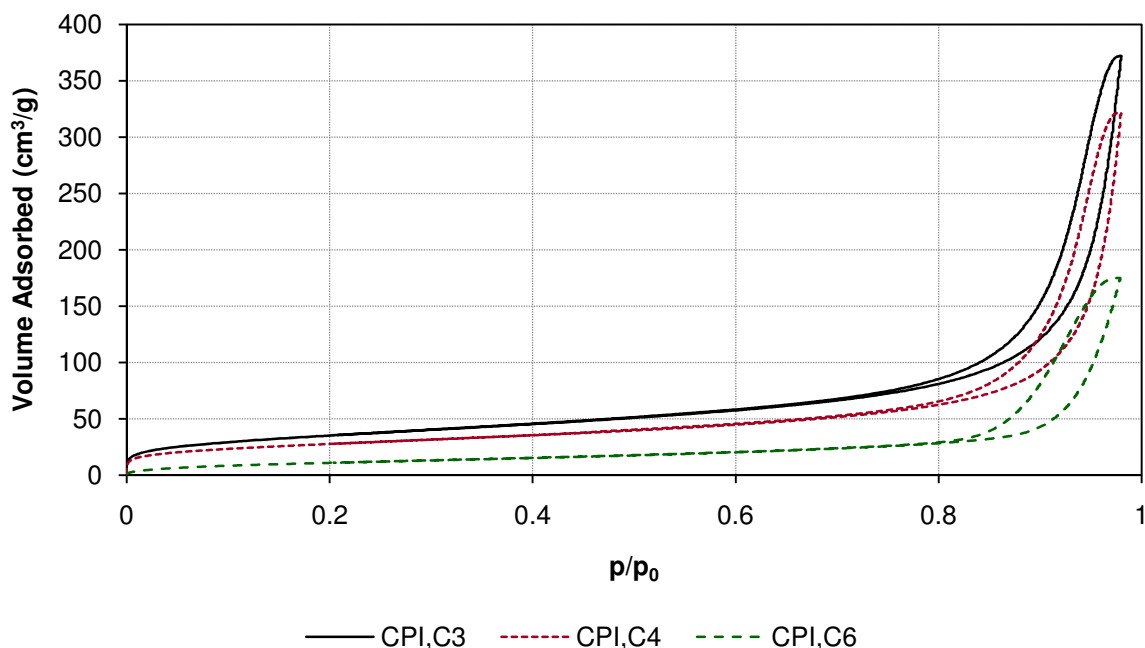


Figure 4.7. Adsorption/Desorption isotherms of $CP_{I,C3}$, $CP_{I,C4}$ and $CP_{I,C6}$

All nitrogen adsorption/desorption isotherms were similar to each other, though $CP_{I,C6}$ showed much lower adsorption capacities. This has been observed by San Miguel et al. (1998) from transition samples (incomplete rubber degradation). The plots show a type IV isotherm. Type IV isotherm has a characteristic hysteric loop. Hysteresis occurs when desorption takes a different path than the adsorption and it is associated with capillary condensation in mesopores (IUPAC, 1985).

Bradley et al. (1995) obtained similar adsorption/desorption isotherms for commercial carbon black grades N330 and N100. The external surface areas obtained show correlation with the total surface areas ($r = 0.96$). Commercially available carbon blacks with similar surface area are of the N100 and N200 series (Wang et al., 2000) which offer high abrasion resistance and are easy to process. However, as it will be discussed in Chapter 6, the chars generated resemble lower grade carbon blacks, such as N772 (surface area = $32 \text{ m}^2/\text{g}$), when applied in rubber formulations.

4.3.3.2 Influence of parameters

The influence of the process parameters were investigated with regard to the carbon content, surface area and pH value for all samples with the exception of $CP_{I,C6}$ (as this sample had not been completely pyrolysed), hence it was excluded from the model application. As this was

the screening test, aimed to understand the key parameters influencing the pyrolysis behaviour, the omission of this sample data was not expected to significantly perturb the results.

4.3.3.2.1 Effect on Carbon Content

Investigating the significant parameters influencing the carbon content, a model is fitted with overall $p\text{-value} = 0.0000$. As stated earlier, the overall model is significant if the $p\text{-value}$ is less than the chosen α level; in this case 0.05. The coefficients of determination are $R^2 = 99.37\%$ and $R^2_{\text{adj}} = 98.73\%$. This means that the model can explain 98.73% of the results. The model consisting of temperature (x1), heating rate (x2), particle size (x4), rotation (x6) and weight (x7), with their corresponding coefficients and $p\text{-values}$ are shown in Table 4.8. The most important parameters are the particle size and the heating rate with 100% significance.

Table 4.8. ANOVA results for C-content

Source	df	SS	MS	F	$p\text{-value}$
Regression	5	57.602114	11.5204	156.68	1.73E-05
Residual	5	0.36765	0.0735		
Total	10	57.9698			
$R^2 = 99.37$ $R^2_{\text{adj}} = 98.73$ stdev = 0.2712					
Parameter	Coefficient	$p\text{-value}$	Significance (%)		
Constant	41.04	7.04E-13	100.00		
x1	0.48	0.0023076	99.77		
x2	-1.01	7.34E-05	99.99		
x4	-1.63	6.91E-06	100.00		
x6	-0.81	0.0002048	99.98		
x7	-0.62	0.0007537	99.92		

The graph in Figure 4.8 gives a visual representation of the main parameters influencing the carbon content, obtained by plotting the average carbon content value at the minimum (-1) and maximum level (+1). The graph shows that the particle size appears to be the most influential parameter (showing the greatest variation).

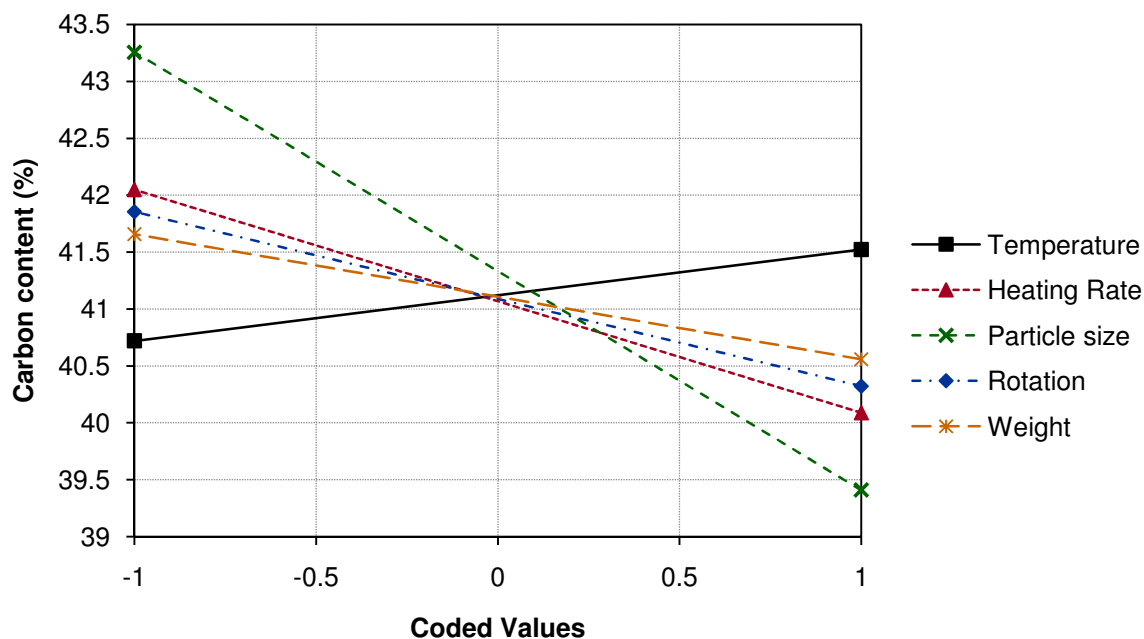


Figure 4.8. Graphical representation of the main effects influencing the carbon content

The influence of particle size in pyrolysis processes has been a subject of investigation by various authors especially for its role in the transport effects with respect to pyrolysis rate. Galan & Smith (1985), Encinar et al. (2000) and Gonzales et al. (2001) summarized these transport effects for pyrolysis on a fixed reactor to (i) intraparticle transport, which depends on particle size, (ii) particle to fluid transport – which is affected by particle size and nitrogen flow, and (iii) interparticle transport which is influenced by the sample masses, i.e. the number of layers of particles. In the current study, the last two effects would also be affected by the rotational speed of the vessel.

For particle sizes between 0.2 mm and 1.6 mm, Gonzales et al. (2001) did not observe any influence on the process rate, though the increase in particle size was expected to cause greater temperature gradients inside the particle resulting in more secondary reactions which would lead to higher carbon content. In the present case, the opposite is observed. This is in agreement with the findings of Mui et al. (2010) who also observed that the carbon content in chars from finer particle precursors was higher. Mui et al. attributed this “... to the tortuous diffusion path between finer particles, which increased the residence time of the volatiles involved in secondary reactions”. This would favour formation of carbon deposits over the surface and increase the carbon content. Senneca et al. (1999) further pointed out that “... carbon black in tyre rubber is likely to act as a nuclei source around which coherent solid carbon grows by cyclisation and/or cross-linking and affects the yields of char”.

Gavalas (1982) who investigated coal pyrolysis pointed out that care must be taken when interpreting results concerning the influence of particle size as there is a chance there is a difference in compositions between different ranges. With the possible variation in rubber formulation between makers, similar effects could be observed for tyres.

Another important parameter is the heating rate. The higher the heating rate, the lower the carbon content observed. As shown in Table 4.7 higher carbon content is observed at the conditions where secondary reactions are favoured – in this case the slow heating rate (Miura et al., 2004).

4.3.3.2.2 Effect on Surface area

Statistical analysis of the BET results was carried out. A model consisting of temperature (x1), heating rate (x2) and nitrogen flow (x5), as well as the interactions of temperature with heating rate (x1*x2) and heating rate with nitrogen flow (x2*x5) as parameters gave a good overall model (p -value = 0.0089) with R^2 and R^2_{adj} of 92.02% and 84.04% respectively. This means that the model can explain 84.04% of the results. The most significant parameters are summarised in Table 4.9.

Table 4.9. ANOVA results for surface area

Source	df	SS	MS	F	p -value
Regression	5	639.299	127.8598	11.533	8.90E-03
Residual	5	55.4332	11.0866		
Total	10	694.7322			
		$R^2 = 92.02$	$R^2_{adj} = 84.04$	stdev = 3.3297	
Parameter	Coefficient	p -value	Significance (%)		
Constant	115.62	1.05E-09	100.00		
x1	-4.44	0.0084312	99.16		
x2	3.43	2.05E-02	97.95		
x5	4.03	0.01	98.76		
x1*x2	-1.80	1.50E-01	85.05*		
x2*x5	-2.42	0.07	93.00*		

* Lower than 95% significance was accepted due to the overall model's and the other individual parameters' high significance

The main effects are illustrated in Figure 4.9. The interaction effects are illustrated by plotting for example the average surface area versus the heating rate at -1 and +1 levels, for each temperature setting (-1 and +1) and connecting these points for the low and high temperature settings to give the two lines as shown in Figure 4.10 (Myers et al., 2009).

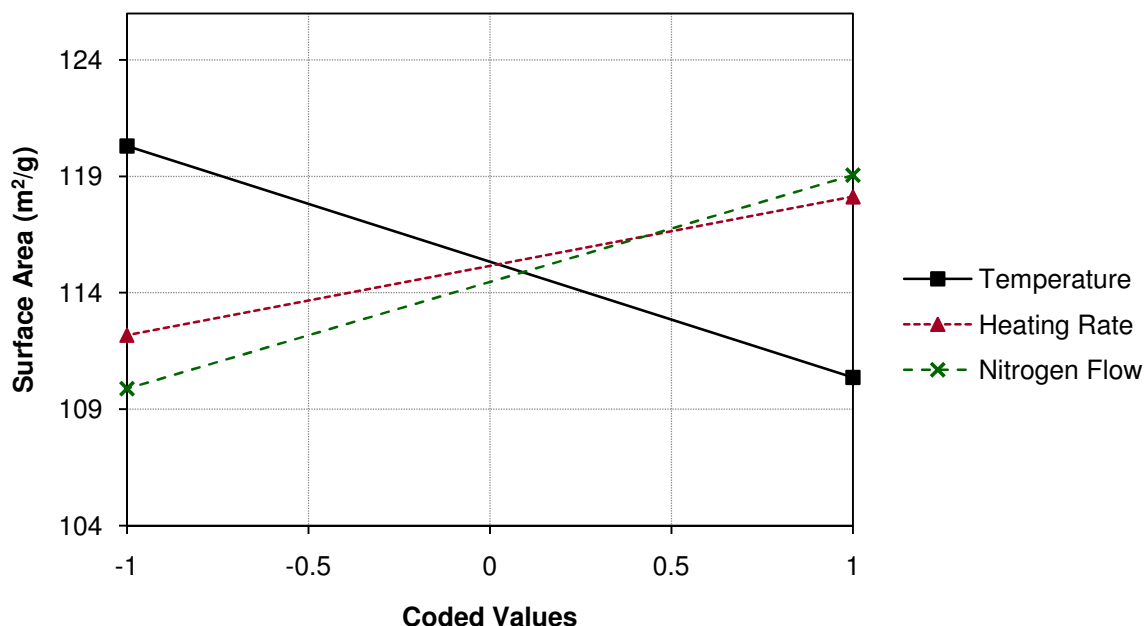


Figure 4.9. Graphical representation of the main effects influencing surface area

The most significant parameter was temperature with 100% significance. Mui et al. (2010) pointed out that temperature is essential to the breakdown of the linkage between polymeric components to the formation of the new pores through rearrangement of carbon atoms. This rearrangement leads to porosity development.

It can be observed from Figure 4.9 that the temperature effect is negative, indicating that for the range studied, higher temperatures give lower BET surface areas. However, Williams et al. (1990) observed that surface areas increased with both the increase in temperature and heating rates for chars generated at 420°C, 600°C and 720°C end temperatures using 5°C/min, 20°C/min, 40°C/min and 80°C/min heating rates. In these experiments chars were held at the end temperature for a minimum of 2 hours or until no further significant release of gas was observed. This means the surface areas could have been affected by this irregular but unaccounted dwell time. Mui et al. (2010), conversely, observed a decrease in surface area at end temperature 500°C (156 m²/g) to 700°C (96 m²/g) which was attributed to the opening and widening of more pores, transforming micropores to mesopores, as a result of the continuous release of volatiles and the collapse of pore walls.

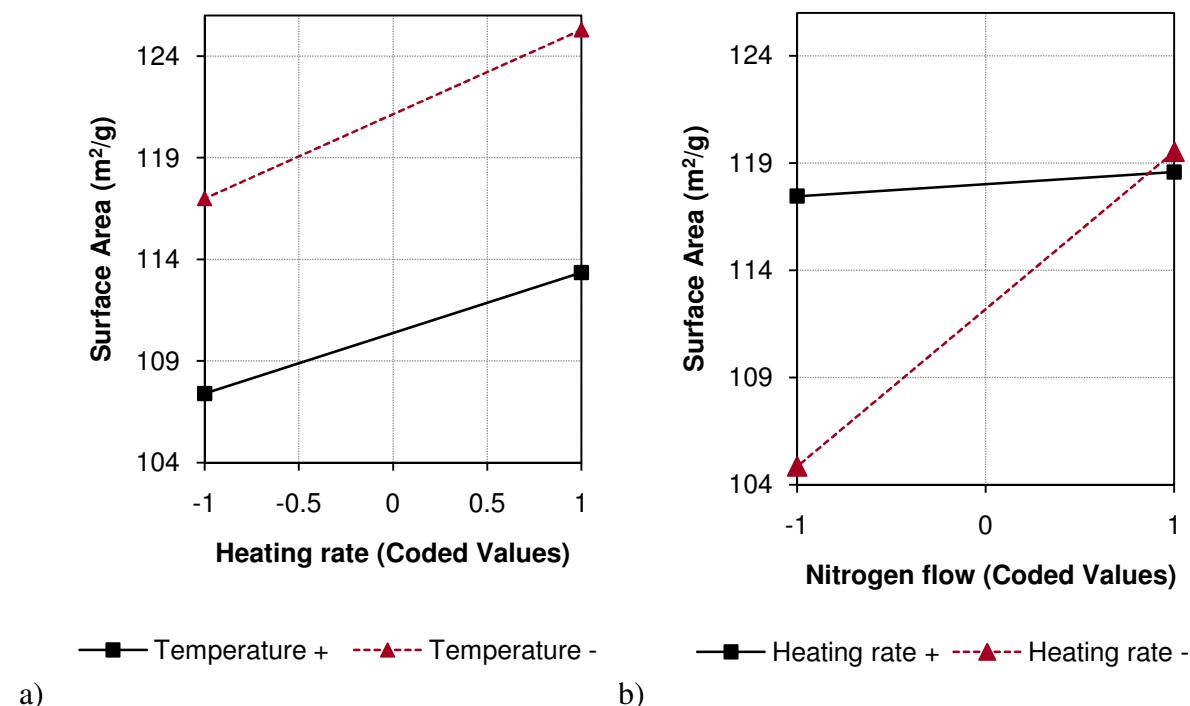


Figure 4.10. Graphical representation of surface area interaction effects: (a) temperature*heating rate and (b) heating rate*nitrogen flow

Further to the temperature effect, Figure 4.10 indicates that the increasing heating rate and nitrogen flow give higher surface areas. In addition, Figure 4.10a shows that for both low and high end temperatures the heating rate has the same increasing trend.

The interaction between heating rate and nitrogen flow is of particular interest. Figure 4.10b indicates that while at high heating rate the nitrogen flow does not seem to influence the process, at low heating rates the nitrogen flow is important. Nitrogen removes generated gases from the hot zone to prevent secondary reactions (Williams et al., 1990). Secondary reactions would block the pores, thus at a high nitrogen flow where gases are removed faster, the surface area is expected to be higher. Slow heating rate may also promote secondary reactions also decreasing the surface area. However other authors have observed the opposite. Mui et al. (2010) observed a decreasing trend of surface area on increasing heating rate. This was explained considering that the time for the evolving gases to be discharged at higher heating rates is less than at lower heating rates leading to an accumulation of volatiles inter- and within particles which favour the possibility of carbon deposits blocking pore entrances.

This observation is associated with the escape of the generated gases which is controlled by the nitrogen flow. The importance of nitrogen flow is highlighted by the significance of the interaction between the heating rate and N_2 flow. In fact, Figure 4.10b predicts in the case of

high nitrogen flow that low heating rate does marginally produce chars with higher surface area as observed by Mui et al. (2010). However, the reverse occurs when low nitrogen flow is used – this highlights the importance of experiments designed with the factors varied together. The differences in observations between authors may be a result of the different reactor shapes and characteristics, which can influence heat transfer, volatile losses and gas flows.

San Miguel (1998) also examined pyrolysis using three different particle sizes (i) powdered sample < 0.42 mm, (ii) granular sample < 2 mm and (iii) cut sample < 9.5 mm. Surface area analysis showed similar adsorption/desorption isotherms but the powdered sample had greater adsorption capacities at $p/p_0 < 0.90$, implying that the smaller the precursor the larger the surface area. In the current study the particle size did not show up as one of the three important parameters – possibly because of the lower range of particle sizes used. However in San Miguel's study, sample (i) and (ii) came from a different supplier than sample (iii) and for the first two samples there is no information if they were shredded from the same feedstock; the differences in surface area could be because of differences in composition.

4.3.3.2.3 Effect on pH-value

Statistical analysis on the effect of the process variables on the pH-value was carried out. Important factors composing a model with overall $p\text{-value} = 0.0003$, $R^2 = 98.11\%$ and $R^2_{\text{adj}} = 96.21\%$ were temperature (x1), heating rate (x2), dwell time (x3), rotation (x6) and weight of sample (x7). The most important factor with the most pronounced effect as shown in Figure 4.11 is temperature.

Table 4.10. ANOVA results for pH-value

Source	df	SS	MS	F	<i>p-value</i>
Regression	5	2.4745	0.4949	51.811	3.00E-04
Residual	5	0.0478	0.0096		
Total	10	2.5223			
$R^2 = 98.11$		$R^2_{\text{adj}} = 96.21$	stdev = 0.0977		
Parameter	Coefficient	<i>p-value</i>	Significance (%)		
Constant	8.06	1.47E-11	100.00		
x1	0.40	4.66E-05	100.00		
x2	-0.16	3.45E-03	99.65		
x3	0.24	5.63E-04	99.94		
x6	0.11	0.0155355	98.45		
x7	-0.10	0.0230549	97.69		

Roy et al. (1995) also observed an increase in the pH-values of aqueous suspensions of tyre pyrolysis chars on increasing the temperature. Studebaker (1957) and Bradley et al. (1995) had measured pH-values of commercial carbon blacks and correlated it to the surface oxygen level – with increasing surface oxygen the pH-values decrease.

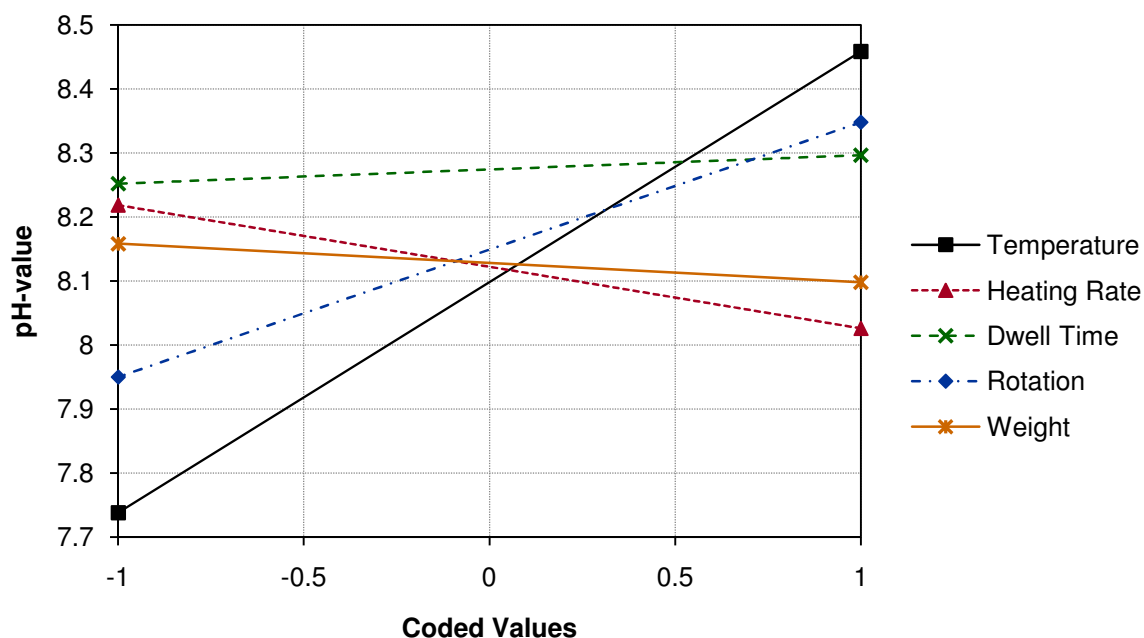


Figure 4.11. Graphical representation of the main effects influencing pH-value

The surface oxygen groups decompose under pyrolysis conditions (heating in inert atmosphere) by releasing CO or CO₂ at different temperatures depending on their stability (Burg & Cagniant, 2008). Temperature-programmed desorption (TPD) methods have been employed to monitor the amount of CO or CO₂ desorbed and assigned to the respective surface oxides. A summary by Figueiredo et al. (1999) is shown in Figure 4.12.

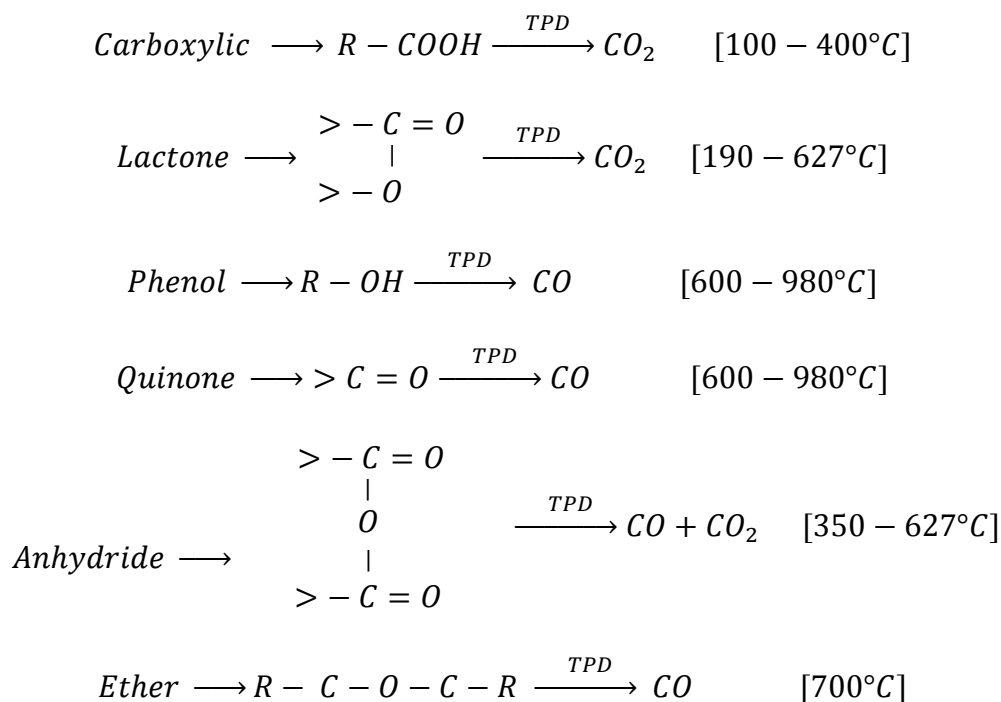
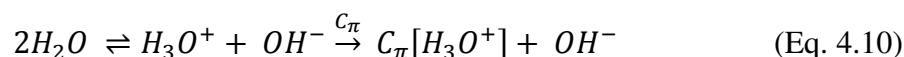


Figure 4.12. Figueiredo's summary of decomposition temperatures of carbon surface groups by TPD studies

Thus once the oxygen is removed, the alkalinity observed is attributed to the Lewis base character of the aromatic π -electrons of the basal planes of the carbon (Boehm, 1994). Lewis bases are electron pair donors and are likely to absorb hydronium ions in water so that the excess of hydroxyl ions remaining would give a basic pH (Studebaker, 1957) according to Equation 4.10 (Fabish & Schleifer, 1984).



C_π was defined by Fabish & Schleifer (1983) "... as the idealized graphitized surface platelet having maximum itinerate π -electrons". Oxygen chemisorbed on the carbons surface results in localisation of the mobile π -electrons towards the periphery of the basal planes, decreasing Lewis basicity.

The other parameters found important could be linked to the temperature factor and their influence on how the heat is transferred. Fast rotation, for example, lowers the heating rate because it reduces the contact time.

4.3.4 Conclusions

Car passenger tyre crumb was pyrolysed in experiments using the Plackett-Burman design to formulate the experiments used to generate chars (38.2 – 49.1 wt.%), oils (44.1 – 53.5 wt.%) and gas (6.4 – 9.4 wt.%) at yields similar to those observed by other authors. Under the conditions used, one char (CP_{I,C6}) was significantly under-pyrolysed (transmittance of toluene extracts = 0%) and was excluded from the model. The chars were alkaline with pH-values of 7.75 – 9.15, had high ash content of between 52.6 and 59.9% (CP_{I,C6} had 45.6%) and surface areas ranging from 101.1 – 128.6 m²/g (CP_{I,C6}: 43.4 m²/g).

The parameters that had the most influence upon the char properties examined further – carbon content, surface area and pH-value – at the selected minimum and maximum ranges were the temperature and the heating rate. These parameters were therefore selected to be used in further experiments described in Part II (Section 4.4) of this chapter along with dwell time (to ensure that complete pyrolysis was achieved).

The Plackett-Burman design used was found to be very suitable for identifying the most important variables in a screening test with a reduced number of experiments. However, it must be emphasised, that this design has its disadvantages, especially compared to the general fractional factorial design which would have resulted in this case in 16 experiments, as they are known to produce ‘messy aliases’ (Montgomery, 2005). Furthermore, the removal of one point due to the incomplete pyrolysis of CP_{I,C6}, introduced further uncertainty in the model, but was necessary as its inclusion created a significant distortion of the data.

4.4 Part II – Fitting a quadratic model

4.4.1 Introduction

The screening test resulted in linear model relationships, identifying temperature and heating rate as the most influential parameters on the characteristics of the char obtained. In this section the possibility of fitting the process parameters into a quadratic model was investigated. To exclude the possibility of having incomplete pyrolysis occurring again, along with temperature and heating rate, a third parameter, dwell time was added to the model.

There is limited literature reporting the use of response surface methodology in studies on waste tyre pyrolysis. Barbooti et al. (2004) studied the influence of pyrolysis temperature (400 – 460°C), nitrogen flow rate (0.2 – 0.5 m³/hour and particle size (2 – 20 mm) to find the optimum conditions for the production of the maximum yields of pyrolytic carbon and oil. Miranda et al. (2010) examined the influence of temperature, reaction time and pressure on a mixture of tyres (30% w/w) and plastics (70% w/w) to optimise the oil yield. The current work is interested in the quality of the products rather than the yields.

4.4.2 Experimental procedure

4.4.2.1 Box-Behnken design

To fit a second order model in the potential relationship between the variables and the responses, at least three levels of each design variable is necessary. Ideally to account for all possible combinations, a full three level factorial design would be required. For 3 variables, this implies 3^N experiments, i.e 27 experiments. There are several designs used in RSM that allow the investigation of 3 variables but with fewer experiments. One of them is the Box-Behnken design. This design, based on the three-level incomplete factorial, can be described by a cube having a centre point, to account for curvature, and the points in the middle of the edges (Figure 4.13) (Ferreira et al., 2007).

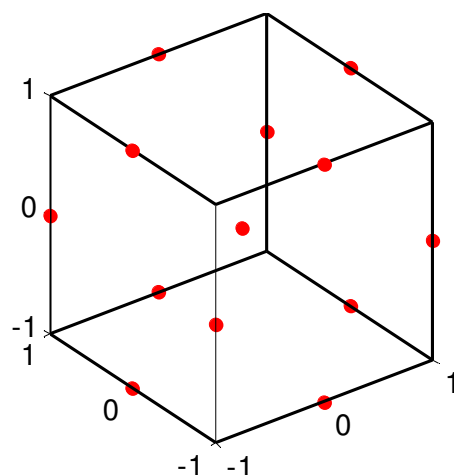


Figure 4.13. Graphical representation of the Box-Behnken design

The appropriate design for three variables is summarised in Table 4.11.

Table 4.11. Box-Behnken design for 3 parameters

Run no.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Code	x_1	-1	1	-1	1	-1	1	-1	1	0	0	0	0	0	0	0
	x_2	-1	-1	1	1	0	0	0	0	-1	1	-1	1	0	0	0
	x_3	0	0	0	0	-1	-1	1	1	-1	-1	1	1	0	0	0

Coded value -1 corresponds to the minimum value of each variable, 0 to the middle and +1 to the highest. Note that the centre point experiment is repeated three times (runs 13, 14, 15) to examine the lack of fit of the model (Section 4.2.2).

4.4.2.2 Experimental conditions

The Carbolite HTR 11/150 laboratory scale rotary furnace described in Section 4.3.1.2 was used for the experiments.

As mentioned in the introduction, the variables chosen to investigate further their influence in tyre pyrolysis were temperature (x_1), heating rate (x_2) and dwell time (x_3).

To ensure complete pyrolysis the temperature minimum value that was used in the screening tests was increased from 500°C to 550°C. For the same reason the minimum and maximum value of dwell time was also increased by 30 minutes.

The complete conditions of the three variables, temperature, heating rate and dwell time, are summarised in Table 4.12. Significant effects of the factors and their interaction effects were tested at 95% confidence interval.

300 g of sample E of particle size between 1 – 2 mm was used for all the experiments. The reaction vessel was set to rotate at 10 rpm, as adopted from the work of San Miguel (1999). The system was purged with nitrogen gas at a constant flow of 500 ml/min, from 20 minutes prior to the start of the experiment until its end and the furnace had cooled down.

In addition, crumb from sample D and commercial carbon black grade N772 were pyrolysed at the centre point. The experiments were performed randomly as noted in the Run Order column but the IDs of the generated outcomes were assigned using the standard order i.e. CP_{II,E}1 identifies the experiment with the conditions listed in standard order 1. CP_{II,E} stands for Conventional Pyrolysis, part II, using crumb sample E.

Table 4.12. Part II design parameters

Std order	Run order	ID	Temp. (°C)	Heating rate (°C/min)	Dwell time (min)
1	7	CP _{II,E} 1	550	2	75
2	3	CP _{II,E} 2	700	2	75
3	8	CP _{II,E} 3	550	10	75
4	9	CP _{II,E} 4	700	10	75
5	2	CP _{II,E} 5	550	6	30
6	11	CP _{II,E} 6	700	6	30
7	10	CP _{II,E} 7	550	6	120
8	5	CP _{II,E} 8	700	6	120
9	6	CP _{II,E} 9	625	2	30
10	1	CP _{II,E} 10	625	10	30
11	13	CP _{II,E} 11	625	2	120
12	4	CP _{II,E} 12	625	10	120
13	14	CP _{II,E} 13	625	6	75
14	12	CP _{II,E} 14	625	6	75
15	15	CP _{II,E} 15	625	6	75
16	16	CP _{II,D} 16	625	6	75
17	17	CP _{II,N772} 17	625	6	75

The same procedure described in Section 4.3.2 was adopted for the characterisation of the chars generated.

In order to investigate further the actual temperature of the crumb during the experiment compared to the reading from the thermocouple in the oven box, an additional thermocouple was placed inside the vessel as shown in Figure 4.14.



Figure 4.14. Thermocouple measurement configuration

4.4.3 Results and discussion

4.4.3.1 General overview

The average of the temperature measurements taken from the furnace reading and the thermocouple at 2°C/min, 6°C/min and 10°C/min was plotted against time as shown in Figure 4.15. The thermal lag is more pronounced as expected at higher heating rates – the maximum difference between furnace and thermocouple reading was 37°C at 2°C/min, 66°C/min at 6°C/min and 88°C at 10°C/min.

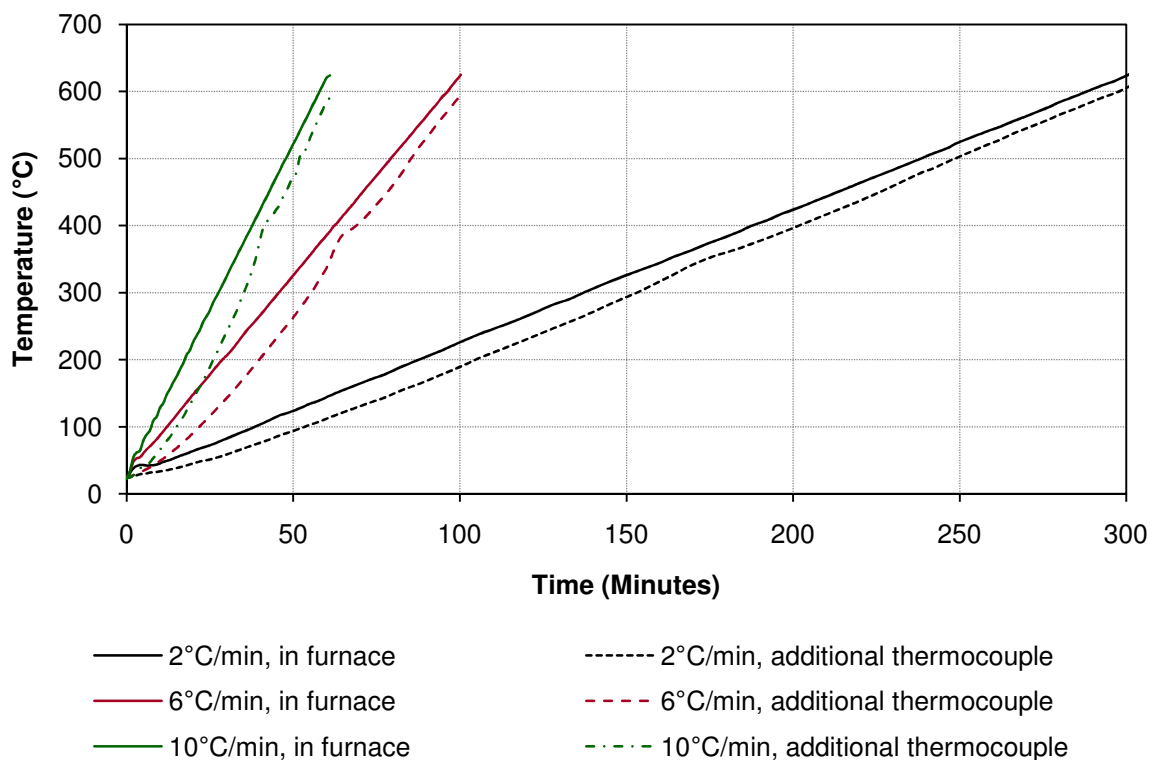


Figure 4.15. Furnace and thermocouple temperature measurements

Though this difference is large at the beginning of the process, the temperature inside the vessel catches up and is at a minimum at 350°C, 390°C and 400°C at 2°C/min, 6°C/min and 10°C/min respectively. Even though tyre pyrolysis is overall an endothermic process, both endothermic and exothermic reactions occur (Cheung et al., 2011). The exothermic reactions are usually associated with chemical reactions such as crosslinking and cyclisation (Brazier & Schwartz, 1978) (see Section 3.3). Yang & Roy (1996) used DTA to examine enthalpy changes on the individual polymers used in tyre manufacture, NR, SBR and PBR, and observed an exothermic period between 300 – 450°C, with maximum rate of exothermicity observed at 378°C for both NR and SBR and 381°C for PBR using a heating rate of 10°C/min. This is the same region where there is an increase in the temperature of the crumb as seen in Figure 4.15 confirming the occurrence of exothermic reactions.

Figure 4.16 shows the heating profile of the pyrolysis of samples D and E, and N772. It can be noted that the exothermic peak is identical irrespective of feedstock composition whereas N772 shows a straight line.

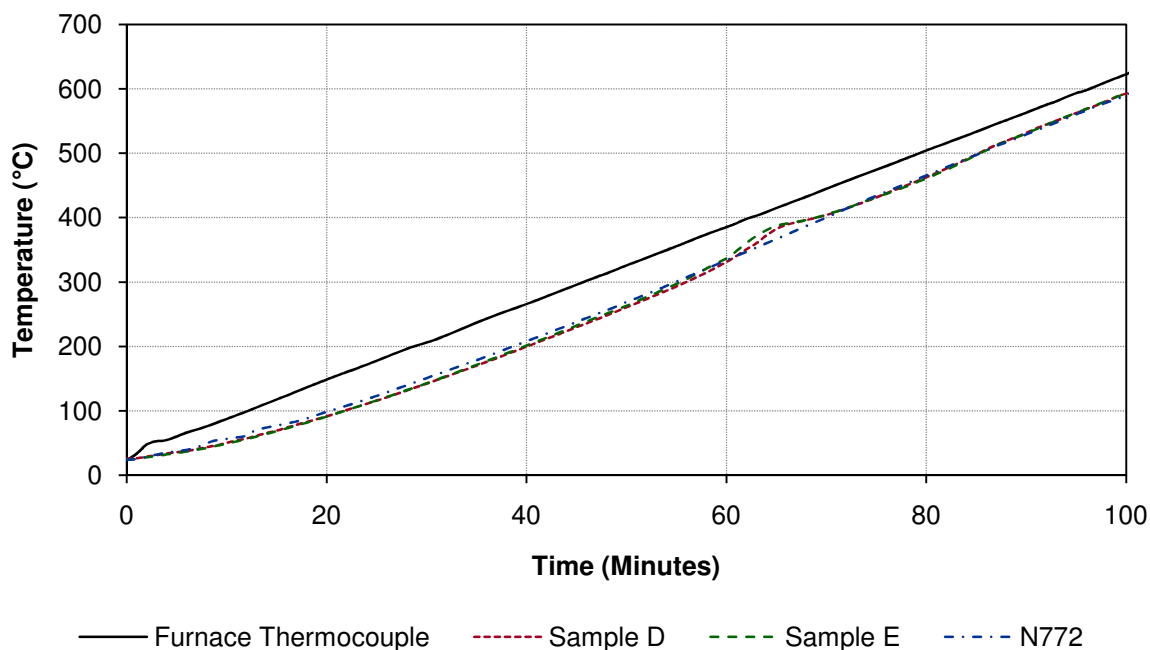


Figure 4.16. Comparison of thermocouple measurements for different samples at 6°C/min

All chars had yields of $40.3 \pm 0.6\%$ as complete pyrolysis was ensured. CHN, ash content and toluene extractable transmission results are summarised in Table 4.13. Only one char, CP_{II,E3}, that was generated at 550°C, 10°C/min and 75 min dwell time had some oils still present (93.3%).

Table 4.13. Char characterisation results of Part II experiments (conventional pyrolysis)

	Ash Content (%)	Transmission of Toluene Extracts (%)	C (%)	H (%)	N (%)	Surface Area (m ² /g)		pH- value
						BET	Meso & Macropore	
CP _{II,E} 1	44.11	99.8	51.77	<0.1	<0.1	112.5	91.0	7.80
CP _{II,E} 2	43.89	99.4	52.99	<0.1	<0.1	94.2	79.3	8.40
CP _{II,E} 3	43.45	93.3	52.61	<0.1	<0.1	105.9	91.9	7.84
CP _{II,E} 4	43.90	99.7	53.61	<0.1	<0.1	97.8	84.1	8.31
CP _{II,E} 5	44.79	98.6	50.79	<0.1	<0.1	113.3	94.1	7.81
CP _{II,E} 6	47.01	99.5	50.21	<0.1	<0.1	102.6	88.0	8.60
CP _{II,E} 7	44.00	99.6	51.86	<0.1	<0.1	113.3	92.6	7.81
CP _{II,E} 8	44.00	99.7	52.93	<0.1	<0.1	98.9	86.1	8.55
CP _{II,E} 9	45.74	99.5	51.14	<0.1	<0.1	109.8	87.7	7.92
CP _{II,E} 10	44.03	98.3	53.12	<0.1	<0.1	105.7	90.8	7.90
CP _{II,E} 11	45.45	99.2	51.39	<0.1	<0.1	106.7	87.2	8.27
CP _{II,E} 12	44.77	99.0	52.35	<0.1	<0.1	103.9	88.5	8.07
CP _{II,E} 13	46.31	99.4	50.88	<0.1	<0.1	102.5	84.9	8.13
CP _{II,E} 14	43.45	99.5	53.56	<0.1	<0.1	100.3	84.9	8.16
CP _{II,E} 15	45.88	99.4	55.87	<0.1	<0.1	105.7	89.1	8.07
CP _{II,D} 16	19.54	98.2	–	–	–	82.3	70.3	9.10
CP _{II,N772} 17	0.75	99.6	–	–	–	35.2	33.2	^b
N772	0.33	73.3	–	–	–	32 ^a	31 ^a	^b

^a Wang et al. (2000), ^b See explanation below

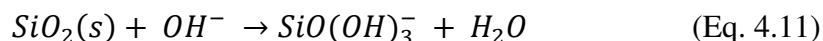
The pH-values of the chars were again in the alkaline region, specifically between 7.73 and 8.60 (Table 4.13). The pH-value of CP_{II,D}16 was 9.10 compared to the 8.12 (average of CP_{II,E}13–15). Table 4.14 shows their differences in composition derived from EDX measurements.

Table 4.14. CP_{II,E}13–15 and CP_{II,D}16 chars composition

	C	Ash	O	Mg	Al	Si	K	Ca	Fe	Zn	SiO ₂	Fe ₂ O ₃	ZnO
CP _{II,E} 13-15	54.8	45.2	22.8	0.2	0.3	19.5	0.0	0.1	0.0	2.0	41.8	0.0	2.6
CP _{II,D} 16	80.5	19.5	8.3	0.0	0.2	6.6	0.1	0.5	0.1	3.1	14.2	0.1	3.8

Though CP_{II,E}13-15 has more oxygen, this is probably bound with the other elements present to form oxides such as SiO₂ and ZnO. Alkali elements that can contribute to the alkalinity are not present in significant amounts, so the difference in pH-values of CP_{II,D}16 and CP_{II,E}13–15 might be because CP_{II,D}16 has a larger carbon percentage, so with the removal of the oxygen

from its surface upon heating, there are more sites that can act as Lewis bases. In addition the SiO_2 , present in $\text{CP}_{\text{IE}}13\text{--}15$ (41.8%), might absorb the freed OH^- (Eq. 4.11).



Commercial carbon black N772 and $\text{CP}_{\text{ILN772}}17$ were also tested under the same conditions. The values recorded changed within minutes to acidic ones and duplicate measurements gave ranges of values between 8.46 and 6.72. Also the filtrate volume was much less than that recovered from the chars, indicating the hydrophilicity of these carbons. This implied that these carbons are more prone to oxygen chemisorptions.

The surface area of the char from sample D was $82.3 \text{ m}^2/\text{g}$ compared to the average of runs 13 – 15 of $102.8 \text{ m}^2/\text{g}$, highlighting again the significance of the composition of rubber to the surface area formation. The presence of inorganics might have a contribution– the surface area of Ultrasil[®] VN3, a form of precipitated silica used as reinforcement filler in the rubber industry is $180 \text{ m}^2/\text{g}$ (Evonik Industries, 2012). The surface area of $\text{CP}_{\text{ILN772}}17$ is expected to increase as volatile content (1.2%) was removed by the pyrolysis process, that could hinder the pores. The removal is evident from the transmission of toluene extracts which increased from 73.3% to 99.6% post-pyrolysis.

4.4.3.2 Influence of parameters

4.4.3.2.1 Effect on Carbon content

An attempt to fit a quadratic model to the carbon content values was unsuccessful, as the model showed no evidence of regression ($p\text{-value} = 0.8356 > 0.05$) (Table 4.15). This might be because by changing the conditions – increasing the end temperature and dwell time minimum – therefore achieving complete pyrolysis, carbon content values become similar provided the feedstock is the same.

Table 4.15. ANOVA results for carbon content value

ANOVA for quadratic model					
Source	df	SS	MS	F	<i>p-value</i>
Regression	9	13.5402	1.5045	0.4871	0.8356
Residual	5	15.4428	3.0886		
LOF	3	2.9699	0.99	0.1587	0.9157
PE	2	12.4729	6.2364		
Total	14	0.8288			
$R^2 = 46.72$ $R^2_{adj} = -0.4919$ $stdev = 1.7574$					
Parameter	Coefficient	<i>p-value</i>	Significance (%)		
Constant	53.44	0.0000	100.00		
x1	0.34	0.6091	39.09		
x2	0.55	0.4166	58.34		
x3	0.41	0.5397	46.03		
x1*x2	-0.06	0.9525	4.75		
x1*x3	0.41	0.6585	34.15		
x2*x3	-0.255	0.7833	21.67		
x1*x1	-0.622083	0.5266	47.34		
x2*x2	-0.069583	0.9423	5.77		
x3*x3	-1.367083	0.1952	80.48		

4.4.3.2.2 Effect on Surface area

The quadratic fit produced a model with $p = 0.0044$ and no evidence of lack of fit. Individual parameters with high significance were temperature (x1), temperature with heating rate (x1*x2) and the dwell time with dwell time (x3*x3) with coefficients all under $\alpha = 0.05$. The difference of $R^2 = 96.32$ and $R^2_{adj} = 89.68$ prompt the investigation for the removal of the non-significant terms and the re-evaluation of the model. The best fit for the overall model ($p = 0.0000$) was obtained using as parameters the temperature ($\alpha = 0$), heating rate ($\alpha = 0.05$), dwell time ($\alpha = 0.08$), temperature with heating rate ($\alpha = 0.009$) and the dwell time with dwell time ($\alpha = 0.0006$). The coefficients of determination were $R^2 = 95.36$ and $R^2_{adj} = 92.78$, which means that the model can explain 92.78% of the results (Table 4.16).

Figure 4.17 shows the response of the model.

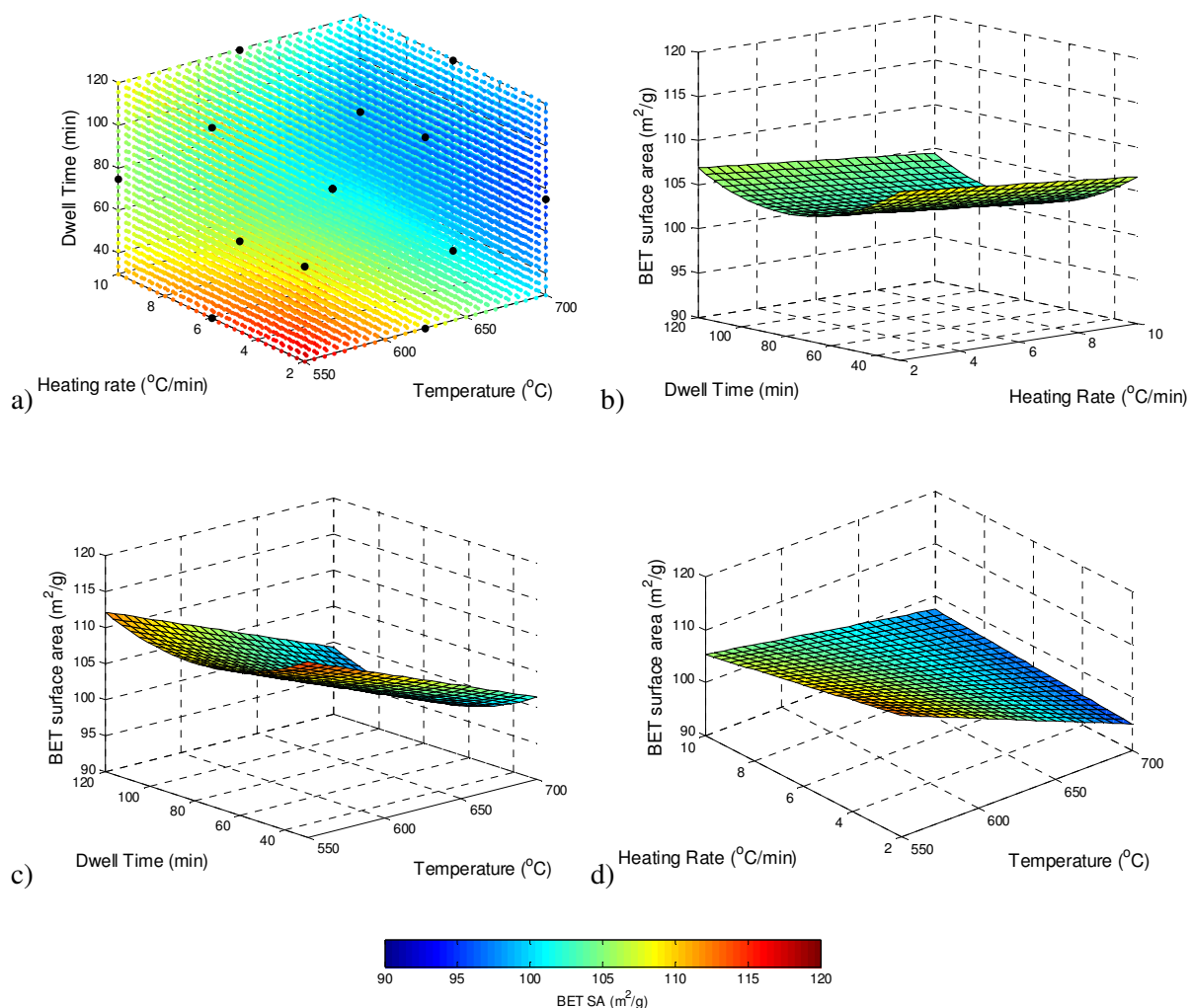


Figure 4.17. Surface area response

The highest surface areas are observed at low heating rates, temperatures and dwell times. Surface area changes more significantly when one of the parameters changing is temperature (Figure 4.17 c & d), than when it is kept constant (Figure 4.17 b). Lowest surface areas were recorded at higher temperatures, irrespective of the heating rate and dwell time.

Table 4.16. ANOVA results for surface area

ANOVA for quadratic model					
Source	df	SS	MS	F	<i>p-value</i>
Regression	9	445.4702	49.4967	14.524	0.0044
Residual	5	17.0392	3.4078		
LOF	3	2.2925	0.7642	0.1036	0.9506
PE	2	14.7467	7.3733		
Total	14	462.5093			
$R^2 = 96.32$		$R^2_{adj} = 89.68$	stdev = 1.8460		
Parameter	Coefficient	<i>p-value</i>	Significance (%)		
Constant	102.83	0.0000	100.00		
x1	-6.44	0.0002	99.98		
x2	-1.24	0.1165	88.35		
x3	-1.08	0.1605	83.95		
x1*x2	2.55	0.0397	96.03		
x1*x3	-0.92	0.3623	63.77		
x2*x3	0.325	0.7391	26.09		
x1*x1	0.1333333	0.8950	10.50		
x2*x2	-0.366667	0.7184	28.16		
x3*x3	4.0583333	0.0083	99.17		

ANOVA Adjusted					
Source	df	SS	MS	F	<i>p-value</i>
Regression	5	441.0318	88.2064	36.962	0.0000
Residual	9	21.4775	2.3864		
LOF	7	6.7308	0.9615	0.1304	0.9828
PE	2	14.7467	7.3733		
Total	14	462.5093			
$R^2 = 95.36$		$R^2_{adj} = 92.78$	stdev = 1.5448		
Parameter	Coefficient	<i>p-value</i>	Significance (%)		
Constant	102.70	3.16E-17	100.00		
x1	-6.44	8.97E-07	100.00		
x2	-1.24	4.97E-02	95.03		
x3	-1.08	8.06E-02	91.94		
x1*x2	2.55	0.0092092	99.08		
x3*x3	4.075	0.0006479	99.94		

4.4.3.2.3 Effect on pH-value

The quadratic fit produced a model with $p = 0.02$ and no evidence of lack of fit at a significance level of $\alpha = 0.05$. The individual parameter with high significance was only temperature $\alpha = 0.0007$. The difference of $R^2 = 92.65$ and $R^2_{adj} = 79.42$ prompted the

investigation of the removal of the non-significant terms and the re-evaluation of the model (Table 4.17).

Table 4.17. ANOVA results for pH-value

ANOVA for quadratic model					
Source	df	SS	MS	F	<i>p-value</i>
Regression	9	0.9438	0.1049	7.0029	0.0226
Residual	5	0.0749	0.015		
LOF	3	0.0707	0.0236	11.218	0.0829
PE	2	0.0042	0.0021		
Total	14	1.0187			
R ² = 92.65 R ² _{adj} = 79.42 stdev= 0.1224					
Parameter	Coefficient	<i>p-value</i>	Significance (%)		
Constant	8.12	0.0000	100.00		
x1	0.33	0.0007	99.93		
x2	-0.03	0.4706	52.94		
x3	0.06	0.2326	76.74		
x1*x2	-0.03	0.6180	38.20		
x1*x3	-0.01	0.8462	15.38		
x2*x3	-0.045	0.4951	50.49		
x1*x1	0.06	0.3894	61.06		
x2*x2	-0.0925	0.2061	79.39		
x3*x3	0.0125	0.8521	14.79		
ANOVA Adjusted					
Source	df	SS	MS	F	<i>p-value</i>
Regression	2	0.8806	0.4403	38.268	0.0000
Residual	12	0.1381	0.0115		
LOF	10	0.1339	0.0134	6.3749	0.1431
PE	2	0.0042	0.0021		
Total	14	1.0187			
R ² = 86.45 R ² _{adj} = 84.19 stdev= 0.1073					
Parameter	Coefficient	<i>p-value</i>	Significance (%)		
Constant	8.16	1.52E-22	100.00		
x1	0.33	1.85E-06	100.00		
x2*x2	-0.10	1.04E-01	89.61		

The best fit for the overall model ($p = 0.0000$) was obtained using as parameter the temperature ($\alpha = 0$). In addition, heating rate*heating rate ($\alpha = 0.10$) was also added to the model to give coefficients of determination of $R^2 = 86.45$ and $R^2_{\text{adj}} = 84.19$, which means that the model can explain 84.19% of the results.

Figure 4.18 illustrates how the pH increases with increasing temperature at constant dwell time of 75 min.

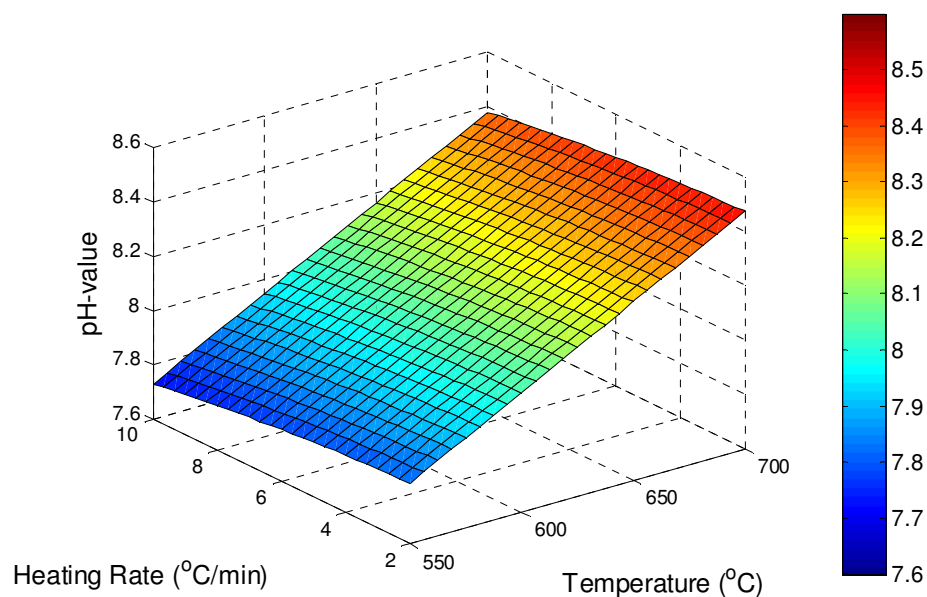


Figure 4.18. Graphical representation of pH-value response

As observed in Section 4.3.3.2.3 increase of pyrolysis temperature results in increase of the pH due to the removal of the surface oxides groups.

4.4.4 Conclusions

Part II of this chapter has analysed the pyrolysis of crumb sample E using a Box-Behnken model. This statistical approach provides a useful tool in fitting a model between the parameters of the tyre pyrolysis experiment and properties of the chars generated. The parameters varied were the temperature, heating rate and dwell time. The most influential parameter identified was temperature. However, the choice of the parameters range limited the variation of the char properties, especially since dwell time was chosen to ensure complete rubber pyrolysis. The model generated data which enabled the next phase of the research, and the results suggested that either a two parameter model of temperature and heating rate would have been more beneficial, or the third parameter could have been the nitrogen flow, rather than dwell time.

5 Microwave-induced tyre pyrolysis

5.1 Introduction

Microwave technology has become very popular for use in waste management. Numerous papers have been published in the last few years examining the use of microwave heating to process wastes such as plastics (Ludlow-Palafox & Chase, 2001), sewage sludge (Domínguez et al., 2005; Tian et al., 2011), coffee hulls (Domínguez et al., 2007), wheat straw (Budarin et al., 2009), municipal solid waste (Li et al., 2011), wood (Miura et al., 2004), bottle waste (Pingale & Shukla, 2008), distillers dried grain with solubles (Lei et al., 2011), contaminated soil (Robinson et al., 2009), corn stalk (Zhao et al., 2010) and oil palm empty bunch biomass (Salema & Ani, 2012). Modified domestic microwave ovens and custom made apparatus were employed and, depending on the dielectric properties of the feedstock, microwave absorbers such as carbon were added to assist the process. In such case, it is the carbon that responds to the microwaves, heats up and then the heat is transferred to the waste. This is especially useful when waste volume reduction in conjunction with generation of useful gas and oil is the main objective.

Published research examining tyre pyrolysis using microwave technology is, however, limited (Pang, 2007; Undri et al., 2011 and Ani & Nor, 2012), even though there is an extensive literature of tyre microwave pyrolysis patents.

5.2 Experimental apparatus for microwave pyrolysis

In this study four different microwave apparatus were tested. The first two comprised of modified domestic microwave ovens, the third a modified microwave synthesis apparatus (the RotoSYNTH) and the last was a custom made furnace manufactured by Cobham Microwave Ltd in collaboration with Imperial College. All the microwave systems used multimode cavities at inert atmosphere (nitrogen gas was used to purge the systems before, during, and after the pyrolysis experiments until the sample had cooled). These systems are described in the following section.

5.2.1 Modified domestic microwave oven I

Preliminary laboratory microwave pyrolysis experiments were conducted in a modified domestic oven (Panasonic model No. NN-SD277S) capable of delivering continuous microwave energy using inverter technology. Two holes were drilled in the oven cavity – one at the back of the oven for the supply of nitrogen gas (N_2) to the system and the other at the side of the oven to allow the discharge of gases generated during the pyrolysis via PTFE tubing (microwave transparent) as shown in Figure 5.1.

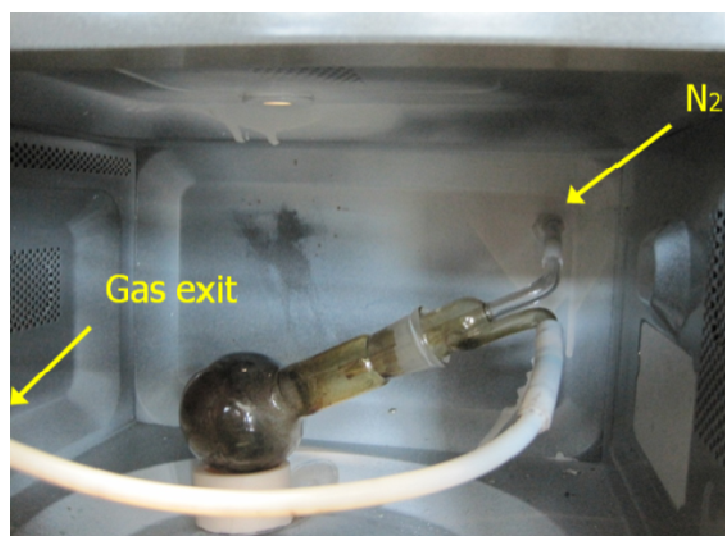


Figure 5.1. Modified domestic microwave oven I

Five grams of sample A were placed in a quartz round bottom flask with a borosilicate drechel head and placed in the microwave oven. The system was then purged with N_2 at a flow rate of 0.6 L/min from 15 min prior to microwave pyrolysis until after the sample had cooled down (post pyrolysis). For the initial trial tests, full power of 850 W was employed for varying periods of time. The conditions are summarised in Table 5.1. Experiments at 1, 2, 3 and 4 minutes were run in triplicate.

5.2.2 Modified domestic microwave oven II

The set-up used in the domestic microwave oven I experiments was modified by Fowler & Goodman (2009) to include an infra-red (IR) sensor and to substitute all glassware with quartz as shown in Figure 5.2. The IR sensor was used to monitor the temperature of the sample. As the quartz vessel is not infra-red transparent, the IR-sensor had to be placed in such a way that it would 'view' the surface of the sample directly. It was placed on the top of

the microwave furnace at a distance dictated by the focal point of the sensor. Nitrogen gas was also introduced from the top, at a flow rate of 1 L/min. A joining collar and a customised drechel head, all made from quartz, were used to connect the system with the round bottom flask. The gases generated escaped the cavity again from the side of the furnace. An ether condenser, which was kept at -10°C (using a grant chiller RC2718 filled with ethylene glycol), was used to aid the condensation of the oil produced. Experiments were run using 20 grams of crumb sample A, 20 minute heating duration and varying power levels as summarised in Table 5.1. Experiments at 250 W were run in duplicate, then at 440 W, 650 W and 850 W in quadruplicate.



Figure 5.2. Modified domestic microwave system II

5.2.3 RotoSYNTH

The RotoSYNTH, which is an equipment used for synthesis experiments, was modified for pyrolysis experiments. Specifically a quartz reactor was custom made and a quartz tube was placed in the middle to provide a discharge route for the gas generated during the pyrolysis experiment (Figure 5.3). The vessel was tilted to 45° and set in constant rotation, and the nitrogen gas flow rate was 1 L/min. Crumb from sample D was pyrolysed at varying power levels (Table 5.1). Temperature was monitored by an IR sensor located on the lower side of the equipment, and the maximum temperature alarm was adjusted to 1000°C .



Figure 5.3. Modified RotoSYNTH

Table 5.1 below is a summary of the experimental conditions in the first three microwave set-ups.

Table 5.1. Domestic Microwave I, II and RotoSYNTH experimental conditions

Domestic microwave I			Domestic microwave II			RotoSYNTH		
Crumb Sample A			Crumb Sample A			Crumb Sample D		
Power (W)	Time (min)	Mass (g)	Power (W)	Time (min)	Mass (g)	Power (W)	Time (min)	Mass (g)
850	0.5	5	250	20	20	300	180	50
	1		440	20		600	60	
	1.5		600	20		750	50	
	2		850	20		750	50	
	3					1000	50	
	4					1200	30	
	5					300	120	100
	6					750	50	
						1000	60	
						1200	30	

5.2.4 Cobham Microwave

A new furnace was developed in collaboration with Cobham Microwave Ltd. This equipment (Figure 5.4) featured a rotary system, similar to the Carbolite rotary furnace previously

described in Section 4.3.1.2. The laboratory unit had maximum power of 2 kW. One of its features was to provide measurement and recording of forward and reverse (reflected) power. In addition an IR sensor was used to provide temperature measurements of the quartz vessel. The quartz vessel was surrounded by microwave-transparent ceramic fibre insulation.

The system was designed taking into consideration the safety of the instrument in compliance with health and safety regulations, for example BS EN 55011:1998 (Industrial, scientific and medical (ISM) radio-frequency equipment - Radio disturbance characteristics - Limits and methods of measurement). For this purpose, choke flanges surrounded the cavity in order to attenuate the microwave radiation which would otherwise be released.

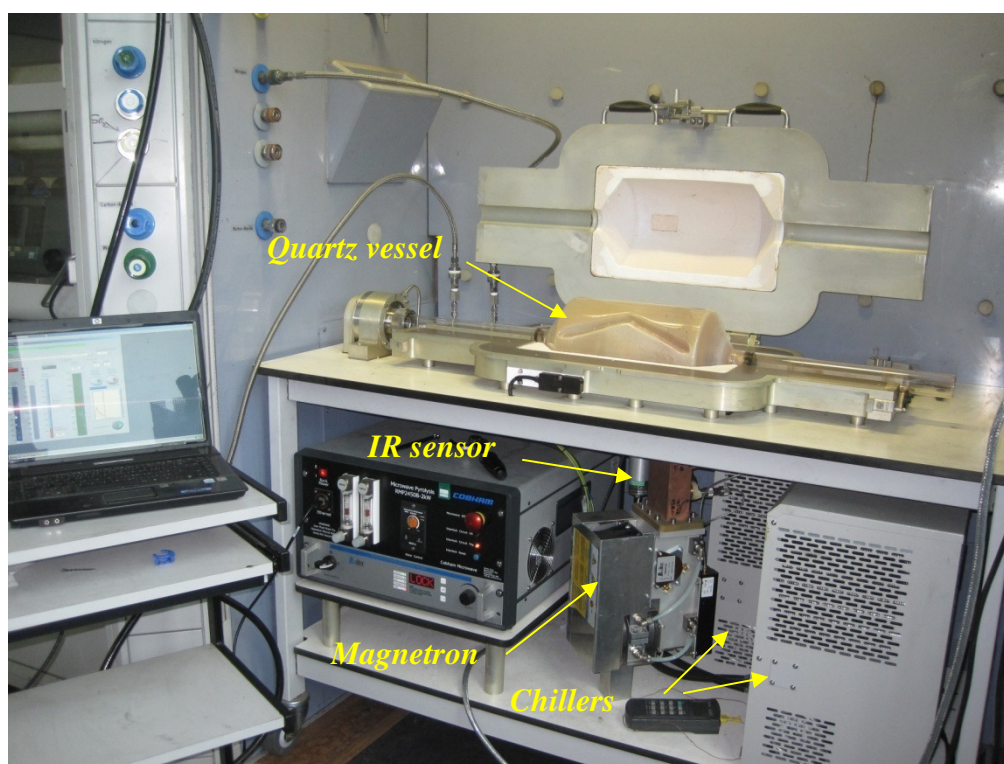


Figure 5.4. Cobham Microwave

Chiller units were used to cool the magnetron and the IR sensor, and an alarm device was used to prevent their overheating. This was set at 80°C. Air was used to prevent the formation of mist on the IR eye. During tyre pyrolysis the equipment was tilted to avoid condensation of oils in the front arm of the vessel.

Using 400 g of sample, a nitrogen flow rate of 2 L/min and a rotation of 10 rpm, two main sets of experiments were performed. The first set (Part I) included 21 experiments using crumb from sample D, different power levels ranging from 650 to 2000 W, and durations of

27 – 265 minutes. This produced completely pyrolysed chars that were then characterised. The second set of experiments (Part II) used crumb from sample F, power levels of 1000 W and 1500 W, and different duration times, to examine the weight loss until pyrolysis is achieved. The experimental conditions are summarised in Table 5.2. The generated outcomes were assigned IDs using the initials CM for Cobham Microwave followed by the crumb sample name, the nominal power used and the duration of the experiment in minutes e.g. CM_D2000_27 identifies with the experiment performed in the Cobham apparatus using crumb from sample D, pyrolysed at 2000 W for 27 minutes.

Table 5.2. Cobham Microwave experimental conditions

Cobham Microwave - 400 g					
<u>Part I</u> Crumb Sample D			<u>Part II</u> Crumb Sample F		
Power (W)	Time (min)	ID	Power (W)	Time (min)	ID
2000	27	CM _D 2000_27	1000	31	CM _F 1000_31
	33	CM _D 2000_33		35	CM _F 1000_35
	40	CM _D 2000_40		38	CM _F 1000_38
1500	40	CM _D 1500_40		41	CM _F 1000_41
	41	CM _D 1500_41a		47	CM _F 1000_47
	41	CM _D 1500_41b		50	CM _F 1000_50
	41	CM _D 1500_41c		70	CM _F 1000_70
	53	CM _D 1500_53		88	CM _F 1000_88
	60	CM _D 1500_60		138	CM _F 1000_138
1200	66	CM _D 1200_66	1500	17	CM _F 1500_17
	70	CM _D 1200_70		18	CM _F 1500_18
	90	CM _D 1200_90		20	CM _F 1500_20
	119	CM _D 1200_119		24	CM _F 1500_24
1000	90	CM _D 1000_90		26	CM _F 1500_26
	120	CM _D 1000_120		32	CM _F 1500_32
	180	CM _D 1000_180		44	CM _F 1500_44
800	97	CM _D 800_97		54	CM _F 1500_54
	160	CM _D 800_160			
	210	CM _D 800_210			
750	142	CM _D 750_142			
600	265	CM _D 600_265			

5.3 Characterisation

Selected outputs obtained from the microwave pyrolysis were characterised using the following procedures:

- pH-value (Chars)
- Ash content (Chars)
- Transmittance of toluene extract (Chars)
- Surface Area (Chars)
- Apparent density (Chars)
- Dielectric Measurements (Chars)
- CHNS analysis (Oils)
- Infrared Spectroscopy (Oils)
- Bomb Calorimetry (Oils)
- Gas Chromatography/ Mass Spectroscopy (Oils)

Only procedures which have not been previously described are introduced in the following sub-sections.

5.3.1 Apparent density

The apparent density of selected chars generated from Part II of the Cobham Microwave experiments, was obtained using a modified ASTM method (ASTM D2854-96). In the experiment, a vibrating feeder was used to fill a graduated cylinder at a uniform rate of between 0.75 and 1.0 ml/s by free fall with the chars to a pre-determined level. This ensured uniform distribution of the chars in the cylinder. The mass of this known volume of chars was then measured, and used to calculate the density. The chars were used as-produced (no preparation, e.g. grinding) and the experimental set-up is shown in Figure 5.5. Equation 5.1 was used to calculate the apparent density.

$$\text{Apparent density} \left(\frac{\text{g}}{\text{cm}^3} \right) = \frac{\text{mass of char}}{\text{char volume}} \quad (\text{Eq. 5.1})$$



Figure 5.5. Apparatus for measuring apparent density

5.3.2 Dielectric measurements

The dielectric properties of selected chars generated from Part II of the Cobham Microwave experiments, were examined using a vector network analyser (Rohde-Schwarz model ZVB4). This analyser includes a microwave generator that can be swept in output frequency over a predefined range and enables the measurement of the phase and amplitude of a reflected and transmitted wave relative to the forward wave from the generator (Meredith, 1998). The frequency range used in this study was between 2.17 GHz and 3.3 GHz. The network analyser generates only low power (tens of milliwatts), which ensures negligible heating and is therefore safe to use. The experimental set up is shown in Figure 5.6, and a detailed description is presented below.

As shown in Figure 5.7, the network analyser is comprised of the signal input (with incident and reflected waves) and the signal output (with transmitted and load reflected waves). These are identified as port 1 and port 2 respectively. The sample or material under investigation is placed in a waveguide which is connected at one end to port 1 and at the other end to port 2. This connection is by coaxial cables through which the signal is delivered. For the dielectric measurements, each sample was placed in a quartz vessel in the centre of the waveguide. To ensure accuracy of the measurements, readings were taken for two positions in the centre of the waveguide: (i) in the geometric middle, and (ii) at the side of the middle of the waveguide, and each measurement was done in duplicate.

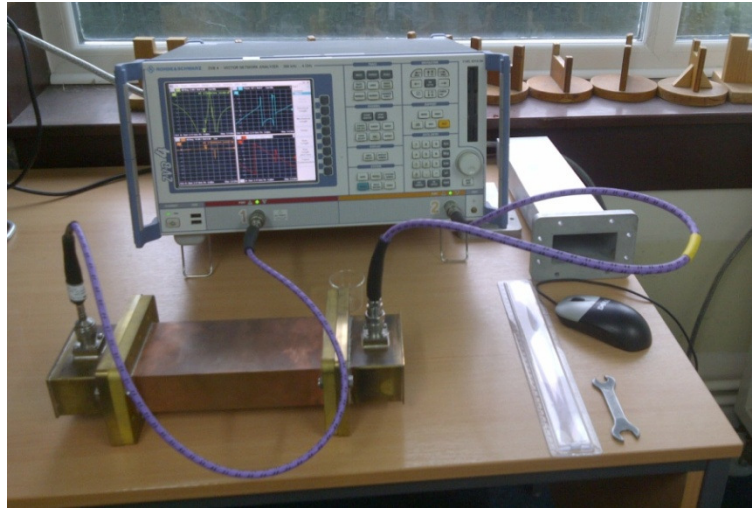


Figure 5.6. Dielectric measurements set-up

Depending on the dielectric properties of the material under investigation, when the signal is delivered, some of it will be reflected, some transmitted, and some absorbed by the material. The analyser measures the voltage of the travelling waves and generates plots representing the amplitude and phase of the Scattering (S) parameters of the system. The S parameters for a 2-port network can be described using equations 5.2 and 5.3, where a_1 and a_2 are the waves entering and b_1 and b_2 are the waves leaving the two-port network system (Bryant, 1993) as shown in the schematic in Figure 5.7:

$$b_1 = a_1 S_{11} + a_2 S_{12} \quad (\text{Eq. 5.2})$$

$$b_2 = a_1 S_{21} + a_2 S_{22} \quad (\text{Eq. 5.3})$$

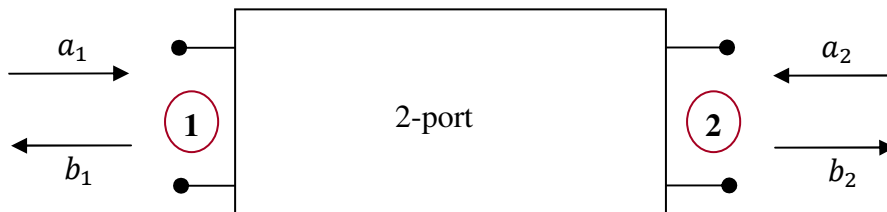


Figure 5.7. Representation of the two-port network system

For a network system where a_2 is zero, known as having a matched load (Bryant, 1993), the equations for S_{11} and S_{21} are linear ratios as follows:

$$S_{11} = \frac{b_1}{a_1} \quad (\text{Eq. 5.4})$$

$$S_{21} = \frac{b_2}{a_1} \quad (\text{Eq. 5.5})$$

S_{11} is the response reflected back to port 1 and is known as Return Loss and its corresponding phase Return Phase. S_{21} is the response at port 2 due to a signal at port 1 and is known as Insertion Loss and its corresponding phase is the Through Phase. These are the two S parameters that are plotted by the analyser.

To ensure accurate measurement of S_{11} and S_{21} , the ports were calibrated initially, using three standards with known reflection coefficients.

Ansoft HFSS (High Frequency Structural Simulator) software was used to build an identical system to the one used and find the best match for the recorded signals by changing the permittivity, $\tan\delta$ and conductivity (Figure 5.8).

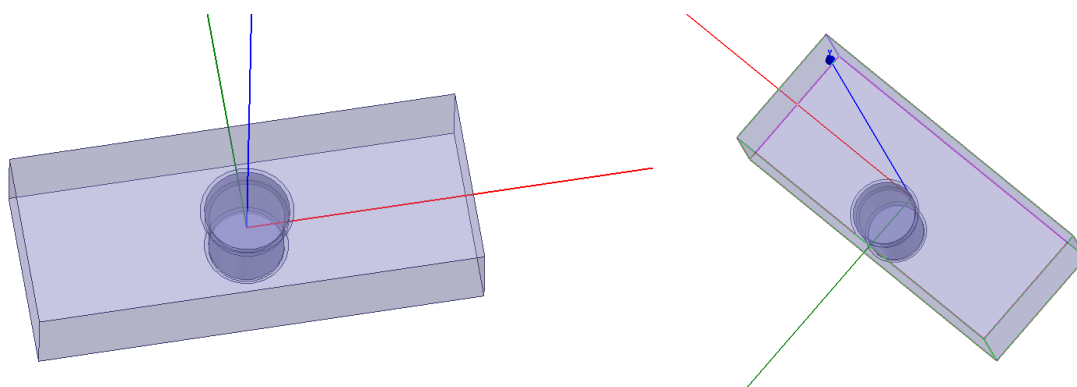


Figure 5.8. Model representation of the sample at the centre and the side of the waveguide

5.3.3 IR Spectroscopy

IR spectroscopy was previously described in Section 4.3.2.5. However, for the analysis of liquids the test sample is analysed directly rather than forming a disk, using a Thermo Scientific Nicolet iS10 spectrometer.

5.3.4 Gas Chromatography/Mass Spectroscopy

Gas Chromatography/Mass Spectroscopy (GC/MS) is an analytical technique that combines gas liquid chromatography and mass spectroscopy to separate, detect and identify the components of a mixture of compounds. In GC/MS the sample is injected through a column

with a stationary phase. Depending on the chemical properties of the components, they will interact differently with the column so that different components will elute from the column at different times. As these molecules leave the column, they are transferred to the mass spectrometer's ionization source, which results in the formation of charged particles. The mass spectrometer then focuses these ions through a magnetic mass analyser, and collects and measures the amount of each selected ion in a detector (McMaster, 2008). The resulting spectra are then compared with libraries to find the best match.

In the current study, a Clarus 500GC and a Clarus 560MS (Ei+ quadrupole mass spectrometer) (Perkin Elmer, NJ, USA) was used, fitted with a Supelco Petrocol DH (100 m x 0.25 mm ID, 0.5 μ m film (non-polar bonded methyl silicone)). Helium was used as carried gas. The analysis program comprised the following steps: a GC initial oven temperature of 40°C was held for 10 minutes, then increased to 300°C at 0.5°C/min where it was held for a further 180 minutes. The chromatograms generated were analysed using Perkin Elmer Turbomass Ver. 5.3.0 software, in which peaks were automatically identified and integrated. Mass spectra were then automatically compared against the 'NIST Mass Spectral Data Library 2005'. Peaks were then identified tentatively with the best spectral match.

5.4 Results and Discussion

The following section contains observations from the microwave experiments covering the interaction of the samples with the microwaves in terms of yield, duration, power and temperature as well as challenges faced. Results from the characterisation experiments are also reported.

The yields of completely pyrolysed chars ranged between 48 – 50 wt.% (domestic microwave I), 45.5 – 46.3 wt.% (domestic microwave II), 43.5 – 46.5 wt.% (RotoSYNTH) and 39.8 – 41.6 wt.% and 40.6 – 41.4 wt.% (Cobham, samples D and F respectively) for all the power levels. As was presented in Chapter 4, the yields for completely pyrolysed chars ranged between 38.2 and 43.1 wt.% (Part I) and 40.3 ± 0.6 wt.% (Part II). The higher yields observed in the domestic microwave set-ups are probably due to the experimental arrangements promoting secondary reactions. A summary of all the yields obtained is presented in Appendix I (Table B). Figure 5.9 shows the char yields obtained by domestic microwave oven I over different durations.

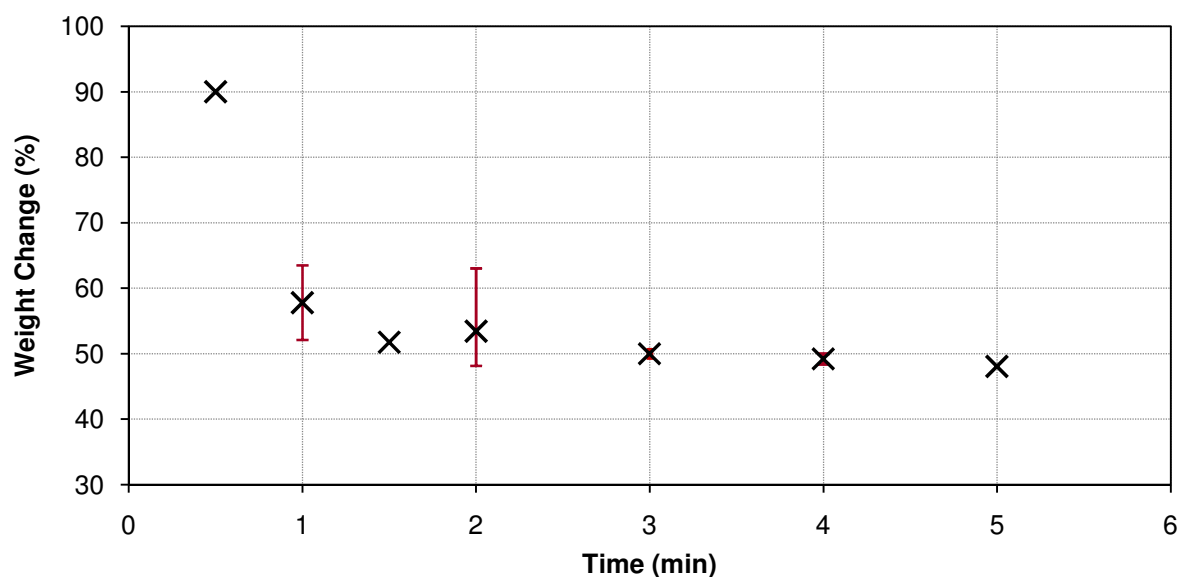


Figure 5.9. Domestic Microwave I char yields at 850 W

Using the domestic microwave set-up I, after 3 minutes at 850 W, the char was essentially pyrolysed. This was confirmed by TG analysis of chars obtained after 3 minutes of pyrolysis which showed insignificant weight change (Appendix II, Figure C). Within 30 seconds (between 0.5 – 1 min) the yield decreased by 32.2 wt.%. This shows that there is no need to add a microwave receptor to tyres to enhance the pyrolysis, though Ani & Nor (2012) included a microwave receptor in their studies on tyre microwave pyrolysis.

The yields of char, oil and gas against time from Part II of the Cobham Microwave experiments at 1000 W and 1500 W is presented in Figure 5.10 and Table 5.3.

Table 5.3. Cobham Microwave Part II Yields (Sample F)

1000 W				1500 W			
Time (min)	Char Yield (wt.%)	Oil Yield (wt.%)	Gas Yield (wt.%)	Time (min)	Char Yield (wt.%)	Oil Yield (wt.%)	Gas Yield (wt.%)
0	100.0	0.0	0.0	0	100.0	0.0	0.0
31	98.0	0.8	1.2	17	98.5	1.3	0.2
35	96.3	2.3	1.4	18	86.3	12.2	1.6
38	86.8	11.4	1.9	20	78.3	19.5	2.1
41	63.4	33.6	3.0	24	58.6	37.7	3.7
47	56.2	40.2	3.6	26	49.6	45.8	4.6
50	52.0	44.3	3.7	32	42.8	53.0	4.2
70	41.2	53.6	5.1	44	41.4	52.6	6.0
88	41.1	53.6	5.4	54	41.1	53.1	5.8
138	40.6	53.1	6.2				

Whereas Undri et al. (2011) successfully pyrolysed 400 g of chopped tyres in 13 minutes using 6 kW of power, and in 39 minutes using 3 kW, their attempt to completely pyrolyse their crumb using 1.5 kW power in 100 minutes was unsuccessful. Their reactor was a static bed reactor and comprised a microwave oven, heat exchanging pipes and collecting flasks. In the current work using the Cobham Microwave (Figure 5.4), however, the complete pyrolysis of the same quantity of tyre crumb was achieved using 1.5 kW of power in 44 minutes, and 1.0 kW in 70 minutes. As shown later in this chapter, complete pyrolysis was also achieved after 27 minutes using 2.0 kW power. This shows that with better design and optimisation of the apparatus much higher efficiency can be achieved.

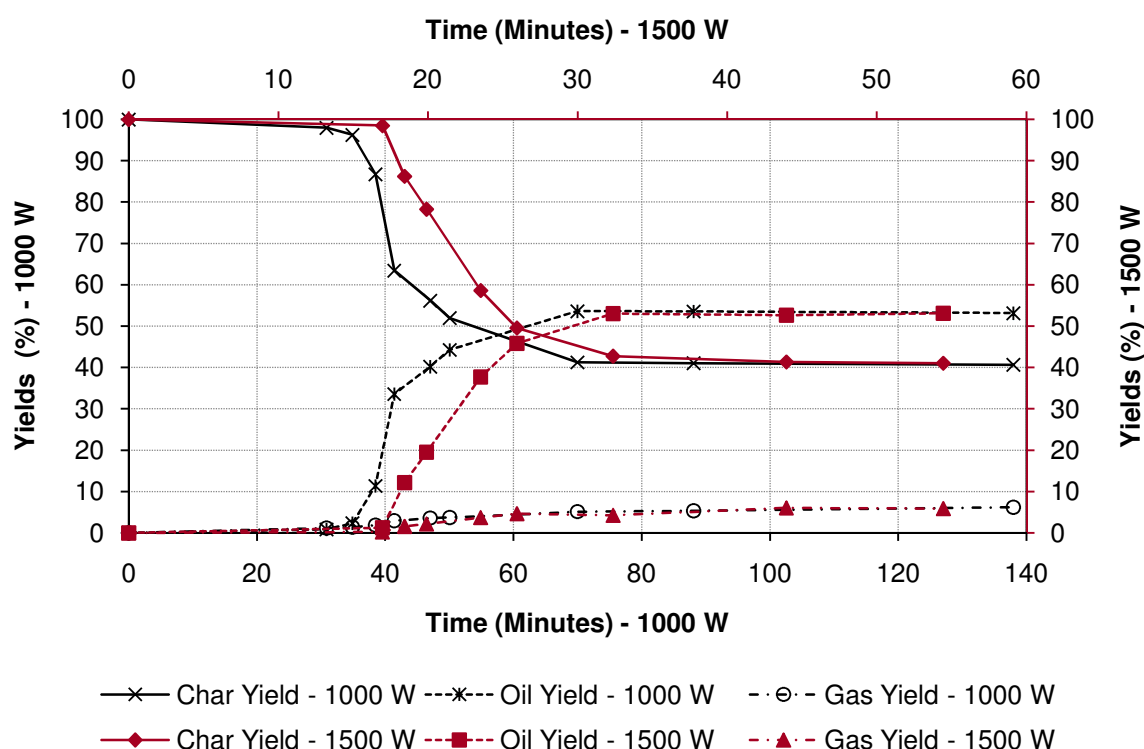


Figure 5.10. Plots of Cobham Microwave Part II yields

Oil yields from the set of experiments using sample D ranged between 52 – 55 wt.% for all powers and 53 wt.% for the experiments with sample F (Appendix I, Table B). Similar oil yields were obtained as with the pyrolysis using conventional means. Undri et al. (2011) measured yields between 37 – 40 wt.% under optimal conditions and gas yields between 12 – 23 wt.%, perhaps because the condensation system was not adequate to handle the rapid generation of gas. For the Cobham system in the current work, a lot of modifications had to be made to achieve optimal condensation and accurate measurement of the oil yields. For this

reason oil yields are only reported for the last series of experiments with the Cobham Microwave. Two initial unsuccessful system set-ups are shown in Figure 5.11 and a final successful set-up is shown in Figure 5.12.



Figure 5.11. First two attempts for efficient condensation system

Initially just a custom made oil trap was used, which recorded 47 wt.%, 44 wt.%, 37 wt.% and as low as 28 wt.% oil yield when using 750 W, 1000 W, 1500 W and 2000 W respectively. In the second set-up, an ether condenser running at -10°C was added to the top of the existing oil trap. Oil yields were improved to 35 – 36 wt.% using 1500 – 2000 W. However, with the introduction of a glass flange on top of the oil trap, to increase the volume of gas that can be accommodated and then piping the gas through two series of cold fingers immersed into liquid nitrogen in parallel, yields of around 53 wt.% were achieved (Figure 5.12).



Figure 5.12. Condensation system using liquid nitrogen traps

One of the biggest challenges in microwave heating is the measurement and control of the temperature. From the four microwave arrangements, described previously, the last three incorporated an IR sensor to give temperature readings. Domestic microwave oven II had an IR sensor ‘viewing’ the sample’s surface directly, from the top, as shown in Figure 5.2.

RotoSYNTH and Cobham microwave had an IR sensor ‘viewing’ the quartz vessel. RotoSYNTH’s IR sensor was pointed at the bottom of the vessel, while the Cobham furnace’s IR was placed on the bottom of the furnace pointing to the middle of the vessel (Figure 5.13).

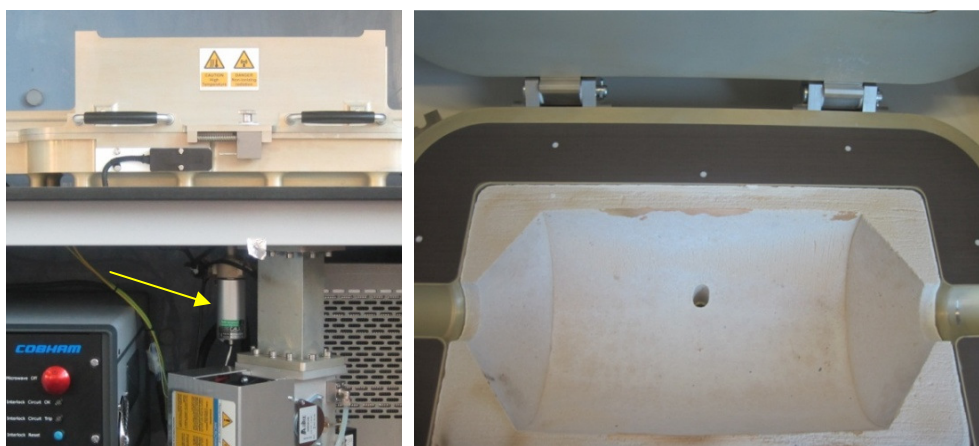


Figure 5.13. IR sensor in Cobham Microwave

As quartz is not infra-red transparent the emissivity of the sensor had to be adjusted for the Cobham furnace (RotoSYNTH’s had been adjusted before arrival at the laboratory). Green & Perry (2007) defines emissivity “...as the ratio of the total radiating power of any surface to that of a black surface at the same temperature”. From literature the emissivity of quartz is 0.93 at 21°C but changes at different temperatures (Green & Perry, 2007). A silicon carbide (SiC) mix provided by Cobham Ltd was used to investigate the best emissivity value at high temperatures. This mix can heat up under microwave radiation without changing consistency and dielectric properties. Values between 0.90 – 0.93 were tested for 400 g of SiC mix at 2000 W. The equipment’s software was recording the thermal profile of the heating and cooling stages. Once the microwaves were turned off at high temperature, a thermocouple was inserted to the middle of the chamber and the temperature of the mix was measured against that recorded by the software (Figure 5.14). The value that gave the best match with the average thermal profile at high temperatures was 0.91 and was selected for the rest of the experiments (Figure 5.15).

As can be observed from Figure 5.15, the thermal profile fluctuates with time – this is because the focal point of the IR changes due to the veins of the reactor (clearly visible in Figure 5.14). For the rest of the experiments the average over a period of 10 was taken.

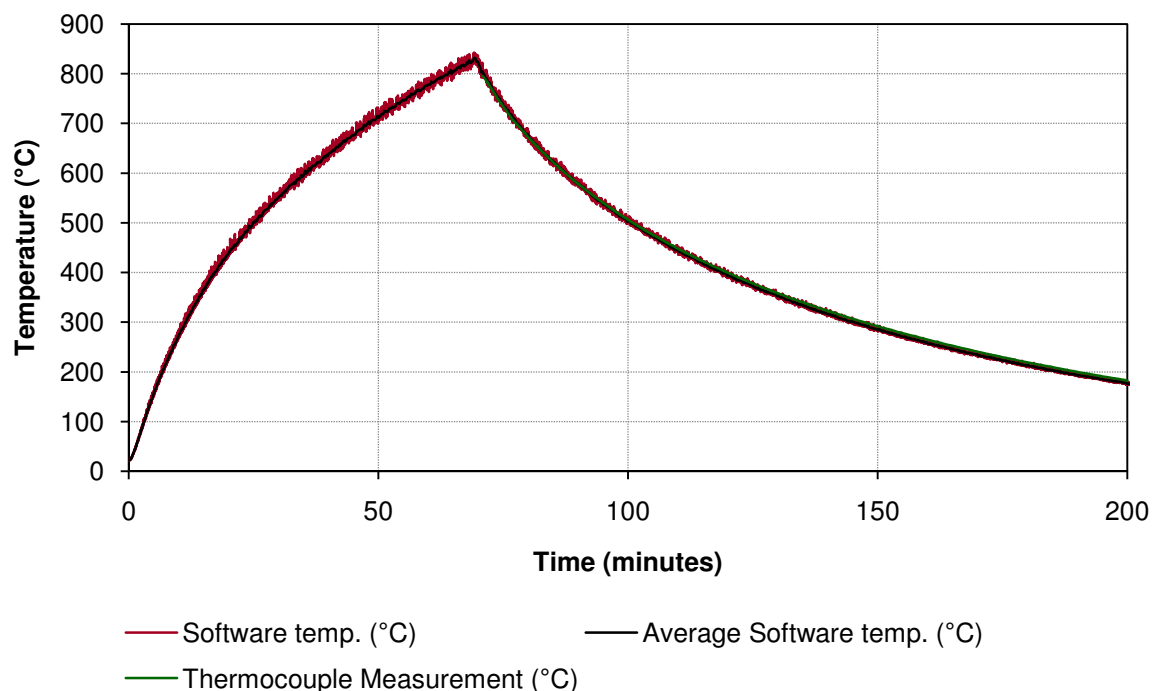


Figure 5.14. Thermocouple measurement of the SiC mix

It should be noted that the IR reading was calibrated for the quartz surface temperature, not the material's temperature. The material's temperature is transferred to the vessel mainly by convection so there will be some thermal lag between the recorded temperature and the instantaneous temperature inside the vessel. However, given the nature of microwaves, the use of an IR sensor to give an indication of the thermal profiles was the only option. Other methods of temperature measurement such as thermocouples or fibre optics are not suitable. As Will et al. (2004) point out, thermocouples cannot be used in an electromagnetic field (EMF) without shielding and grounding as they would cause interactions with the field or even be destroyed. Even with these precautions taken, interactions of the thermocouple with the electric field can never be completely excluded (Will et al. 2004). In fact when Pert et al. (2001) placed a K-type thermocouple in a microwave cavity and applied 150 W for 10 minutes they recorded a thermocouple measurement of 100°C while the ambient temperature was only 26°C. This supports the view that the thermocouple can be directly heated by microwaves. Furthermore, when Pert et al. (2001) heated zinc oxide samples with and without a thermocouple using identical conditions and monitored the temperature using a pyrometer, it was observed that the surface temperature of the sample was twice as much in the presence of the thermocouple than without. However, thermocouples are still used in microwave pyrolysis (for example Ani & Nor, 2012). Commercially available fibre optic

thermometers are restricted by a maximum temperature limit of 400°C, and cannot therefore be used in this research (Undri et al., 2011).

a)



b)

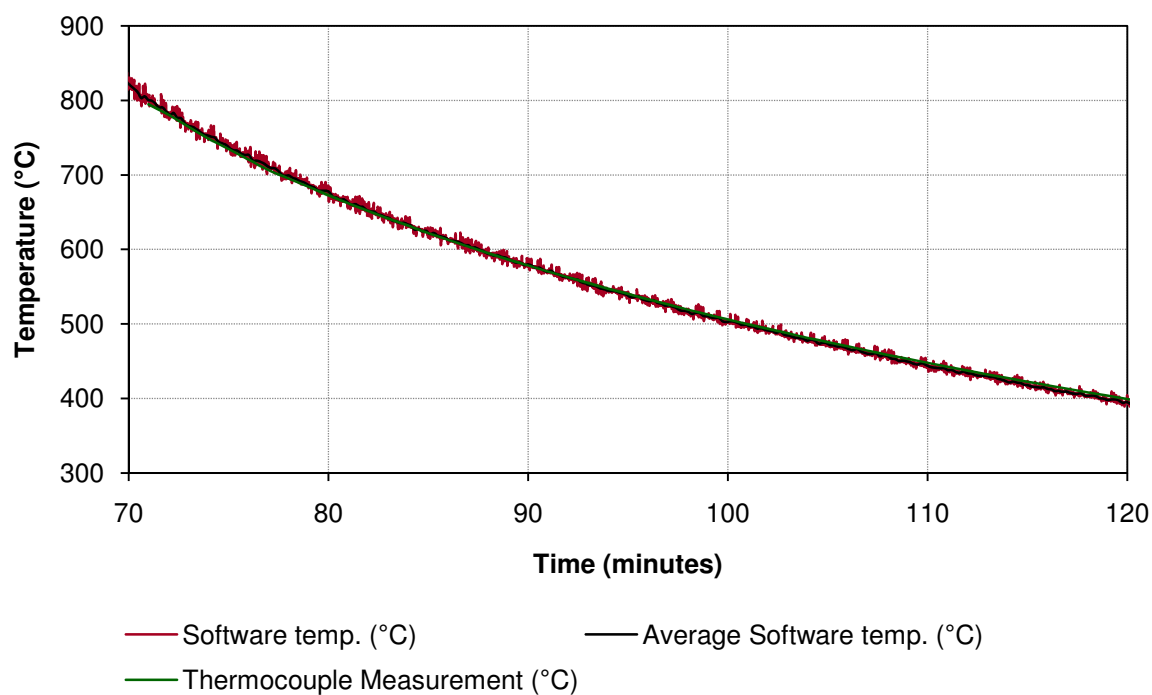


Figure 5.15. SiC mix temperature measurements a) time range 0 – 200 minutes and b) time range 70 – 120 minutes

The thermal profiles from domestic microwave II, RotoSYNTH and Cobham are shown in Figures 5.16, 5.17, 5.18a&b and 5.19. The average of experimental runs at the same power was used.

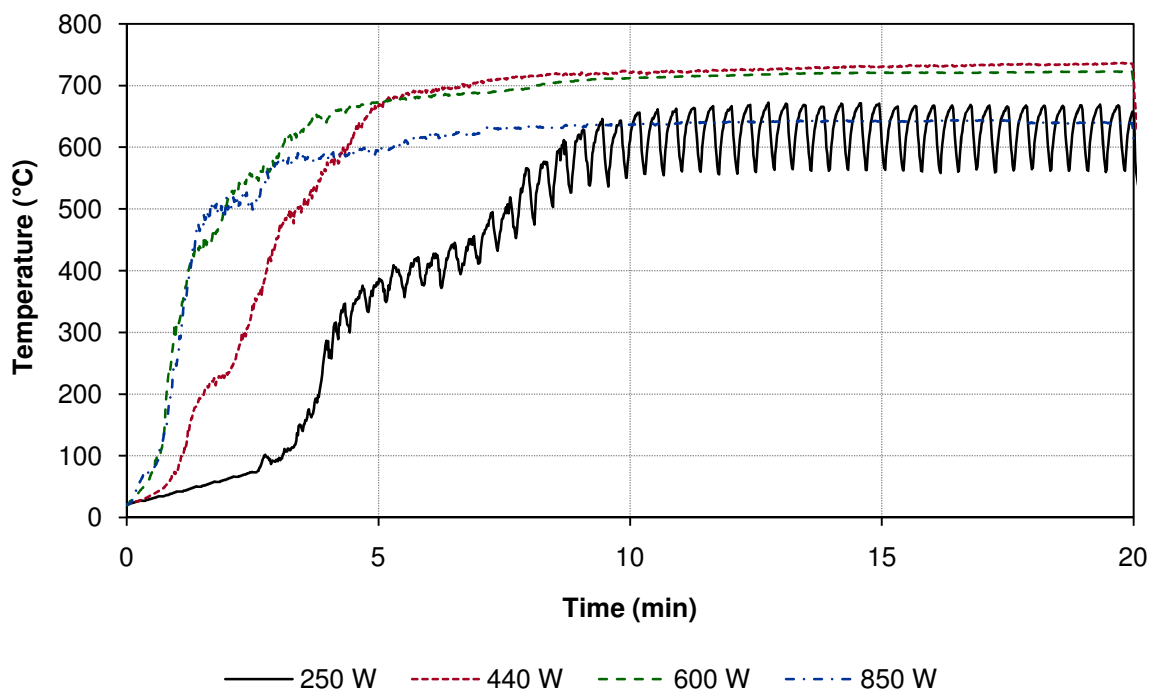


Figure 5.16. Domestic microwave II average thermal profiles at different powers

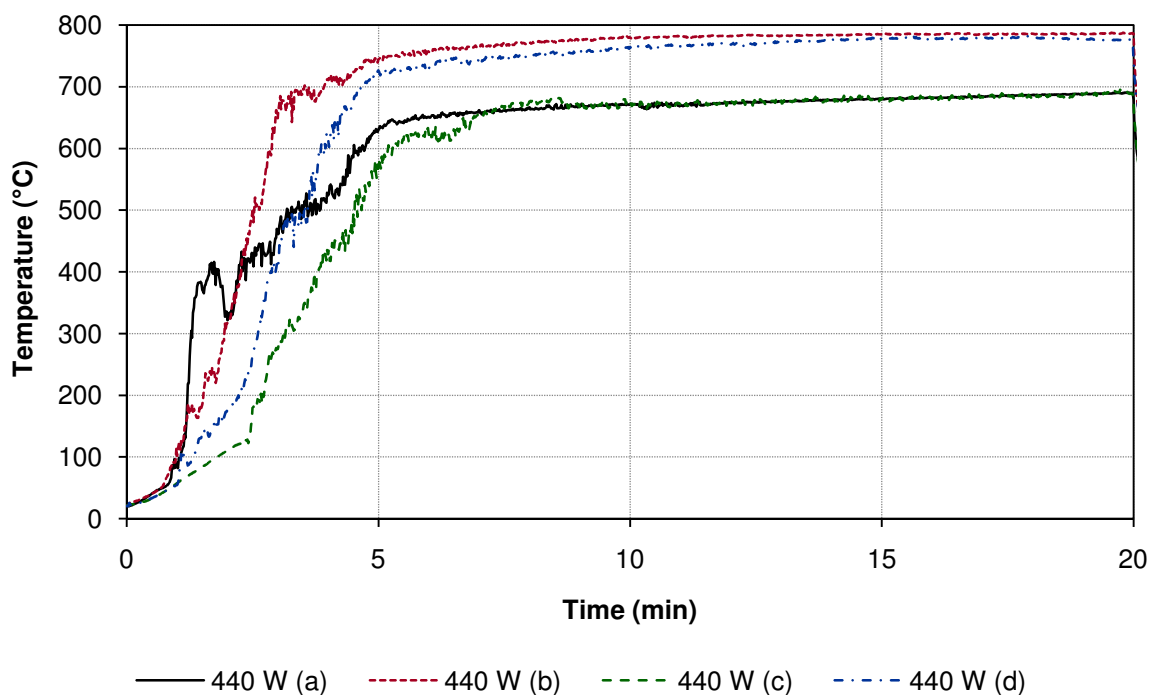
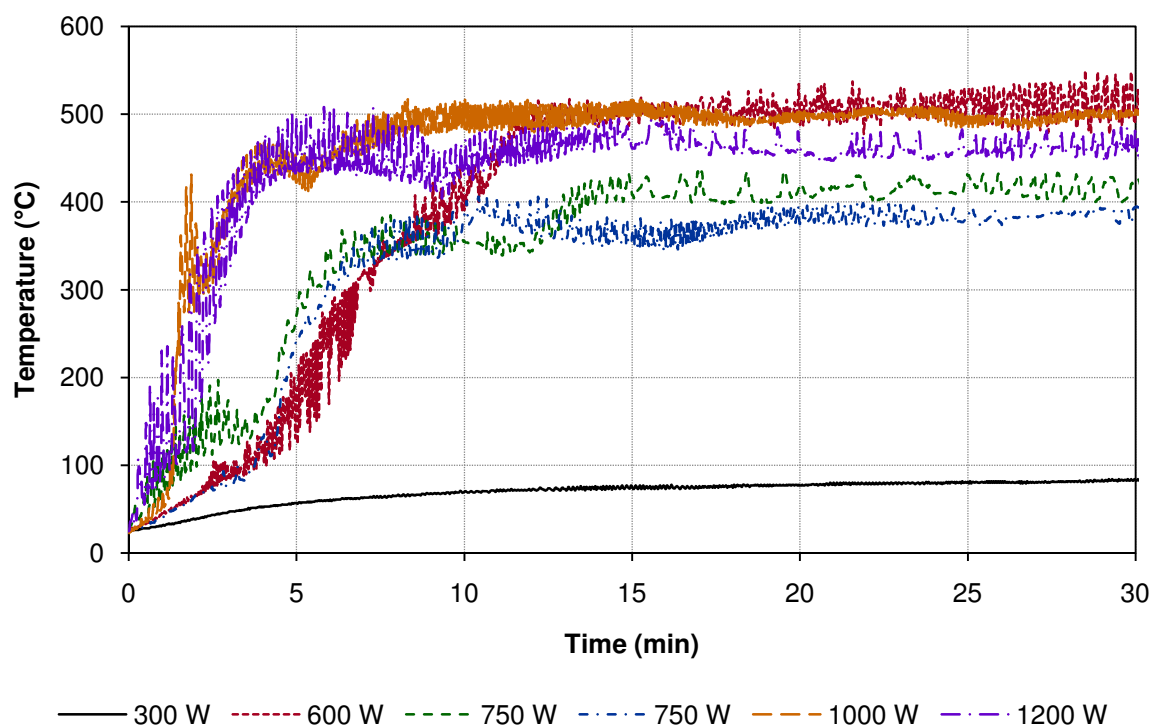


Figure 5.17. Domestic microwave II thermal profiles at 440 W

a)



b)

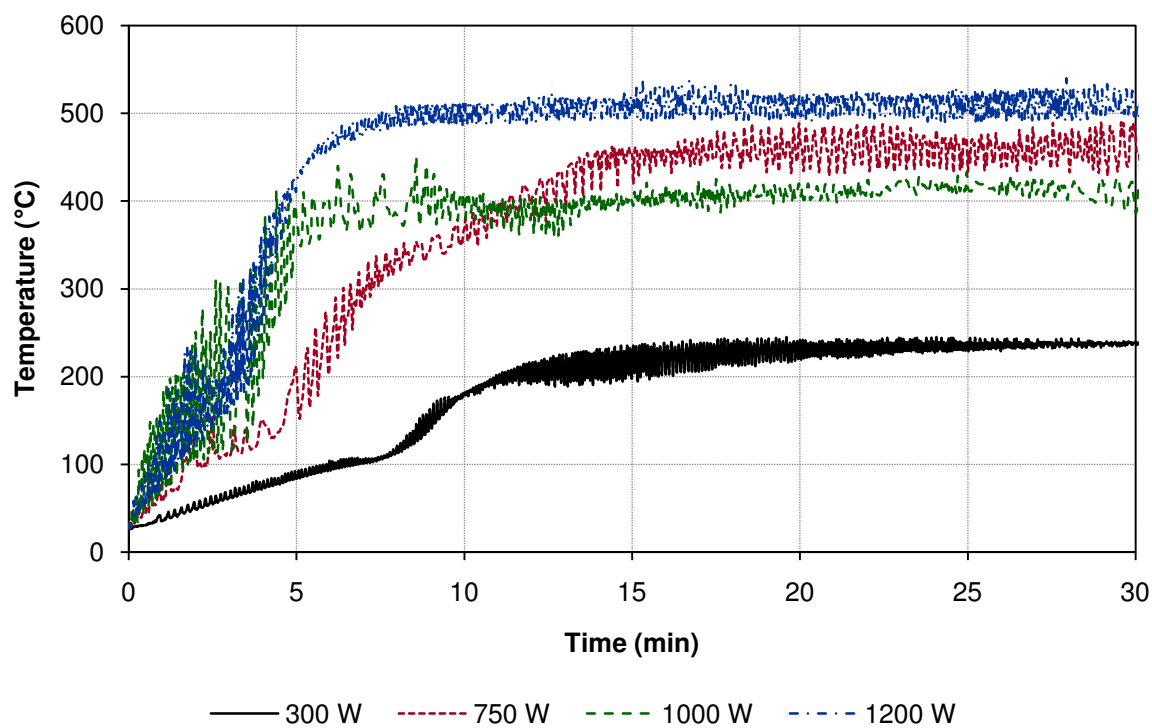


Figure 5.18. RotoSYNTH thermal profiles a) for 50g and b) 100g

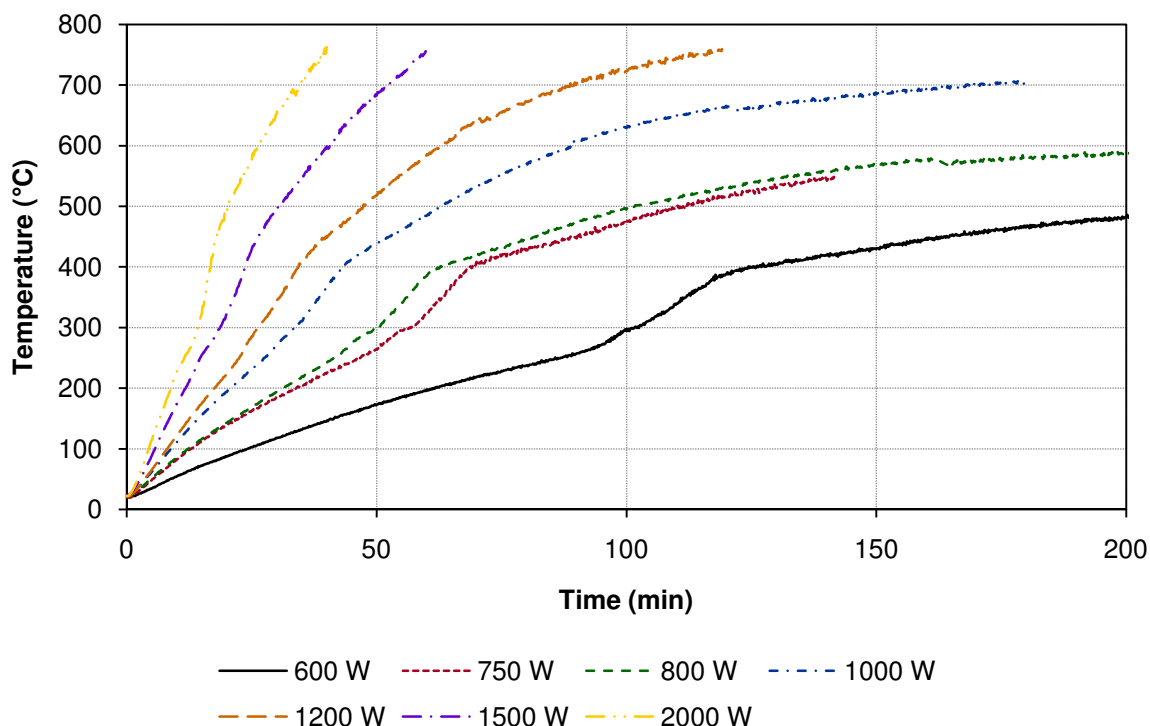


Figure 5.19. Cobham microwave average thermal profiles at different powers

All thermal profiles demonstrate a similar pattern. There are three regions better identified by the RotoSYNTH and Cobham microwave experiments. First there is an initial warm up where release of some volatiles was observed followed by a steeper slope where violent generation of gases occurred and then a slower increase of temperature that, depending on the power and duration of the experiment, reached or did not reach a plateau.

The profile of the domestic microwave II shows a pulse-shaped curve at 250 W. This is as a result of how the oven operates and varies its power. At higher power levels there is a continuous supply of voltage to the magnetron, and therefore the sample under investigation is exposed to a continuous microwave field for the entire duration of the experiment. Different power levels are achieved by varying the amount of voltage. At 250 W and below, it is the magnetron that is turned on and off, instead, creating this pulse effect.

The thermal profiles of the domestic microwave II showed differences during repeated runs, especially during the first minutes. This is illustrated in Figure 5.17 for 440 W. Differences in repeated measurements at short durations is supported by the high standard deviation (8%) calculated on the char yields from the domestic microwave I arrangement (Figure 5.9 and Appendix I, Table B). Furthermore, all the thermal profiles obtained for the domestic microwave II show that a plateau was reached at approximately 5 minutes. At this point,

where the temperature stopped increasing, all the volatiles had been released and the heat applied is equal to the heat being lost to the surroundings. However, there are differences in the final temperature reached which varied by up to 150°C (Figure 5.17).

In addition, the generation of gas during the experiments, which signified the start of the rubber degradation, was observed at surface temperatures lower than expected for rubber degradation, i.e. from 300°C onwards. In fact, it was observed at temperatures ranging from 100 – 125°C. This can be due to inaccurate measurements of the temperature. Also the system was static and hot spots observed, so even though the IR-sensor was viewing a surface of lower temperature, a different area within the sample might have been experiencing higher temperatures.

All these differences can be attributed to specific effects; differences between the position of the glassware within the cavity and the use of different, yet almost identical glassware sets between runs. This causes the sample to experience a slightly different electromagnetic field. The inconsistencies observed at shorter durations can also be due to the rapid generation of a large amount of gas that prohibited the direct measurement of the surface temperature. Problems associated with the lack of controllability and reproducibility have been identified in the use of domestic microwaves in organic synthesis and have been reported by Lidström et al. (2001). In the current work, these problems can be due to a number of factors as described below.

In multimode cavities, the sample does not experience a uniform electromagnetic field but rather nodes and antinodes of the electromagnetic waves, and, parameters such as different positions of the glassware (equipment orientation) between each run or the heterogeneity of the sample can make a significant difference. In addition, the non-uniformity of the EMF makes the system prone to the creation of hot spots, which were observed during the experiment. As explained in Section 1.4.7 this occurs when there is variation in temperature within the sample. Provided that the permittivity of the sample increases with temperature increase, the temperature of the specific region of the sample increases rapidly and reaches a critical temperature that makes it much hotter than the rest of the sample. Further, carbonaceous residues left in the flask between runs worsen this problem, since they have high dielectric constant and selectively couple with the EMF.

Figure 5.20 shows the divitrification of the round bottom flask from a domestic microwave I experiment at a hot spot area. The temperature reached during this experiment must have exceeded the softening temperature of the borosilicate glassware, as the borosilicate dreschel head was deformed. This occurs at temperatures between 750 and 800°C (Shelby, 2005). It was suggested that the introduction of a rotary system would reduce the formation of hot spots, and this theory was subsequently tested.

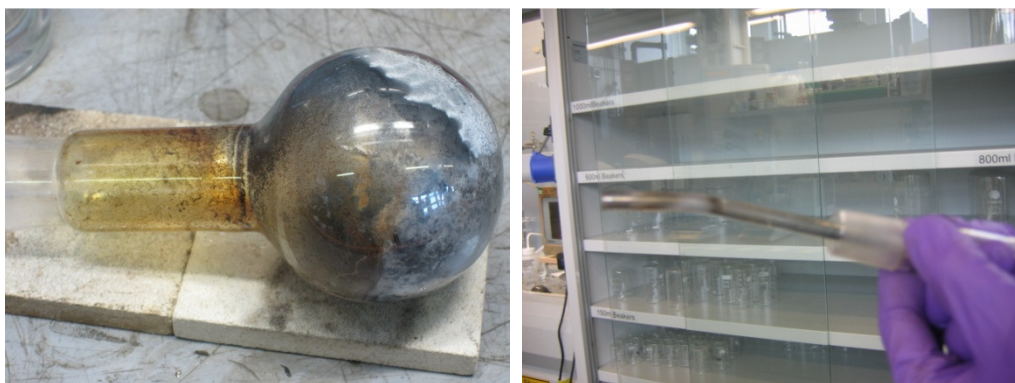


Figure 5.20. Illustration of hot spots and its effects on the glassware

The RotoSYNTH set-up, incorporating a rotary system, generated thermal profiles with pronounced temperature fluctuations, especially at high powers and in the middle area where the rubber degradation occurs. Irrespective of the rotation, hot spots were still observed during the experiment. These were not localised however and evidence of non uniform heating was obtained by the visual examination of the char produced post-pyrolysis (Figure 5.21).



Figure 5.21. RotoSYNTH reactor after pyrolysis

The char presented big lumps on the top and fine particles on the bottom of the reactor. The big lumps might have formed during the onset of devulcanisation. In addition the temperature

readings recorded are likely to differ from the actual temperature of the sample. All the chars, with the exception of those produced at 300 W, were fully pyrolysed, as confirmed by insignificant weight losses observed in TG analysis. This means that whereas some of the RotoSYNTH thermal profiles show maximum temperature of less than 400°C, the samples must have experienced temperature minimums of between 480 – 500°C (Figure 5.18). Differences were expected between the readings and the samples' real temperature as the IR-sensor records the vessel's surface temperature. The sample's heat is transferred to the vessel mainly by convection, however the reactor is not insulated and the cavity has a forced-air cooling flow, so some of the heat will be lost to the surroundings. Furthermore, the rotation of the vessel may have been too fast, resulting in insufficient continuous contact between the sample and the surface of the vessel. In addition, sticky, incompletely pyrolysed rubber had been deposited on the surface of the vessel along with oil residues, which might have increased the inaccuracy of the sample temperature measurements, by providing an insulating layer.

The rubber heated under 300 W power was not completely pyrolysed; 100 g of tyre crumb were reduced to 52.9% (47.1% loss) of their initial weight after 2 hours, whereas 50 g were reduced to 96.4% (3.6% loss) after 3 hours.

The Cobham microwave generated fewer fluctuations in the thermal profiles. The thermal profiles presented in Figure 5.19 are the averages of at least three runs apart from 600 W and 750 W. Identical conditions generated similar profiles, given that microwaves are sensitive to small differences in composition, even from extensive usage of the equipment. Khraisheh et al. (1997) pointed out that microwave apparatus are subject to magnetron aging. In addition, operation of the magnetron for long periods of time may cause the heating of the magnets and consequently the reduction of the magnetic field. This in turn leads to the reduction of the operating voltage, thereby causing the power output to reduce (Khraisheh et al., 1997). Higher power profiles had higher temperature standard deviations, especially in the middle section where the degradation occurs. The graphs obtained show that the three sections are recorded at different temperatures depending on the power. This is expected as the heating rate changes with power, so a similar effect to the TGA change of heating rate is expected (see Section 3.3).

In both domestic microwave systems and the RotoSYNTH (all the configurations that allowed viewing of the chamber), sparks were observed sometimes for a few seconds and

sometimes throughout the experiment. In addition, domestic microwave I encouraged what could be plasma formation that lasted for more than a minute (Figure 5.22). For carbon materials this can occur when the kinetic energy of some of the delocalised π -electrons might have increased to such an extent that enables them to jump out of the material, resulting in the ionisation of the surrounding atmosphere (Menéndez et al., 2010).

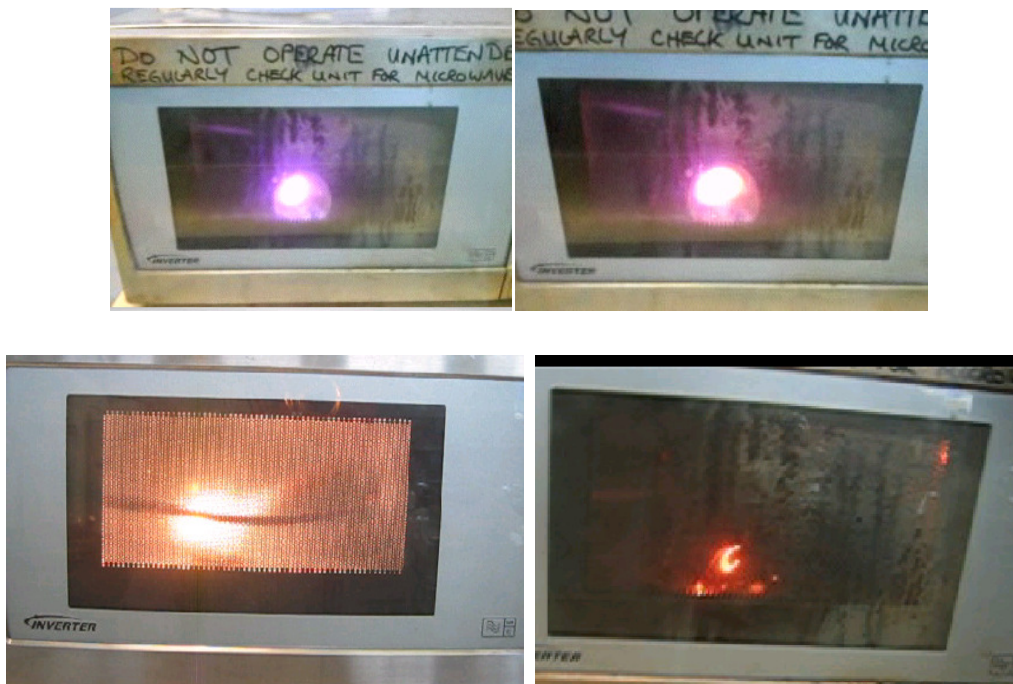


Figure 5.22. Plasma and arching during microwave pyrolysis

Menéndez et al. (2011) also reported plasma formation of different carbon materials undergoing microwave heating, and classified these into two types: ball lighting and arc discharge plasmas. They looked very similar to the ones presented in Figure 5.22, however, in their experiments they only lasted for a few seconds. In addition, the photographic evidence presented in their report used set-ups that included a thermocouple, which would encourage such behaviour, though the authors state that they also observed this phenomenon in the absence of the thermocouple.

The Cobham microwave had the facility to measure and record the forward power (nominal power) and the reflected power – the power not absorbed by the material. By subtracting the former from the latter an evaluation of the power used in the chamber was obtained. Figure 5.23 shows the corresponding net power into chamber at 1000 W with the thermal profile and weight loss. Accordingly the system absorbs less power at the initial warm up but progressively increases as the volatiles start to get released (with the formation of radicals)

and the major weight loss occurs. There is a two peak area that might be related to the degradation of natural and synthetic rubber as observed in the TGA plots reported previously (see Figure 3.9).

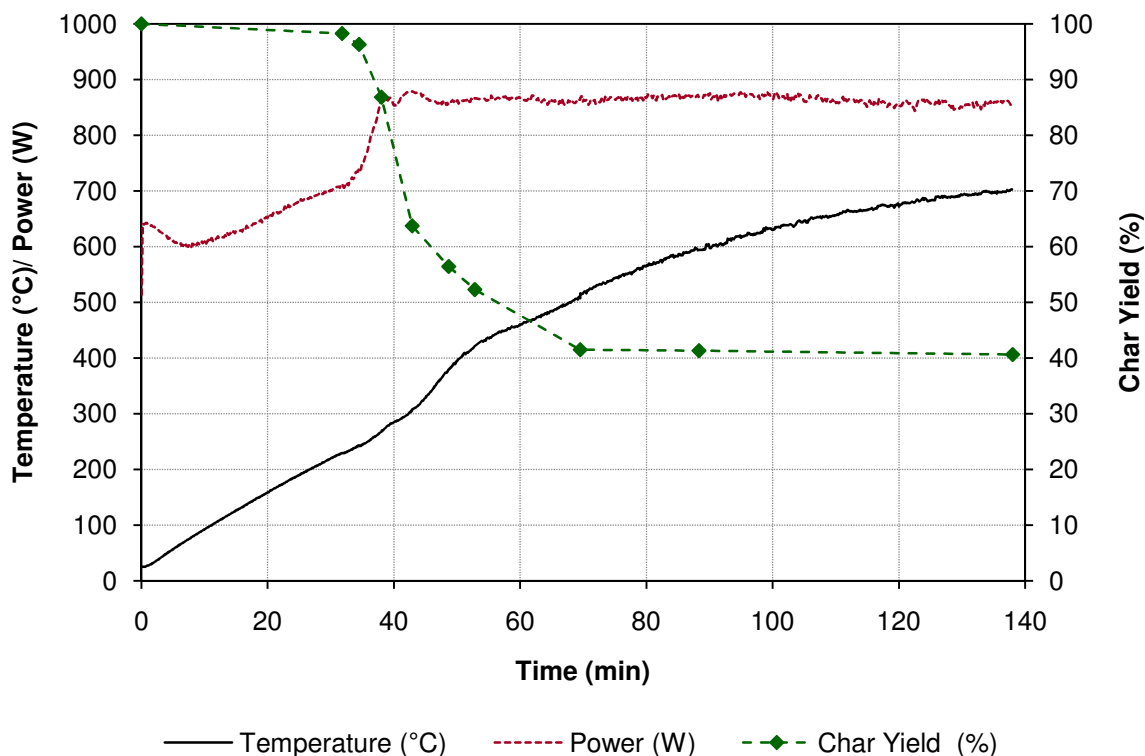


Figure 5.23. Relationship of power and temperature measurements with weight change at 1000 W

The steep slope between 300 and 400°C in the temperature profile in Figure 5.23 corresponds to this degradation area. This is the area where exothermic reactions are expected to occur (see Section 4.4.3.1), along with a change of dielectric properties of the material.

The dielectric properties of the chars generated were examined using the equipment described in Section 5.3.2. The measurements from the network analyser confirmed the change of the complex permittivity from 2 to 8.8 and the change of conductivity from 0 to 0.09 with the major change occurring between 267°C ($\epsilon^* = 2.7$) to 360°C ($\epsilon^* = 7.5$) as shown in Table 5.4. The increase in dielectric properties is expected as the material becomes more carbon concentrated due to the increasing electron mobility via the transfer of the π bond electrons along the aromatic layers (Dodds, 2006).

Dodds (2006) measured the dielectric constant and loss factor at 2.45 GHz of activated carbon to be $\epsilon' = 8.4$ and $\epsilon'' = 1.4$, which give $\epsilon^* = 8.5$ and $\tan\delta = 0.16$, values close to the

ones observed from the chars generated at high temperatures where carbon is the predominant element. In addition, in a review by Menéndez et al. (2010) the $\tan\delta$ values of charcoal, carbon black and activated carbon were stated as between 0.11 – 0.83 at room temperature. These values are comparable to or higher than the $\tan\delta$ value of water (0.1), which is commonly known as a good microwave absorber (Lam & Chase, 2012). The $\tan\delta$ values calculated from the dielectric measurement experiments in this work are in the lower range as stated by Menéndez et al. (2010) possibly because of trapped air (the chars were not ground to ensure dense packing).

Table 5.4. Dielectric Properties

	ε^*	$\tan\delta$	σ	End Temperature (IR-sensor)
Sample F	2	0.03	0	0
CM _F ,1000_31	2	0.03	0	247.6
CM _F ,1000_35	2	0.03	0	258.3
CM _F ,1000_38	2.7	0.06	0.01	267.6
CM _F ,1000_41	5.2	0.08	0.03	304.8
CM _F ,1000_47	7.5	0.08	0.03	360.3
CM _F ,1000_50	7.5	0.08	0.03	395.7
CM _F ,1000_70	8.4	0.10	0.02	495.0
CM _F ,1000_88	8.4	0.10	0.02	602.0
CM _F ,1000_138	8.8	0.13	0.09	702.6

It should be noted that these values are approximate as it was very difficult to achieve an exact match from the simulations and especially the relationship between ε^* and σ . This is because these two parameters are connected with each other in a way that a combination of a higher $\tan\delta$ and lower σ would give a similar result to a lower $\tan\delta$ and a higher value of σ (Balanis, 1989). In addition, for the simulations it was assumed that the parameters do not change in the range of frequencies used, even though they would change slightly as shown in the plots generated from the network analyser for the materials under investigation. Figure 5.24, for rubber F placed in the centre of the waveguide, is a typical example.

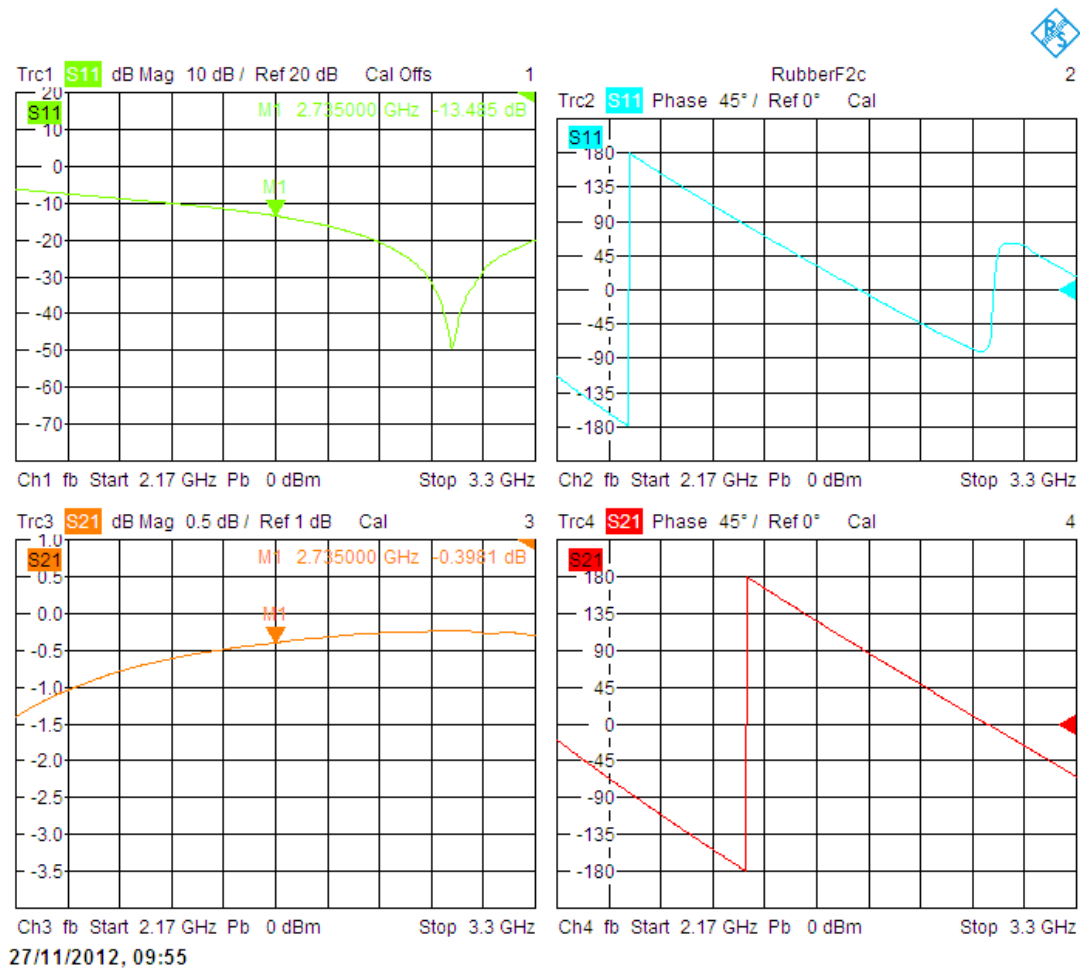


Figure 5.24. Typical plots obtained by the network analyser showing the amplitude and phase of Return and Insertion Loss. Here shown for rubber F placed in the centre of the waveguide

Combining the observations from Figure 5.23 and Table 5.4, even though the material becomes more microwave-responsive the heating rate starts to decline. This is probably due to thermal energy losses occurring in the surroundings (due to conduction, convection and radiation of heat from the crumb to the quartz vessel, insulation, casing etc.). The external aluminium casing of the reactor reached a temperature of 100°C at high internal temperatures indicating these losses to the surroundings.

It must be highlighted that all values used in the dielectric measurements were recorded at room temperature, and it is possible that at the high temperatures of the experiments the dielectric values will vary (Meredith, 1998).

In addition to the sample F and chars generated from it, the dielectric parameters of samples D and E were also measured. Samples D and F, both originated from whole passenger tyres showed the same responses ($\epsilon^* = 2$, $\tan\delta = 0.03$ and $\sigma = 0$). Vulcanized rubber measured at

40°C and 2.45 GHz had $\varepsilon^* = 2.6$ (Komarov, 2012). Sample E was less responsive with $\varepsilon^* = 1.5$, $\tan\delta = 0.02$ and $\sigma = 0$. Sample E was crumb from the tread of car passenger tyres that were contaminated with fibres like nylon which are expected to be less microwave-responsive.

In the current work, a statistical model was going to be formed to examine the relationship between the independent variables, in this case time and power, with the dependent variables, such as char characteristics, as in Chapter 4. To achieve this, the independent variables of the process would be assigned values so that the correlation between them would be zero. However, the very nature of microwaves made this impossible for this setting. For example, in reference to Table 4.3, consider a power setting of minimum 600 W and maximum 2000 W and time range of minimum 27 minutes and maximum 265 minutes. The combination of 600 W, 265 minutes (-1, +1) and 2000 W and 27 minutes (+1, -1) is achievable. A combination of 600 W, 27 minutes (-1, -1), however, would result in non-pyrolysed rubber whereas 2000 W and 265 minutes (+1, +1) would probably not be achieved as the cavity will be heated up to a level high enough to trigger the high temperature alarm. This comes as a result of the non-linear relation and dependence of the change of dielectrics during the process.

Other authors have tried to use response surface methodology on microwave pyrolysis; Lei et al. (2011) used power, time and temperature as independent variables and Ren et al. (2012) used power and temperature to find a relationship between these variables and the oil, char and syngas pyrolysis yields of distillers dried grain with soluble and Douglas fir sawdust pellets respectively. Relationships were achieved with regression coefficients ranging between 83 and 95% for the former and 99 and 100% for the latter. However and as noted in the papers the duration value was recorded after the ideal temperature was achieved, which by definition makes this variable dependent.

The three sections from the thermal profiles for the Part I set of 21 experiments were manually divided to (i) the initial warm up – the first linear section (ii) the main volatile release section and (iii) up to 600°C. The average power absorbed by the sample was then calculated for each section. Figure 5.25 shows the relationship between the power and the time. All sections form power relations with the equations given in Table 5.5.

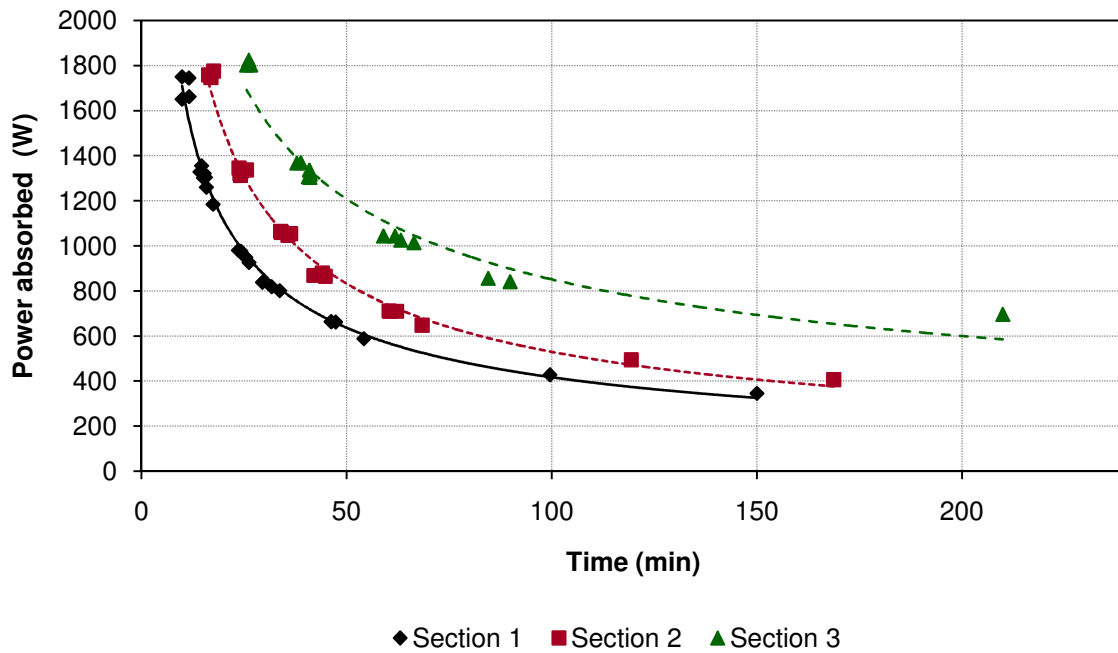


Figure 5.25. Cobham Microwave system power absorption and time relationship

The power has a linear relationship with the heating rate (Figure 5.26). Huang et al. (2008) determined a linear relationship between the power and the heating rate (dT/dt) from a series of experiments using a single mode microwave to pyrolyse rice straw using powers between 50 W – 500 W. As the thermocouple can interfere with the electromagnetic radiation, it was placed at the bottom of the sample holder to give an indication of the nearby thermal effects and the heating rate was calculated from the slope of the linear regression of temperatures from the 1st till the 4th minute. Huang et al. (2008) noted that to initiate a rise in temperature sufficient power input is needed. Similarly, from the equations below, for a heating rate equal to zero there is a certain amount of power required for each section. For section 3, it was not possible to achieve 600°C as a final temperature using nominal powers of 600 W and 750 W, as they only provided average power to the chamber of 492 W and 588 W. These values were below the y value of 616.31 W, derived from equation in Table 5.5. Figure 5.19 shows this effect.

Note that for section 2, the dielectric properties change drastically (Table 5.4) therefore a lower R^2 is obtained as shown in Table 5.5.

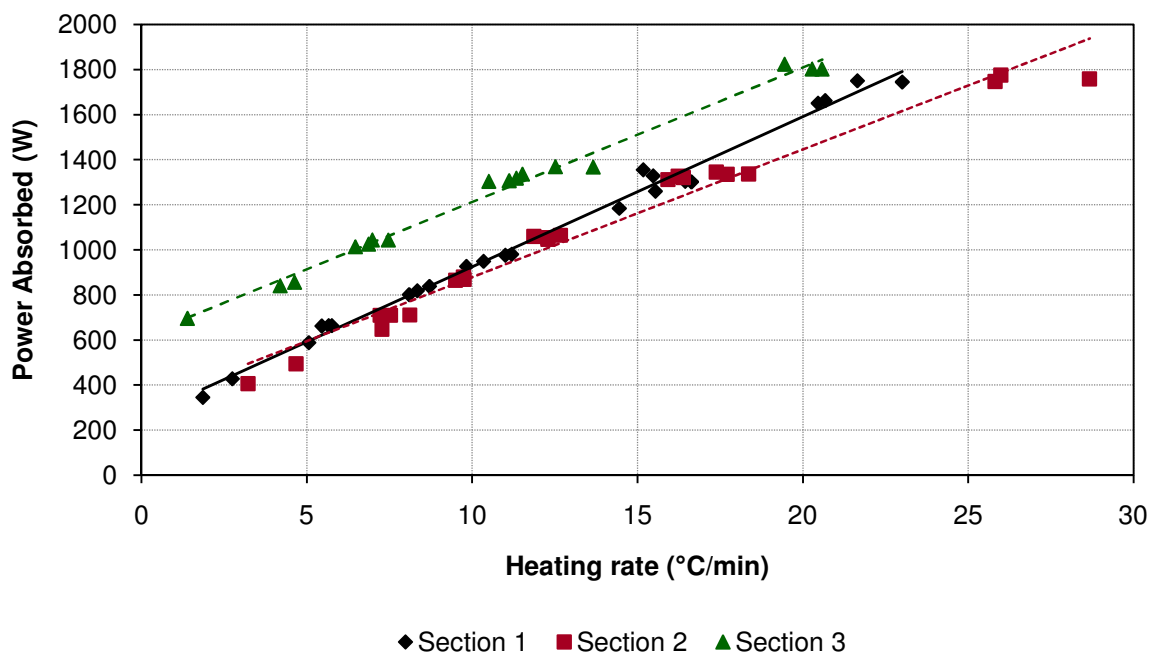


Figure 5.26. Cobham Microwave system power and heating rate relationship

Table 5.5. Empirical relationships between power vs. time and power vs. heating rate

Power vs. Time			Power vs. Heating Rate	
	Equation	R ²	Equation	R ²
Section 1	$y = 6707x^{-0.602}$	0.9958	$y = 67.743x + 250.11$	0.9929
Section 2	$y = 10720x^{-0.653}$	0.9911	$y = 56.723x + 310.64$	0.9707
Section 3	$y = 8711x^{-0.505}$	0.9428	$y = 59.651x + 616.31$	0.9903

The chars generated from sample D in Part I of the Cobham Microwave experiments were characterised, and the results obtained are reported in Table 5.6. The toluene extractables transmission confirmed that all chars had been completely pyrolysed. The surface areas ranged from 76.2 to 96.3 m²/g. Identical runs at 1500 W and 41 minutes had average surface area of 84.5 m²/g with standard deviation of 2.25. Overall, the longer the duration of the experiment and the higher the temperature reached, the lower the surface area. The ash content ranged between 18.61 and 19.40% with no obvious trend clearly observed, as the chars were completely pyrolysed and any differences could arise from minor crumb composition variations. The pH-values were between 8.23 and 10.02 – the longer the duration and the higher the end temperature, the higher the pH-value, as expected from the discussion in Section 4.3.3.

Table 5.6. Cobham Microwave (Part I) experimental conditions and results

ID	Last Average Temp. (°C)	Surface Area (m ² /g)	Ash Content (%)	pH-value	Transmission of Toluene Extracts (%)
CM _D ,2000_27	602	83.6	18.61	9.35	99.5
CM _D ,2000_33	697	78.0	18.74	9.49	99.7
CM _D ,2000_40	764	76.2	18.70	9.60	99.9
CM _D ,1500_40	622	86.1	18.96	8.99	100.0
CM _D ,1500_41	602	83.9	18.91	9.17	99.5
CM _D ,1500_41	605	87.1	18.81	9.16	99.3
CM _D ,1500_41	604	82.5	18.90	9.13	99.4
CM _D ,1500_53	700	83.0	18.93	9.55	99.8
CM _D ,1500_60	754	79.5	18.96	9.53	99.8
CM _D ,1200_66	599	89.8	18.93	8.68	99.7
CM _D ,1200_70	653	87.6	19.23	9.22	99.8
CM _D ,1200_90	700	85.9	18.95	9.27	99.6
CM _D ,1200_119	759	78.1	19.02	10.02	99.7
CM _D ,1000_90	589	92.0	19.40	8.94	99.8
CM _D ,1000_120	671	87.9	19.35	9.39	99.7
CM _D ,1000_180	707	84.9	19.29	9.28	99.5
CM _D ,800_97	499	96.3	19.20	8.23	99.5
CM _D ,800_160	587	95.5	19.07	8.79	99.8
CM _D ,800_210	592	90.2	19.39	9.41	99.6
CM _D ,750_142	552	90.1	19.20	9.53	99.6
CM _D ,600_265	510	91.1	19.31	9.19	99.7

The weight loss experienced by samples of crumb F in Part II of the Cobham Microwave experiments as a function of temperature was compared to experiments with the same crumb but using the Carbolite thermal furnace used in Chapter 4 (Figure 5.27). Three hundred grams were pyrolysed at different end temperatures using 6°C/min heating rate. The nominal end temperatures were related to the ones assumed to be experienced by the sample using the thermocouple data from Section 4.3.3.1 (Table 5.7).

Table 5.7. End temperatures for conventional thermal pyrolysis

Nominal End Temp. (°C)	313	358	390	435	468	494	535	625	700
End Temp. (°C)	250	300	350	400	425	450	500	600	673

The results, as shown in Figure 5.27, would imply possible differences in the decomposition temperature. However, it should be noted that the temperature measurements (especially

using the IR sensor) would show lower values than the real ones, for the reasons highlighted previously, as well as that emissivity changes with temperature. In this case, the IR sensor was calibrated to high temperatures – at lower temperatures the recorded value may be even less than the actual value, and this is why the profiles possibly do not match. Similarity between the char characteristics show that the same results are obtained by both forms of heating.

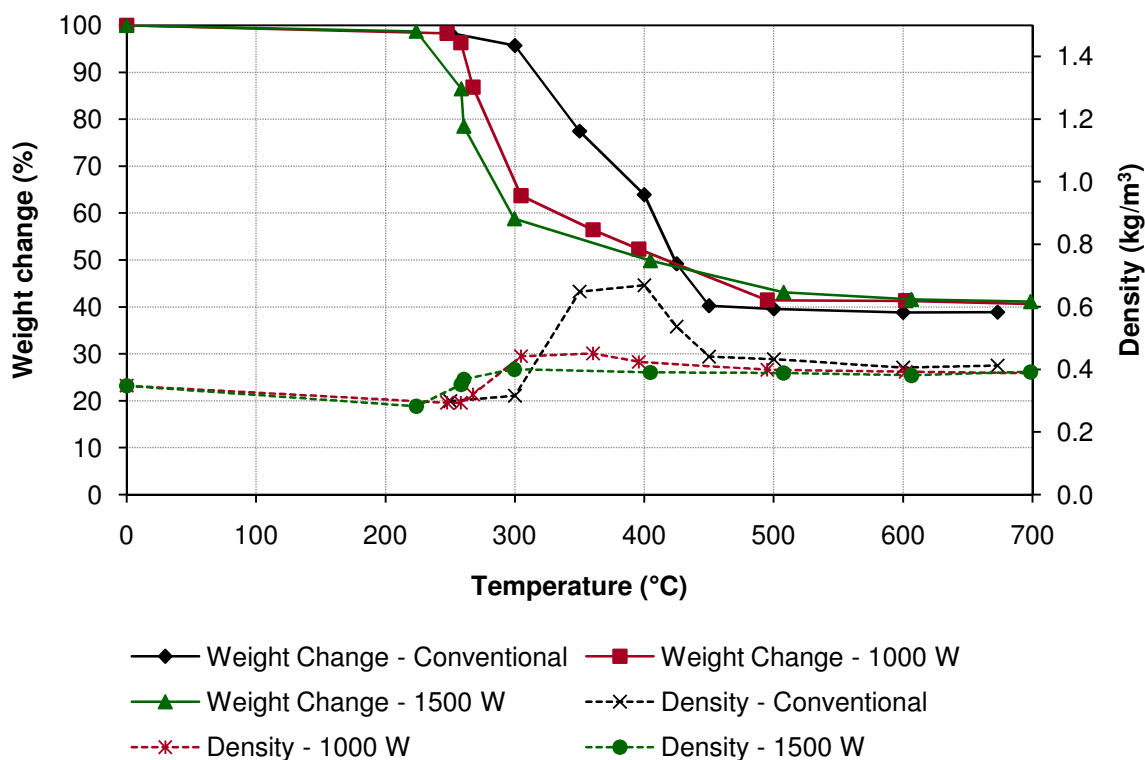


Figure 5.27. Weight change and density of chars produced using conventional and microwave pyrolysis at 1000 W and 1500 W (Sample F)

However the differences in the density of the material is notable as the carbonaceous residue formed from conventional means has much higher density at the point where most volatiles are removed compared to the ones from microwaves. This could support the volumetric heating mechanism by microwaves, which heat from the inside out as opposed to thermal heating from the outside to inside by convection. In any case, care should be taken when direct comparisons are made as even though the design is similar, the volumes of the reactors are different, and different sample masses were used. The question is posed as to whether this effect is really a microwave effect or if it is down to the design and the conditions of the experiment.

Selected oils obtained from the earlier mentioned Cobham Microwave Part I experiments were also characterised using CHNS analysis, calorific value measurements, FTIR and GC/MS. Oils derived from tyre pyrolysis are very complex, reflecting the presence of the various polymers and chemical additives associated with different degradation temperatures, leading to a number of reactions occurring in parallel and in series (Williams & Besler, 1995). Thus, the highly heterogeneous nature of oil makes it difficult to analyse (Galvagno, 2002).

All spectra obtained using FTIR and GC/MS were very similar, irrespective of the different conditions. Significant differences between the oils would have been expected if the experiments had been done at end temperatures lower than the complete pyrolysis; however all oils examined were produced at temperatures higher than 500°C.

The oils were dark brown coloured with intense odour. Sulfur is present in tyre oils (Table 5.8) mostly in theophene derivative compounds and contributes significantly in the oils' malodour (Pakdel et al., 2001). The CHNS analysis gave results almost the same as the ones observed by Laresgoiti et al. (2004) and Cunliffe & Williams (1998a), though the content of nitrogen was lower. The high calorific value was confirmed (42.3 MJ/kg).

Table 5.8. CHNS analysis and calorific value of tyre oil (600°C end temperature)

Reference	C (%)	H (%)	N (%)	S (%)	Calorific Value (MJ/kg)
In current work	87	11	< 0.1	1.6	42.3
Laresgoiti et al., (2004)	86.2 ± 1.0	10.2 ± 0.1	0.4 ± 0.03	1.2 ± 0.1	42
Cunliffe & Williams (1998a)	87.9	10.1	0.5	1.3	41.2

The oil is a mixture of both aliphatic and aromatic chemicals. FTIR spectroscopy (Figure 5.28) confirmed the presence of alkanes by the intense peaks at 2960 – 2850 cm⁻¹, 1470 – 1450 cm⁻¹ and 1370 – 1350 cm⁻¹. The presence of alkanes and aromatics groups is indicated by the peaks between 675 – 900 cm⁻¹ and around 1600 cm⁻¹. Table 5.9 gives a summary of the peaks possible assignments.

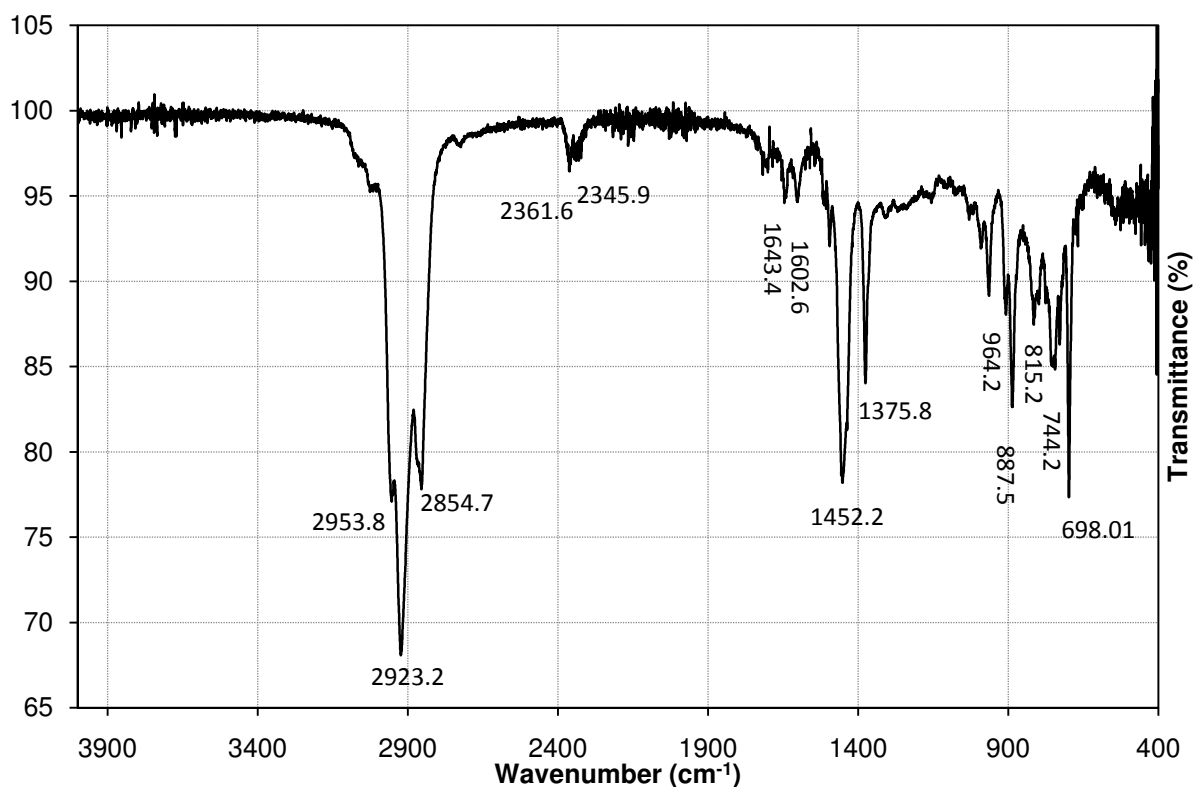
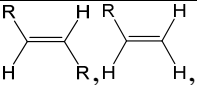
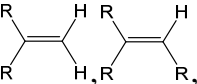
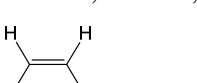
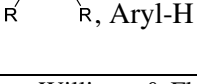
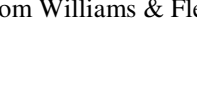


Figure 5.28. FTIR spectrum of oil generated at 1500 W

Table 5.9. FTIR spectrum peak assignment

Peak absorption (cm ⁻¹)	Possible Group Assignment	Band (cm ⁻¹)*	Comments
> 3000	$\text{>C=C}^{\text{H}}/\text{Aryl-H}$	3040-3010	C-H stretching (alkene and aromatic C-H) - often obscured by the stronger bands of saturated C-H below 3000 cm ⁻¹
2953 2923 2854	-CH_2 & -CH_3	2960-2850	-C-H stretching (Saturated C-H)
2346	O=C=O	2349	Appears in spectra due to inequalities in path length
1643	>C=C< , Dienes, trienes	1680-1620, ~1650	Alkenes
1602	Aromatic Rings/dienes	~1600	Aromatic Compounds/alkenes
1452	-CH_2 & -CH_3	1470-1430	-C-H deformation (Saturated C-H)
1376	-CH_3	1390-1370	-CH_3 symmetrical deformation (Saturated C-H)

Peak absorption (cm ⁻¹)	Possible Group Assignment	Band (cm ⁻¹)*	Comments
964		970-675	C-H out of plane deformation (alkene and aromatic C-H)/ aryl-H vibration
875			
815			
744			
698			

* Band frequencies from Williams & Fleming (1995)

The complexity of the oil composition was verified by GC/MS analysis, which presented a large number of different peaks (more than 800), most of them with very small peak areas (Figure 5.29).

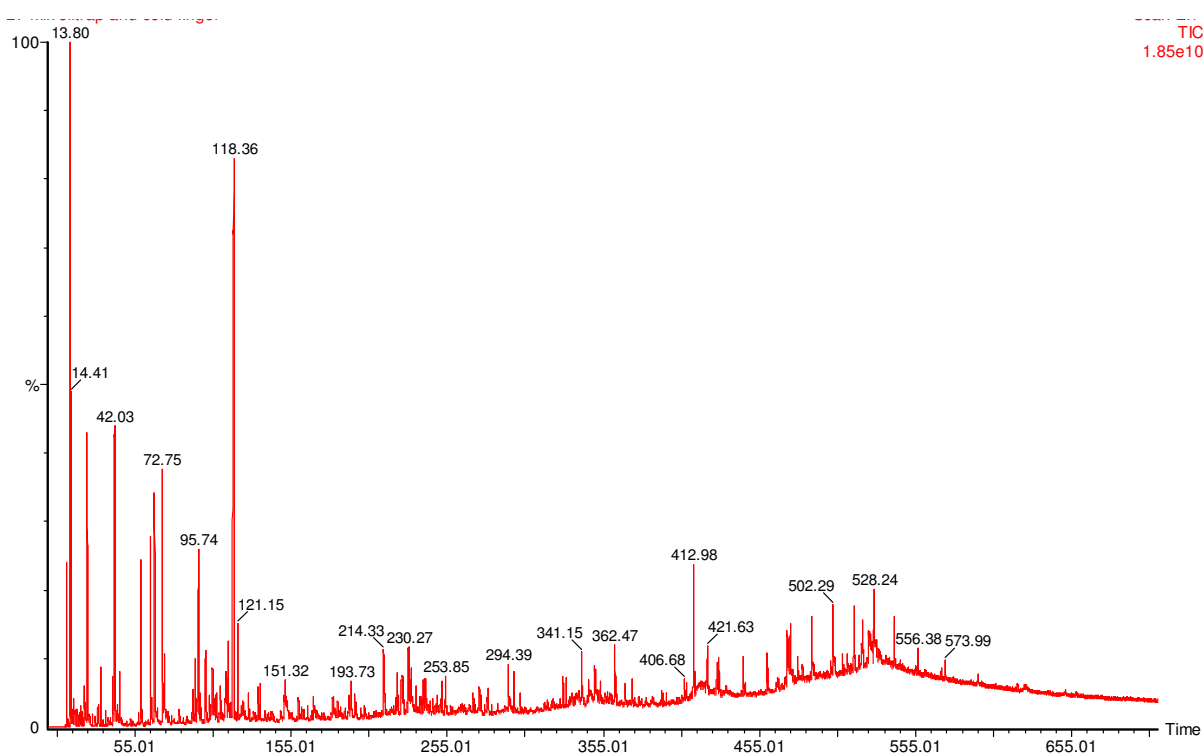


Figure 5.29. GC/MS spectrum of oil generated at 2000 W

Table 5.10 presents the possible assignments of the peaks with percentage area more than 1%. The most abundant peak was identified as C₁₀H₁₆, possibly in the form of limonene (both

enantiomers) (15.4%). Other aliphatic compounds present in the oil mixture included C_5H_8 possibly in the form of 2-methyl-1,3-butadiene (isoprene), which is the monomer of natural rubber (polyisoprene), and 4-ethenylcyclohexene. The most abundant aromatic compounds were toluene, xylene/ethylbenzene and styrene. In addition, 6PPD, which is a compound most commonly used in tyre formulations as an antioxidant, was also identified. The presence of the most abundant chemicals can be attributed to the decomposition of the main rubber constituents of tyres (natural rubber, polybutadiene and SBR).

Table 5.10. GC/MS spectrum peak assignment

Retention Time (min)	Percentage Area (%)	Molecular Formula	Possible assignment
13.8	1.6	C_5H_8	3-methyl-1,2-butadiene (Isoprene), 2,3-pentadiene, 1,3-pentadiene
24.5	1.2	C_6H_6	benzene, 1,5-hexadiyne
42.0	2.8	C_7H_8	toluene, 1,3,5-cycloheptatriene
58.9	1.0	C_8H_{12}	4-ethenylcyclohexene
65.0	1.8	C_8H_{10}	ethylbenzene
67.6	2.3	C_8H_{10}	1,3-dimethylbenzene (m-benzene), p-xylene, o-xylene, ethylbenzene
72.7	2.0	C_8H_8	styrene
95.7	1.6	$C_{10}H_{16}$	D-limonene, 4-ethenyl-1,4-dimethylcyclohexene
100.2	1.2	C_9H_{10}	methylstyrene
118.4	13.8	$C_{10}H_{16}$	Limonene
413.0	1.6	$C_{18}H_{24}N_2$	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)

Isoprene and limonene are the two main products generated from the thermal degradation of natural rubber (Chien & Kiang, 1979; Groves et al., 1991; Chen & Qian, 2002). The degradation of natural rubber is predominantly initiated by a β -chain scission with respect to the double bonds of the polymer. This generates two allylic radicals, stabilised by resonance, as shown in Figure 5.30 (Golub & Gargiulo, 1972). Isoprene can then be formed mainly by unzipping mechanism of the polymer chain with regeneration of the original radical (Figure 5.31) (Groves et al., 1991). Limonene forms by either a monomer recombination via Diels-Alders mechanism (Groves et al., 1991; Chen & Qian, 2002) or intramolecular cyclisation followed by scission (Golub & Gargiulo, 1972) (Figure 5.32). It is possible that both mechanisms occur, but depending on the conditions of the experiments one is favoured (Pakdel et al., 2001). In this case, limonene formed by Diels-Alder is possibly the favoured

mechanism as it results in reduction of the amount of isoprene, explaining the difference in abundance of the two chemicals present in the oil. Limonene is considered an important chemical as it finds wide industrial applications. In fact, it is the main ingredient of household cleaning agents and industrial hand cleaners (Pakdel et al., 1991).

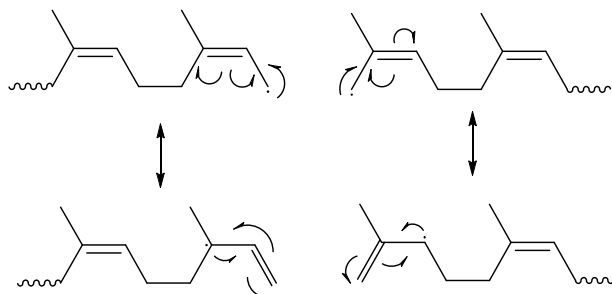


Figure 5.30. Resonance of radicals formed by β scission of natural rubber

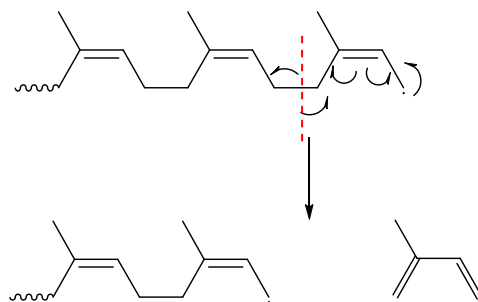


Figure 5.31. Monomer Formation

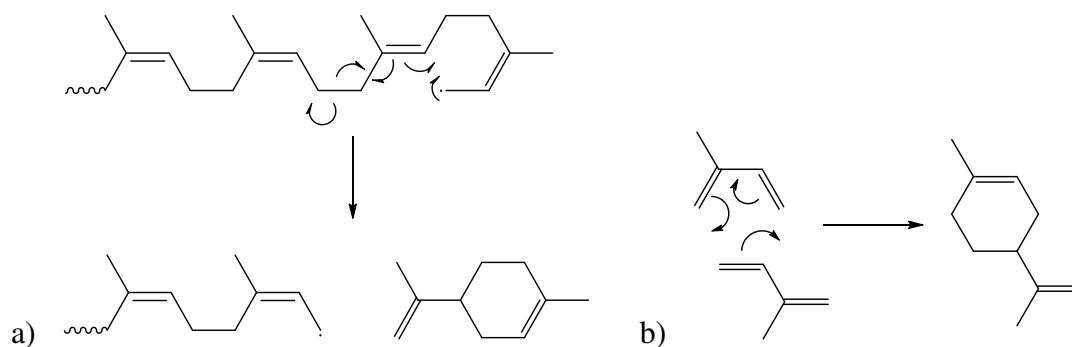


Figure 5.32. Limonene formation mechanism by a) intramolecular cyclisation followed by scission b) Diels-Alder reaction

Other products can be attributed to carbon-carbon scissions followed by intramolecular hydrogen or group transfer, or radicals formed from α -scission and second carbon-carbon bond cleavage, which leads to a stable product, for example formation of ethene (Figure 5.33) (Chien & Kiang, 1979).

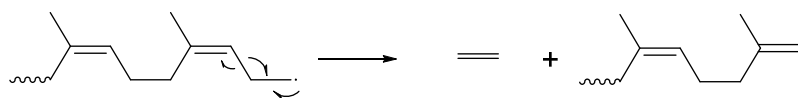


Figure 5.33. Ethene formation from natural rubber

In addition, minor quantities of benzene, toluene and xylene have been observed during the thermal degradation of natural rubber using pyrolysis/gas chromatography especially at high temperatures, possibly due to Diels-Alder reactions between short chain alkenes followed by dehydrogenation (Chen & Qian, 2002).

The thermal degradation of polybutadiene, like natural rubber, is also possibly initiated by β -chain scission with respect to the double bonds. Butadiene and 4-ethenylcyclohexene have been identified as the main products formed (Golub & Gargiulo, 1972; Choi, 2001). The mechanisms of their generation are likely to resemble the ones shown in Figures 5.31 & 5.32 respectively, with the methyl group on the polymer chain substituted with hydrogen.

Chen & Qian (2000) have studied the thermal degradation of a styrene-butadiene rubber using pyrolysis-gas chromatography (py-GC). There are various carbon-carbon bonds that are susceptible to β -chain scission in this polymer, some with respect to 2 double bonds and some with respect to one, the first being the more favourable to occur (Figure 5.34).

The main products identified by Chen & Qian (2000) from the corresponding content areas of the chromatograph for temperature range between 510 and 600°C were methane (7.59%), C₂-components (20.67%), C₃-components (5.42%), C₄-components (3.26%), 4-ethenylcyclohexene (8.93%), xylene (4.46%), styrene (3.76%) and indene (1.31%). Similarly, Choi (2002) studied the thermal degradation of SBR rubbers with differing microstructures using py-GC as well and identified the major products according to their relative peak intensities of the chromatograph as butadiene (31.4 – 41%), 4-ethenylcyclohexene (6.9 – 14.2%) and styrene (6.2 – 30.2%). The differences of component percentages between the two authors highlight the importance of the microstructure of the SBR.

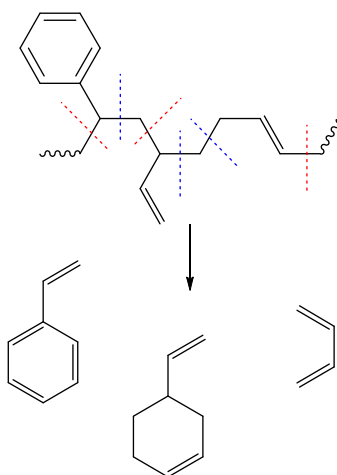


Figure 5.34. SBR β -chain scission possibilities (red - with respect to 2 bonds, blue - with respect to 1 bond) and the main products from SBR degradation (Adapted from Choi, 2002)

The styrene was produced mainly by the styrene unit of the polymer. This was confirmed by Choi (2002), who observed increased styrene presence from the polymers with higher styrene content. In addition, other aromatics like toluene can be formed by direct bond scission from SBR (Kwon & Castaldi, 2009). However, the presence of aromatics is not just because of the aromatic nature of the polymer. Like in the case of natural rubber and polybutadiene, aromatic compounds can be generated by the dehydrogenation of cyclised molecules, formed possibly by Diels-Alder mechanisms. Styrene, for example, can also be formed by dehydrogenation of 4-ethenylcyclohexene (Figure 5.35) (Chen & Qian, 2000). In fact, hydrogen is one of the main gases identified from tyre pyrolysis (21.7 vol% by Kyari et al., 2005).

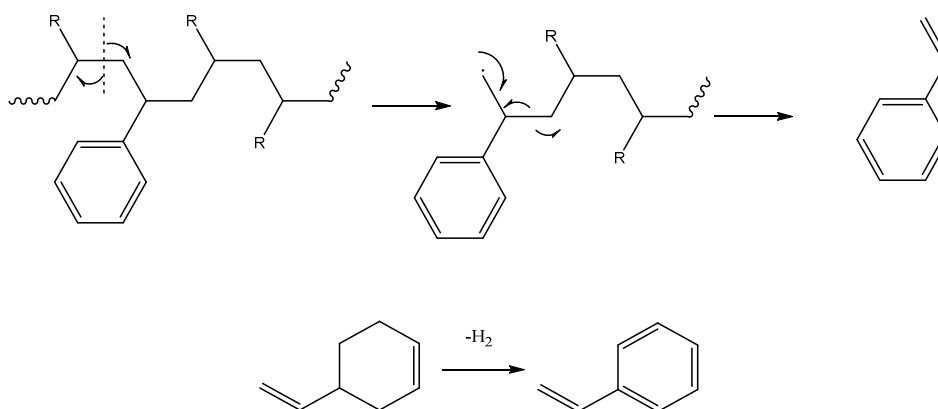


Figure 5.35. Possible mechanisms of xylene formation from SBR degradation

Thus, in the case of tyre pyrolysis, products from the individual polymers are expected to be generated as seen from the GC/MS results. The major compounds identified from the oil

derived from microwave pyrolysis are compared to the ones identified by other authors using conventional tyre pyrolysis as well as to the major components of oil generated from the CP_{II,D}16 experiment (Chapter 4).

Table 5.11. Major tyre pyrolysis oil components from different research

	Current work		Arabiourrutia et al. (2007)	Kyari et al. (2005)	Laresgoiti et al. (2004)	
	Rotary Furnace (Microwave)	Rotary Furnace (Conv.)	Conical spouted reactor	Fixed Bed Reactor	Autoclave	
End Temperature (°C)	600	600	500	500	500	600
Dwell Time (hr)	-	-	-	1	0.5	0.5
<i>Compounds</i>	% area	% area	% area	% area	% area	% area
toluene	2.8	1.7	0.8	3.5	4.4	2.81
ethylbenzene/xylene	4.1	3.4	1.8	4.1	6.3	3.93
styrene	2.0	<1	2.2	2.2	2.5	1.94
Limonene	15.4	16.2	26.8	13.8	5.1	3.19
6PPD	1.6	1.3	0.3	na	na	na

The major component is, as expected, limonene (though Laresgoiti et al. (2004) observed it in much less quantities). The quantities of the main compounds identified from the microwave generated oil are very similar to the ones identified by Kyari et al. (2005). Differences in the percentage compositions in comparison with the other authors are probably due to different experimental conditions, such as the reactor's design, that may or may not promote the secondary reactions and cracking of the oils, and possibly the composition of the tyre rubber, that may or may not contain more natural rubber, SBR or PBR, rather than the form of heating.

Whereas the properties of the chars and oils obtained by both conventional and microwave-induced pyrolysis are similar, microwave heating should offer an advantage in the area of energy efficiency through volumetric heating. As the energy is transferred electromagnetically and not as heat flux (as occurs in conventional pyrolysis), there are no longer limitations related to the thermal diffusivity and surface temperature (Meredith, 1998). This implies a significant reduction in heating times, using an optimal design chamber with no losses to the surrounding environment; Meredith (1998) states a possible reduction to less than 1% compared to conventional heating. In addition, the power conversion (electrical to microwave) is more efficient in microwave heating. Using a 2450 MHz generator this

efficiency is between 50 – 70%, whereas for a 915 MHz generator this reaches more than 80% (personal communication with experts in the microwave industry). At an industrial scale, using 915 MHz would be more beneficial due to this conversion efficiency. Meredith (1998) also states that the magnetron life is 8000 – 12000 hours at 915 MHz compared to 4000 – 6000 hours at 2540 MHz. The latter frequency is commonly used in small scale applications such as in the current work, being widely available and cheaper because of its use in domestic microwaves.

5.5 Conclusions

In this chapter it has been shown that microwave technology can be used for the microwave-induced pyrolysis of tyres. Issues related to the temperature measurements inside a microwave cavity were highlighted and the importance of the system design has been emphasised using four different apparatus configurations, including a prototype custom-made rotary furnace. The behaviour of tyre rubber under microwaves was related to the change of its dielectric properties. The latter were measured for chars produced at increasing temperatures using a network analyser at room temperature, and it was found that the complex permittivity, $\tan\delta$ and σ , were increased from 2, 0.03 and 0 (raw tyre rubber) to 8.8, 0.13 and 0.09 (char generated at an end temperature as recorded by the IR sensor of 703°C) respectively. Similarities between properties of the chars (surface area, ash-content, pH-values) and oils (CHNS, individual components as identified by GC/MS) generated from microwave and conventional heating have been observed. Overall, microwave heating would have an advantage in this type of application through a careful cavity design that would ensure uniform heating (to minimise hot-spot formations) and be optimised to achieve maximum energy efficiency.

6 Recovery of value from pyrolysed chars

6.1 Introduction

In this Chapter the recovery of value from pyrolysed tyre chars is investigated by examining the use of selected chars produced in Chapters 4 and 5 as reinforcement filler replacement in rubber compound formulation.

Tyre rubber compound formulation was discussed in Chapter 1, as well as the use of carbon black as reinforcement filler in the rubber formulation. Published research in the use of waste as filler replacement report varying levels of success – due primarily to comparability issues; there are different grades of fillers and therefore different reinforcement performance expectations. The wastes that have been investigated include rice husk ash (da Costa et al., 2000) and pyrolysed chars (Cataldo, 2005), discussed in Section 6.2 below.

Reinforcement can be defined in general as the enhancement of specific and measurable physical performance properties to exceed typical expectations for the material in its intended application. For example, glass fibre reinforced composites and steel-reinforced concrete. In polymer reinforcement, these properties include tensile strength, tear resistance, abrasion resistance, modulus of elasticity (Fröhlich et al., 2005; Boonstra, 1979), etc. Reinforcement in elastomers is considered for specific applications, such as increasing the service life of a tyre by using carbon black as reinforcement filler to improve the abrasion resistance. Typically, there are trade-offs in the overall characteristics of the resulting material, as the use of a reinforcement to improve a particular property, e.g. modulus of elasticity, may have a corresponding negative effect on a different property. For example, an increase in hardness results in a decrease in deformation at break. Donnet & Custodero (2005) refer to this as “*a fascinating paradox that explains the ability of reinforced elastomers to provide unique material properties and applications*”.

The reinforcement of rubber by filler is a complex phenomenon influenced by a number of factors such as the polymers properties, the filler properties and the processing of the rubber compound. Fröhlich et al. (2005) summarised the main factors related to the filler properties as follows:

- i) the primary particle size or specific surface area – this relates to the effective contact area between the filler and polymer matrix,
- ii) the structure of the filler – this influences the degree of restrictive motion of elastomer chains under strain, and
- iii) the surface activity – this determines the filler-filler and filler-polymer interaction.

Wolff & Wang (1993) state that all these properties contribute to the reinforcement of the rubber through mechanisms such as interfacial interaction between the rubber molecules and the filler particles, filling up of the voids present in the filler aggregates by polymer, and further aggregation or clustering of the filler aggregates in the polymer matrix. These mechanisms cause the rubber compound to display properties expected of a compound into which a higher volume of filler has been added to it, than is currently the case, based solely on the filler density and loading.

The effective filler volume can be influenced by interfacial interactions between the rubber and the filler, which lead to the adsorption of the polymer molecules on the surface of the filler. This adsorption causes a restriction in molecular mobility of the polymer chains in the vicinity of the filler (Donnet & Custodero, 2005; Wolff & Wang, 1993; Boonstra, 1979). This surface interaction, which depends on the surface area and surface activity of the filler, can be measured by bound rubber measurements. These measurements involve the determination of the portions of the rubber that are insoluble in good rubber solvents (Donnet & Custodero, 2005).

In addition, the filling up of the voids in the filler aggregates, known as occlusion of rubber, causes that rubber to behave more like filler than as a rubber matrix, by resisting deformation. Occluded rubber is a function of the structure of the filler (Wang, 1998).

Furthermore, the aggregates of the filler tend to form agglomerates (filler-filler interactions) which lead to the formation of a filler network or secondary structure. Within these structures rubber is trapped which also contributes to the effective volume of the filler. All the above are illustrated in Figure 6.1.

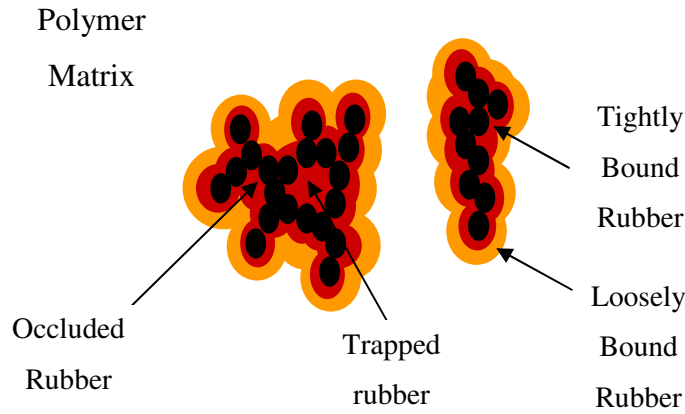


Figure 6.1. Illustration of the filler polymer interactions (Adapted from Sosson et al., 2010)

For further insight on the filler-polymer and filler-filler interactions, the dynamic properties of the elastomers are usually investigated, typically by Dynamic Mechanical Analysis (DMA). In DMA, the application of an oscillating force to a material causes that material to deform (Menard, 2008). This force is applied as stress (σ) and the resultant deformation is measured as strain (γ), and these are defined by the following equations:

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (\text{Eq. 6.1})$$

$$\gamma = \gamma_0 \sin \omega t \quad (\text{Eq. 6.2})$$

Where t = time, δ = phase angle between stress and strain, and γ_0 and σ_0 are the maximum amplitude of strain and stress respectively. The dynamic stress-strain behaviour of an elastomer can then be described by the complex modulus G^* , the elastic modulus G' and the viscous modulus or loss modulus G'' using the following relationships (Eq. 6.3 – 6.6):

$$G^* = \frac{\sigma_0}{\gamma_0} = G' + iG'' \quad (\text{Eq. 6.3}) \quad \sigma = \gamma_0 G' \sin \omega t + \gamma_0 G'' \cos \omega t \quad (\text{Eq. 6.4})$$

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \quad (\text{Eq. 6.5}) \quad G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad (\text{Eq. 6.6})$$

Elastic modulus represents the energy returned to the system, whereas viscous modulus is related to the energy lost (Wang, 1998). Figure 6.2 below shows a typical plot of a filled rubber obtained through DMA, in which the Shear Modulus has been plotted against the Double Strain Amplitude (DSA). Note that modulus can be characterised by either G or E , depending on whether the deformation is shear or compression-extension (Payne, 1962a).

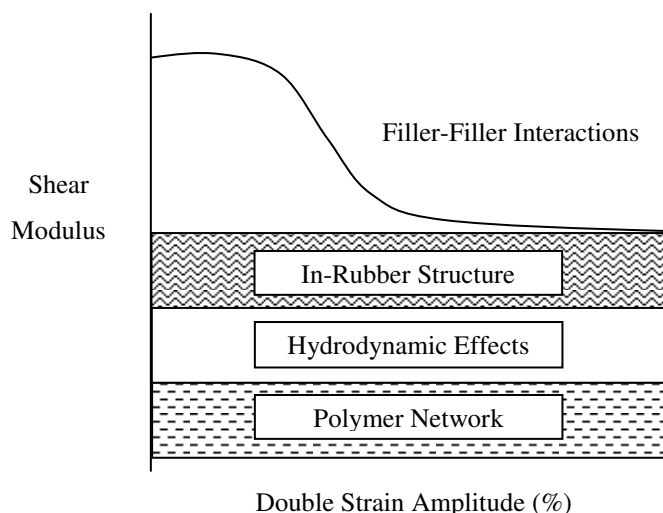


Figure 6.2. Payne effect illustration (Adapted from Meon et al., 2004)

As shown in Figure 6.2 there are two parts that contribute to the modulus, a strain dependent and a strain independent part. The strain independent part of the modulus is a function of the following elements as summarised by Fröhlich et al., (2005), Meon et al., (2004) and Payne (1962b):

- i) the polymer network (depends on the crosslinked density and the nature of the polymer)
- ii) the hydrodynamic effect (caused by the addition of a non deformable filler to the viscoelastic rubber matrix – dependent on the shape of the filler)
- iii) the in-rubber structure (related to the likelihood of the filler preventing the deformation of the rubber)

In the strain dependent part, the modulus decreases with strain increase. This effect, known as Payne effect, defined as the difference between modulus values measured at low and high strains (ΔG^*), is attributed to interaggregate interaction (Meon et al., 2004; Wolff & Wang, 1993). With increased strain this filler-filler network breaks down, releasing trapped rubber, thus reducing the apparent filler volume.

The following section discusses some previous research in the use of material derived from waste, as an alternative to commercial fillers in rubber formulation.

6.2 Fillers from waste

Similar to the current work, chars were generated by Cataldo (2005) from pyrolysis of crumbs derived from tyre tread. Using a heating rate of 50°C/min, the crumbs were heated up to 700°C under inert conditions (nitrogen atmosphere) and held at this temperature for 10 minutes. The char obtained was evaluated as a filler replacement in a natural rubber/SBR compound formulation without any treatment, by replacing partially or completely carbon black grade N339. This grade of carbon black was chosen due to its surface area proximity (90 m²/g) to the surface area of the generated char (81 m²/g). The mechanical properties of the compounds containing the pyrolytic char, however, showed inferior reinforcing effect compared to the control compound.

More recently, Ivanov & Mihaylov (2011) also examined the possibility of replacing the filler in rubber compounds using a material obtained from the pyrolysis-cum-water vapor of 'green' tyre tread. Ivanov & Mihaylov report that the material was found to contain mainly silicon dioxide (65%) and carbon (30%) following characterisation. The material, identified as SiO₂D, (75 parts per hundred rubber, phr) was mixed in an SBR/BR blend and other additives and tested for its curing characteristics, mechanical and dynamic properties. The results were compared to two controls: one containing silica (50 phr) and the other containing silica (50 phr) and carbon black N330 (25 phr). The SiO₂D filled compound showed similar mechanical and dynamic properties as the compound filled with the blend of silica/N330, though the former had a much shorter optimum curing time.

Furthermore, the potential for replacing commercial filler with rice-husk ash generated from the incineration of rice husk waste has been investigated in various rubber blends by Sae-Oui et al. (2002), Ismail et al. (1997) and da Costa et al. (2000 & 2003). Rice husks can be separated to white husk ash (95% SiO₂) and black husk ash (55% SiO₂, 45% carbon) depending on the conditions they are generated (Klingensmith & Rodgers, 2004). The white rice husk ash used by da Costa et al. (2000) was either simply milled or milled and then chemically treated in rubber compounds at various loadings (0 – 50 phr), and compared to N774 (20 phr) and precipitated silica (20 phr). Under some conditions comparable results were obtained, for example the tensile strength of a compound containing 20 phr of treated rice husk ash was 26.0 MPa compared to 22.0 MPa of a compound containing N774. However, for most properties examined the overall results obtained were slightly inferior to the results obtained from the controls.

Nabil et al. (2012) investigated the effect of partial replacement of commercial fillers by recycled Poly(ethylene terephthalate) (PET). Physical properties such as tensile strength and modulus showed inferior results when compared with the compounds containing carbon black N550 and silica.

Other wastes examined for their potential as fillers in rubber compounds include palm ash (Ismail & Haw, 2008), recycled newspaper (Ismail et al., 2008) and cocoa pod husks and rubber-seed shells (Okieimen & Imanah, 2005). Physical characteristics examined by these authors suggest that the filler has semi to non-reinforcing properties. Table 6.1 below is a summary of some previous investigations on the use of materials derived from waste as an alternative to commercial fillers in rubber compound formulation.

In addition to the summary above, RockTron (<http://rktron.com/>) has developed a technology that enables the use of fly ash from coal power stations as filler in various applications including in polymers and elastomers. This application however is not presented in publicly available literature in sufficient detail, but is claimed (on RockTron's website) to be the first and only commercial solution to recovering value from fly ash waste by its transformation into an *eco-mineral* filler.

6.3 Experimental procedure

In the current work, selected ground chars (< 150 μm) were examined for their performance as filler replacements in rubber compounds. The selected chars included four chars generated using conventional pyrolysis; CP_{II,E}1 and CP_{II,E}2, (generated using the same heating rate and dwell time but different end temperature, 550 and 700°C respectively) and CP_{II,E}15 and CP_{II,D}16 (identical conditions but different source of feedstock). In addition, two chars obtained by microwave-induced pyrolysis: one using relatively low power and long duration (CM_D800_210) and one obtained using relatively high power and short duration (CM_D1500_41a) were also selected.

Table 6.1. Summary of the conditions used in some of the studies investigating the replacement of fillers by waste products

Researcher	Cataldo (2005)	Ivanov & Mihaylov (2011)	da Costa et al. (1999)	Nabil et al. (2012)
Filler substitute	Pyrolytic carbon from waste tyre crumb	Pyrolytic material from waste tyre tread	Rice husk ash	Recycled Poly(ethylene terephthalate) powder
% Filler Replacement	12.5 - 100	100	100	20 - 100
Pretreatment	-	n.a	MHA: milled for 5 hours, < 63 μm , Treated Husk Ash: MHA with 20% NaOH and 12N HCl, dried at 120°C for 24 hrs before use	ground to particle size 125 - 212 μm , dried in vacuum oven at 80°C for 24 hrs before use
Mixing	Internal mixer (2.2 L)	Brabender mixer (1st stage) followed by external mixer (Blending rollers) (2nd stage)	laboratory size two-roll mill	laboratory size two-roll mill (160 x 320 mm^2)
Curing	Natural rubber/SBR	sSBR/BR	Natural rubber	Natural rubber
Testing Properties measured	MDR testing (M_L , M_H , $T_{S1,2}$, T_{C90}), Tensile strength, stress at 25, 50, 100, 200, 300% elongation, elongation at break, Hardness, $\tan\delta$	MDR testing (M_L , M_H , T_S , T_{C90}), Tensile strength, stress at 100% & 300% elongation, elongation at break, residual elongation, hardness, abrasion, Dynamic Properties	FTIR, MDR testing (M_L , M_H , T_{C90}), tensile strength, tear strength and abrasion resistance, hardness, SEM	MDR testing (M_L , M_H , T_{S2} , T_{C90}), Tensile strength, stress at 300% elongation, elongation at break, swelling test, SEM
Controls	N339	N330, Silica	precipitated silica, N774	N550, precipitated silica, Halloysite nanotubes
Results	Inferior results	Some comparable mechanical properties of rubber compounds containing waste filler (75 phr) and blend Silica (50 phr)/ N330 (25 phr)	Mainly inferior results	Inferior results

Two rubber formulations, containing different commercial fillers were used as control samples: one from the N300 series considered a high reinforcing grade usually used in tyre tread (N339) and the other from the N700 series, considered a semi-reinforcing grade (N772) (Wampler et al., 2004). N339 has a higher surface area ($91 \text{ m}^2/\text{g}$) and higher structure (Oil Absorption Number (OAN) = $120 \times 10^{-5} \text{ m}^3/\text{kg}$) whereas N772 has lower surface area ($32 \text{ m}^2/\text{g}$) and OAN = $65 \times 10^{-5} \text{ m}^3/\text{kg}$ (Wampler et al., 2004). Further, two blends of N772/Silica were used in the ratio 50/10 and 36/24 to account for the silica amounts in crumb D and E respectively.

A summary of the experimental process used in this work is presented in Figure 6.3 and described below.

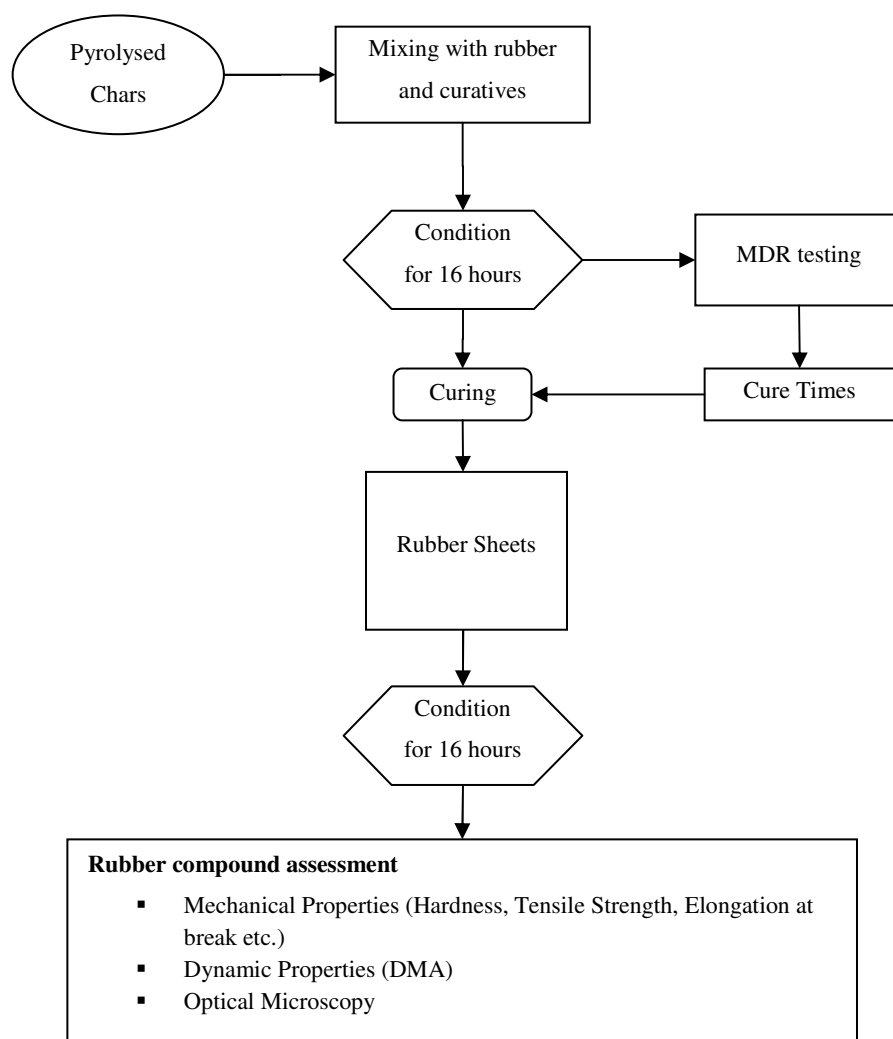


Figure 6.3. Experimental process for rubber compounding formation and testing

6.3.1 Formation of rubber compounds

The formation of the rubber compound sheets involved the mixing of the compounds and the curing assessment. The chars were mixed with compounding ingredients as described in Section 6.3.1.1 and allowed to rest for a minimum of 16 hours before undergoing a curing assessment (Moving Die Rheometer test) described in Section 6.3.1.2. From this test, information on the cure times for each char was obtained, which was then used to mould test sheets. The moulded samples were then conditioned for a minimum of 16 hours at 23°C prior to being assessed.

6.3.1.1 Mixing

A Brabender Plasticorder mixing machine with a small chamber of 50 ml volume was used due to the limited sample size of char available (40 g). The ingredients, comprising the rubber, filler, vulcanising agent, accelerators and antioxidants, shown in Table 6.2 as parts per hundred rubber (phr), were accurately weighed to 2 decimal places accordingly to fill 94% of the chamber volume.

Table 6.2. Rubber formulation

<i>Ingredients</i>	<i>phr</i>
Rubber (SBR)	100
Process Oil	10
ZnO	5
Stearic acid	2
Anti-oxidant (6PPD)	1.5
Accelerator (TBBS)	1.5
Sulfur + mineral oil	1.5
Filler	60

Excluding the rubber, all the ingredients were blended to form an add-mixture. The following mixing sequence was used at 55 rpm rotor speed: At 0 minutes, the polymer was added, followed by the add-mixture, the ram was then lowered. After 1 minute the ram was raised to brush down the feed throat area and lower the ram again. After 2 minutes the mixer was stopped.

The material was then removed from the mixing chamber and placed into a steel bowl. The batches were then blended immediately on the ARTIS 13" 2-roll mill to take the heat out and

prevent scorching (premature activation of the cure reactions which prevent flow in the mould if this happens) using a nip setting of 5. Any remaining loose powders were added to the nip and the batch was passed through the nip 6 times to ensure dispersion of any powder. Material was then removed from the mill using a nip setting of 10, to give a sheet thickness of around 4 mm for subsequent moulding operations.

In addition, the formulation and mixing process was modified for the formation of 2 rubber compounds to investigate the effect of using a coupling agent. These rubbers were formed using char generated from the Cobham Microwave furnace at 1500W for 41 minutes and crumb from sample E (< 500 μm). More details are presented in Appendix III.

6.3.1.2 Curing and Moving Die Rheometer testing

A rubber test piece is examined for its vulcanisation characteristics using a Moving Die Rheometer (MDR) test according to BS ISO 3417:2008. This testing was conducted by ARTIS using an MDR 2000 by Alpha Technologies. A fixed volume of sample of the mixture (4.5 cm^3) is placed between polyester films on a biconical disc in a temperature-controlled die cavity. The disc is oscillated through $\pm 0.5^\circ$ amplitude, exerting shear strain to the sample. On the upper die the torque required to oscillate the disc is measured and recorded as a function of time. The torque value depends on the stiffness of the sample (BS ISO 3417:2008). Typical graphs produced in an MDR test are shown in Figure 6.4, where:

M_L = Minimum torque (N.m)

M_H = Highest torque (N.m)

t_{s1} = time to an increase of one unit of torque above M_L (minutes)

$t_c(90)$ = cure time to 90% of maximum torque developed during the test (minutes)

As seen in the graph there is an initial area known as the scorch time that covers the shaping and processing operations of rubber. This is the time required at a specified temperature for the pre-crosslink insertion chemistry to take place (Dick, 2001), defined as the time until one torque unit rise above the minimum is achieved (t_{s1}). After this, the torque increases as permanent crosslinks are formed as part of the vulcanisation process; thus increasing the resistance to deformation. $t_c(90)$ is the time where 90% of the cure measured is achieved, and this is used to approximate the curing time of the rubber mixture and identifies the point

at which the product can be removed from the mould. Following this it can either cure to equilibrium (Figure 6.4a), cure to a maximum torque with reversion (Figure 6.4b) or cure to no equilibrium in maximum torque (Figure 6.4c). The route followed by the cure will depend on the polymer and the cure system chosen.

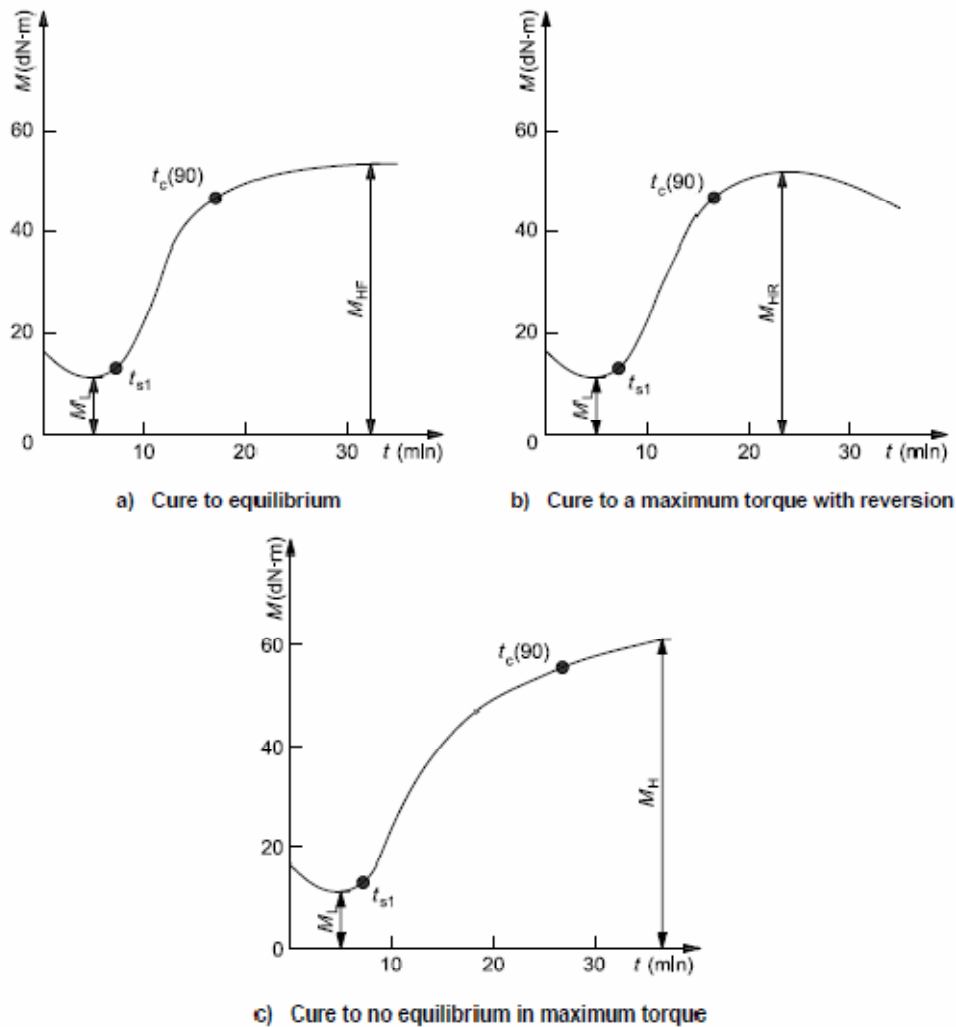


Figure 6.4. Typical MDR plots (BS ISO 3417:2008)

In the current work, a tensile test sheet of 150 x 150 x 2 mm was moulded using cure times based on the MDR $t_c(90)$ values (i.e. cure time = $t_c(90) \times 1.75$). The equipment used recorded the torque values in inch pounds.

6.3.2 Assessment of rubber compounds

The following properties of the rubbers produced were assessed using techniques described below:

- Dynamic mechanical analysis isothermal strain sweep at 40°C
- Hardness
- Tensile properties (M100, M300, Elongation at break and tensile strength)
- Optical Microscopy

A selected char was also characterised using Transmission Electron Microscopy.

6.3.2.1 *Dynamic Mechanical Analysis*

The dynamic properties of the samples were measured by performing strain sweeps at constant frequency and temperature. The double strain amplitude varied between 0.05 to 4% at 40°C in tensile mode using frequency of 10 Hz. These experiments were performed by ARTIS and plots were obtained for modulus against DSA.

6.3.2.2 *Hardness*

The hardness of the cured rubber compounds was measured according to the British Standard for Determination of indentation hardness, Part 1: Durometer method (Shore Hardness), BS ISO 7619-1:2010. In this method the hardness of the test sample is measured by applying a load on the surface using an indenter for a given period of time. This measurement was carried out by ARTIS, using a type A durometer with the indenter applied for 3 seconds. The hardness is obtained by the following relationship:

$$F = 550 + 75H_A \quad (\text{Eq. 6.7})$$

where F is force applied in millinewton and H_A is the hardness reading taken from the type A durometer. As performed by ARTIS, five readings were taken at different positions on the test sample and the median value was determined.

6.3.2.3 *Tensile properties*

The tensile stress-strain properties were determined according to BS ISO 37:2005. The following properties were determined as defined by the Standard: Tensile strength (the maximum tensile stress recorded in extending the test piece to a breaking point), Elongation at break (the tensile strain in the test length at breaking point), and stress at a given elongation (stress required to produce an elongation, in this instance an elongation of 100% and 300%).

In these experiments, carried out by ARTIS, the test pieces were cut to a dumb-bell shape, stretched in a tensile-testing machine at a constant rate and readings of force and elongation taken as required. The different properties are calculated using the equations below.

$$\text{Tensile strength, } TS = \frac{F_m}{wt} \text{ (MPa)} \quad (\text{Eq. 6.8})$$

$$\text{Elongation at break, } E_b = \frac{100(L_b - L_0)}{L_0} \text{ (\%)} \quad (\text{Eq. 6.9})$$

$$\text{Stress at given elongation, } M_e = \frac{F_e}{wt} \text{ (MPa)} \quad (\text{Eq. 6.10})$$

Where F_m = maximum force recorded (N)

W = width of the narrow portion of the die (mm)

t = thickness of the test length (mm)

L_0 = initial test length (mm)

L_b = test length at break (mm)

F_e = the force recorded at a given strain (N)

The median of three runs was determined. A laser extensometer was used to measure the strain in the gauge length of the sample.

6.3.2.4 Optical Microscopy

Optical Microscopy was used to assess the dispersion of the filler in rubber compound. This is a morphological analysis technique in which visible light in conjunction with a system of lenses is used to magnify samples (Brandon & Kaplan, 2008). The analysis was performed by ARTIS using a Leica MZ6 microscope with Leica DFC 280 camera at x 40 magnification.

6.3.2.5 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a similar technique for microstructural analysis like SEM (Section 4.3.2.6) but in TEM the electron beam is transmitted through the material under investigation (Brandon & Kaplan, 2008). Using TEM, images are obtained at much higher resolutions than SEM. Images of selected chars in ethanol were obtained using a JEOL

2010 TEM in the Materials department at Imperial College London, using x 300, x 4000 and x 20000 magnification.

6.4 Results and discussion

Using MDR testing, plots were generated for torque against time for rubber compounds containing selected chars obtained in the previous chapters. Values were obtained for t_{s1} , $t_c(90)$, M_L and M_H , as shown in Table 6.3. Also shown in Table 6.3 are values for surface area, pH-value and ash content obtained for the respective chars from the characterisation section in Chapters 4 and 5, as well as values from MDR testing for compounds containing the commercial fillers.

Table 6.3. Summary of properties of the rubber compounds and their respective filler

	t_{s1} (sec)	$t_c(90)$ (sec)	M_L (lb.ic)	M_H (lb.ic)	Surface Area (m ² /g)	pH- value	Ash Content (%)
CP _{II,E} 1	65	231	1.88	11.76	112.5	7.80	44.0
CP _{II,E} 2	53	191	1.79	12.60	94.2	8.40	44.0
CP _{II,E} 15	58	196	1.89	11.94	105.7	8.07	45.9
CP _{II,D} 16	53	177	1.6	10.66	82.3	9.10	19.5
CM _D 800_210	52	207	1.36	10.07	90.2	9.41	19.4
CM _D 1500_41a	57	191	1.57	12.13	83.9	9.16	18.9
N339	73	254	2.45	15.5	91 ^a		
N772	80	221	0.98	12.64	32 ^a		
N772/Silica (50/10)	80	228	1.06	11.22	32/180 ^b		
N772/Silica (36/24)	122	287	1.89	7.97	32/180 ^b		

^a Wampler et al. (2004), ^b Evonik Technology (2012)

MDR testing gives an indication of the vulcanisation characteristics of a rubber compound. As stated in Section 1.2, vulcanisation is the process where crosslinks are inserted between polymer chains. This results in a compound with increased elasticity that is essentially insoluble in any solvent and cannot be processed further using techniques that require it to flow (Coran, 2005).

The most widely used system is the accelerated-sulfur vulcanisation. Even though there are still differences between researchers as to the exact mechanism of the vulcanisation, there is a general agreement on the basic steps involved (Ghosh et al., 2003). These include the following as summarised by Ghosh et al. (2003):

- i) Formation of an active-sulfurating agent
- ii) Formation of a crosslink precursor
- iii) Formation of initial crosslinks, and
- iv) Reactions that lead to crosslink shortening and crosslink degradation

Initially, the accelerator and the activator react to give an active accelerator complex which then reacts with the sulfur to form a sulfurating agent. The latter reacts with the rubber chain to form a crosslink precursor (accelerator-terminated polysulfidic pendant groups) which can then react with additional unsaturated sites on the rubber to give polysulfidic crosslinks. These can form shorter crosslinks or degrade to cyclic sulphides or other main chain modifications (Ghosh et al., 2003).

In the current study, N-t-butylbenzothiazole-2-sulfenamide (TBBS) was used as an accelerator, with zinc and stearic acid as the activator system. With the addition of sulfur a sulfurating agent is formed, with possible structures as shown in Figure 6.5.

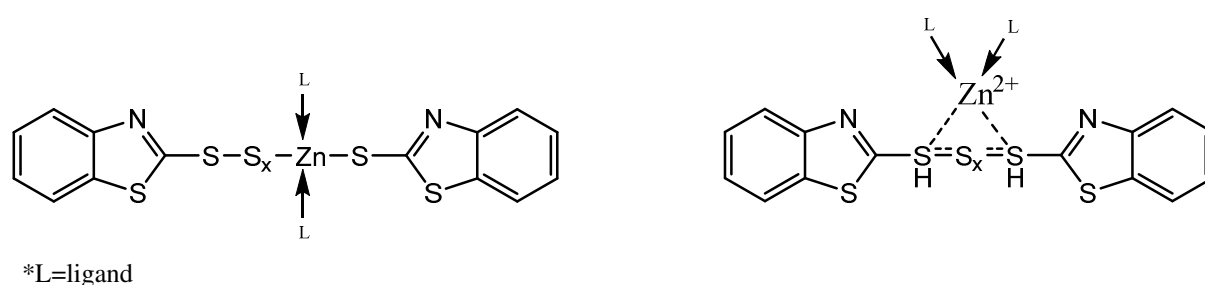


Figure 6.5. Sulfurating agent

The t_{s1} values of the tested compounds (Table 6.3), that denote the end of scorch time and start of the crosslinking, are much shorter for the compounds with added pyrolysed chars than for the compounds with added commercial fillers. This must be related to the presence of ash in these chars. This ash consists mainly of zinc oxide (ZnO), sulfur and silica (SiO₂), along with other minor metal oxides. It is possible that t_{s1} is faster due to the overall higher amount of ZnO present in the system compared to the compounds with commercial carbon blacks. In the presence of stearic acid, the increased zinc ions (Zn²⁺) cause an overall increase in the rate of the early reactions, which lead to the formation of rubber-S_x-Accelerator (Coran, 2005) (Figure 6.6).

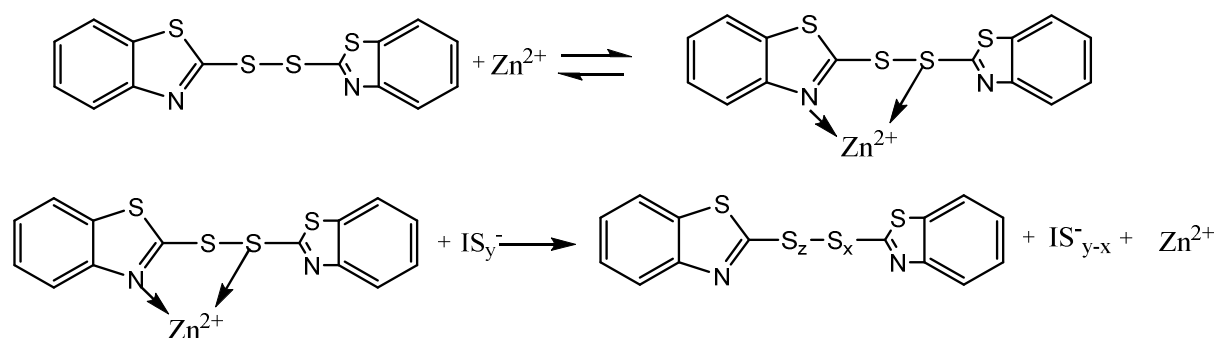


Figure 6.6. Zn^{2+} interaction with the sulfurating precursor, where IS_y^- is an ionised form of linear sulphur (Coran, 2005)

In the current work, however, there was insufficient information on the form of the inorganics present, to provide more definite conclusions on the reactions taking place. For example, even though the presence of sulfur was confirmed ($\sim 2\%$) using CHNS analysis, this does not give any information of whether the sulfur is bound or free (i.e. organic sulfur or 'S'). Presence of free sulfur would also affect the cure kinetics. In addition, the presence of silica usually increases t_{s1} as seen by the compounds filled with blends of N772/Silica. This is because the activator/accelerator system reacts with silica and slows down the reactions. It is likely that the surface of the silicate in the chars may be less available or the 'Si-OH' groups are perhaps shielded in some way.

Nevertheless, scorch time is an important parameter as there has to be sufficient delay to enable mixing, shaping, forming and flowing in the mould before vulcanization starts (Coran, 2005). Even if a system shows short scorch time, there are ways to overcome this, for example by adding a premature vulcanization inhibitor such as N-(cyclohexylthio)phthalimide (CTP).

Compounds filled with pyrolysed chars also showed faster $t_c(90)$ than those filled with commercial carbon blacks, apart from CP_{IL}E1. This char is compared with CP_{IL}E2 in Figure 6.7 as both chars were generated using the same heating rate ($2^\circ\text{C}/\text{min}$) and dwell time (120 minutes) but different end temperatures (550°C and 700°C respectively). In addition, lower maximum torque values were obtained for the compound containing the char generated at a lower end temperature.

Many factors related to the filler's properties can affect the vulcanisation characteristics. One of the most important factors is the surface activity. It is known that oxygen-containing

groups and increased acid concentration on the carbon's surface has a retarding effect on the rate of vulcanisation (Wiegand, 1937; Parkinson, 1951; Cotten, 1972). As shown in Chapter 4, increase in pyrolysis temperature increased the pH value of the char (used to give an indication of surface activity), which would explain the faster cure characteristics of CP_{II,E}2 compared to CP_{II,E}1.

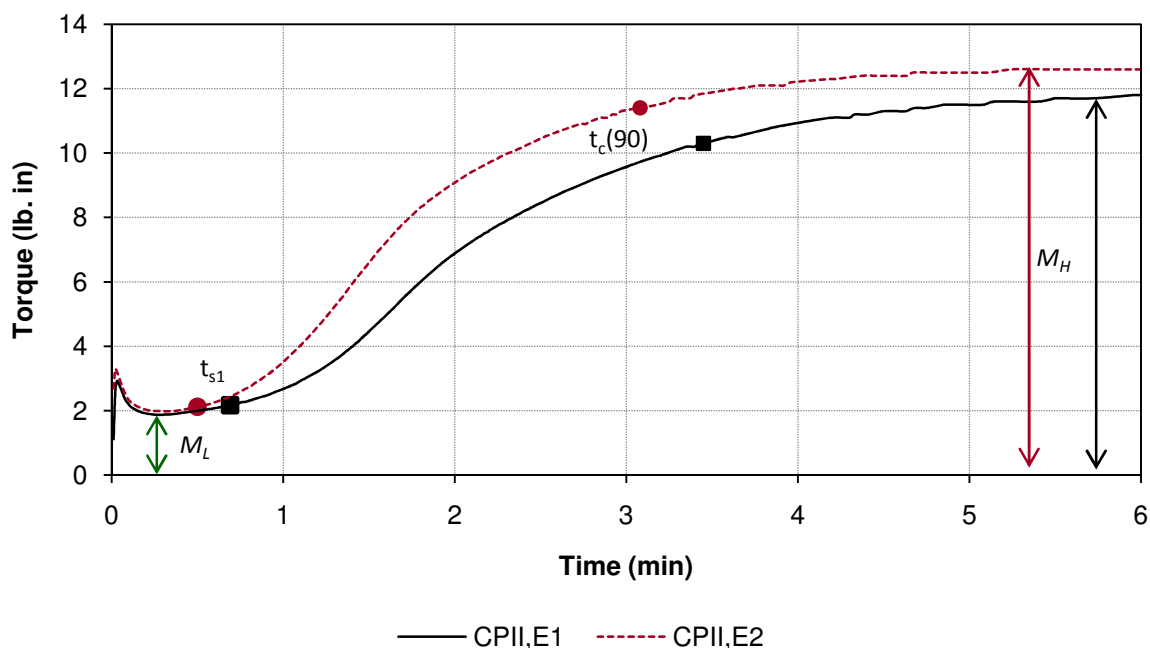


Figure 6.7. MDR plots of CP_{II,E}1 and CP_{II,E}2

The minimum torque values (M_L) depend on the stiffness and viscosity of the unvulcanized compound at a low shear rate (BS, 2008). Compounds filled with the high reinforcing grade, N339 are expected to have high viscosity. Its high surface and structure compared to N772 encourage more rubber to become trapped within its aggregates or bound on its surface as described in Section 6.1, which will increase its viscosity. The values of the compounds with added chars are in between the ones observed for the compounds with N772 fillers and those with N339 fillers. These chars have surface area values similar or higher to the N339 surface area. However, the presence of ash has a detrimental effect on their properties, as it can not only affect the surface area by reducing the availability for interaction with the polymer, but can also affect its surface activity. This is evident when comparing the two chars generated under identical conditions, but using different feedstock, CP_{II,E}15 and CP_{II,D}16.

TEM analyses of CM_D1500_41a and N772 at different magnifications are shown in Figure 6.8.

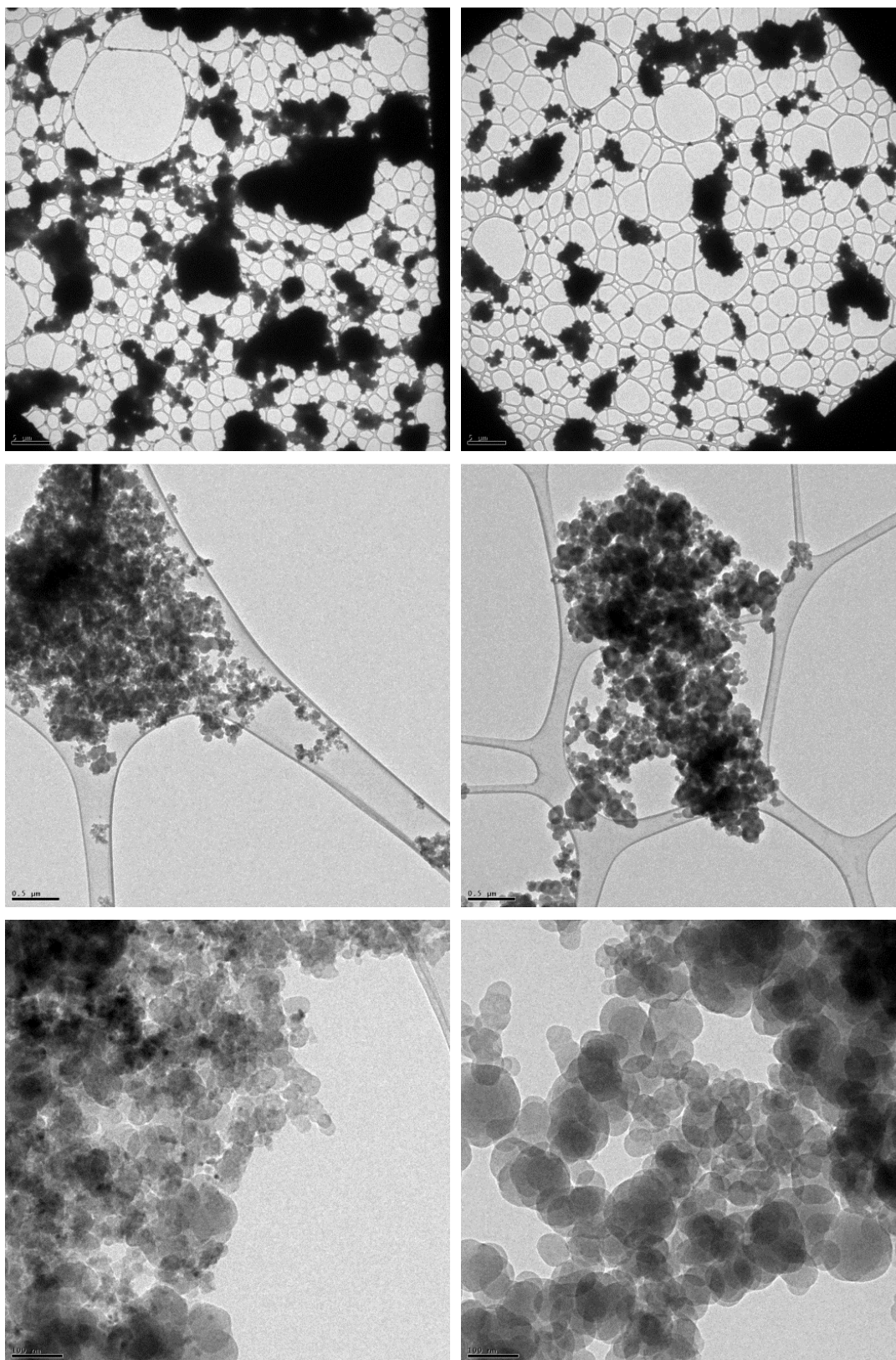


Figure 6.8. TEM images of CM_p1500_41a (left) and N772 (right) at x 300 (unit = 5 μm), x 4000 (unit = 0.5 μm), and x 20000 (unit = 100 nm)

At lower magnifications, the char and filler appear very similar, with grape like clusters observed in both samples. However, the char shows a larger variety of particles size distribution, with the smaller ones (probably due to the inorganic components) trapped within the larger particles making it effectively one big chunk and reducing the availability of space where the rubber would normally get trapped.

The increase of torque during MDR testing is proportional to the number of crosslinks formed per unit volume of rubber (Coran, 2005). As expected from a high reinforcing filler, N339 shows a high value of maximum torque (M_H) and a higher difference between the maximum and minimum torque values ($M_H - M_L$), as this implies better reduction of mobility of the macromolecular rubber chains, thus greater interaction between the filler and the rubber matrix (Table 6.3). N772 filled compounds have slightly higher $M_H - M_L$ values and similar M_H values to the ones obtained from the pyrolysed char filled compounds which imply that the mechanical properties of the last two may be similar.

As seen in Table 6.4 the physical properties of the compounds with pyrolysed chars are close to that with N772 control. Hardness results (these give an indication of the elastic modulus of a vulcanisate) ranged between 56 and 61 for the compounds filled with pyrolysed chars. The hardness of N772 filled compounds was within this range (58), whereas N339 filled compound had a higher value of 68. Tensile strength (TS) and elongation at break values for the compounds with pyrolysed chars ranged between 16.3 – 18.6 MPa and 605 – 702% respectively, also close to the N772 filled compound (18.9 MPa and 625%). In higher modulus vulcanisates, there are relatively short chain lengths between crosslinks and filler particles, so they reach their limit of extensibility at lower strains. This is why the vulcanisate filled with the highly reinforcing carbon black grade N339, as presented in Table 6.4, had the highest tensile strength (24.5 MPa) and the lowest elongation at break (493%).

The rubber compound containing CM_D1500_41a had a higher modulus at 100% elongation (2.02 MPa) than that with N772 (1.74 MPa) but a slightly lower modulus at 300% elongation (7.43 MPa compared to 7.89 MPa). Also in Table 6.4, the rubber compound filled with CP_{II,D}16 char had higher modulus than that with CP_{II,E}15 (both produced under the same conditions but different feedstock). This is possibly due to the presence of less inorganic components (lower ash content, Table 6.3) which would imply less occlusion of active sites.

Table 6.4. Mechanical properties of the rubber compounds

	Hardness	TS (MPa)	M100 (MPa)	M300 (MPa)	E _b %
CP _{II,E} 1	58	18.6	1.78	6.37	673
CP _{II,E} 2	59	17.4	1.86	7.00	624
CP _{II,E} 15	60	18.2	1.72	6.21	676
CP _{II,D} 16	57	17.7	1.93	7.65	605
CM _D ,800_210	56	16.3	1.49	5.69	702
CM _D ,1500_41a	61	16.6	2.02	7.43	635
N339	68	24.5	2.99	14.9	493
N772	58	18.9	1.74	7.89	625
N772 /Silica (50/10)	58	20.4	1.56	6.10	721
N772/Silica (36/24)	52	20.2	1.24	3.79	845

The compound with the lowest reinforcing properties was CM_D800_210, generated at low power and long duration. This might be because the low power resulted in slow heating rate, which would promote secondary reactions of the generated volatiles. This would cause “*the formation of hard-to-break agglomerated particles...*” which lower the quality of the char and reduce its reinforcing capabilities (Roy et al., 1995). In addition, the long exposure of the crumb to heat (210 minutes) would eliminate most surface functional groups. Furthermore, this compound showed significant deviations on repeated measurements. Low mechanical properties might be related to poor dispersion in the polymer matrix.

To investigate the dispersion issue, optical microscopy was employed at x 40 magnification. This confirmed the uneven dispersion of all the chars examined indicating that the filler-rubber interactions are not ideal. Figure 6.9 presents the optical microscopy results for vulcanisates filled chars CM_D800_210 and CM_D1500_41a compared to one filled with N772.

Commercial carbon blacks are normally pelletized during the manufacture process and these pellets disintegrate during the rubber formulation mixing process. In the current work, the pyrolysed chars, however, do not completely disintegrate during formulation mixing, giving rise to the uneven dispersion of the char filler on the formed rubber compound. This is an aspect that can be investigated further.

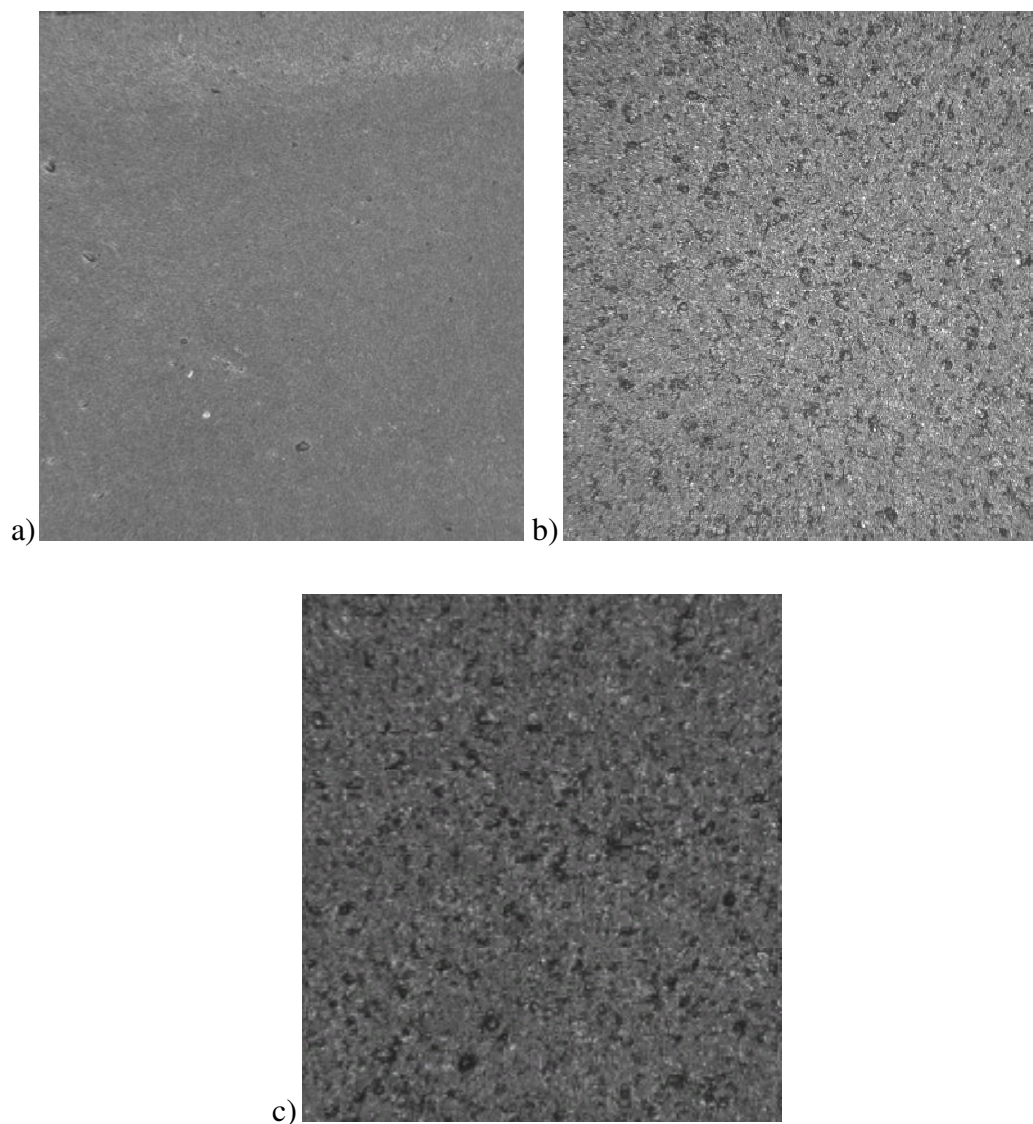


Figure 6.9. Optical microscopy of rubber compounds containing a) N772, b) CM_p1500_41a and c) CM_p800_210

Nonetheless, even with a non-ideal dispersion, the compounds generated with the chars had similar properties with the one filled with N772. The DMA studies also confirm this similarity in the properties of the vulcanisates. Figures 6.10 and 6.11 show the elastic modulus and $\tan\delta$ plots against the double strain amplitude for selected vulcanisates and Table 6.5 presents the percentage increase in the following dynamic properties: (i) the elastic modulus, from the initial value (E'_i) to the last value measured (E'_l), (ii) the viscous modulus, from the initial value (E''_i) to the maximum value (E''_{max}), and (iii) the $\tan\delta$, from the initial value ($\tan\delta_i$) to the maximum value recorded ($\tan\delta_{max}$).

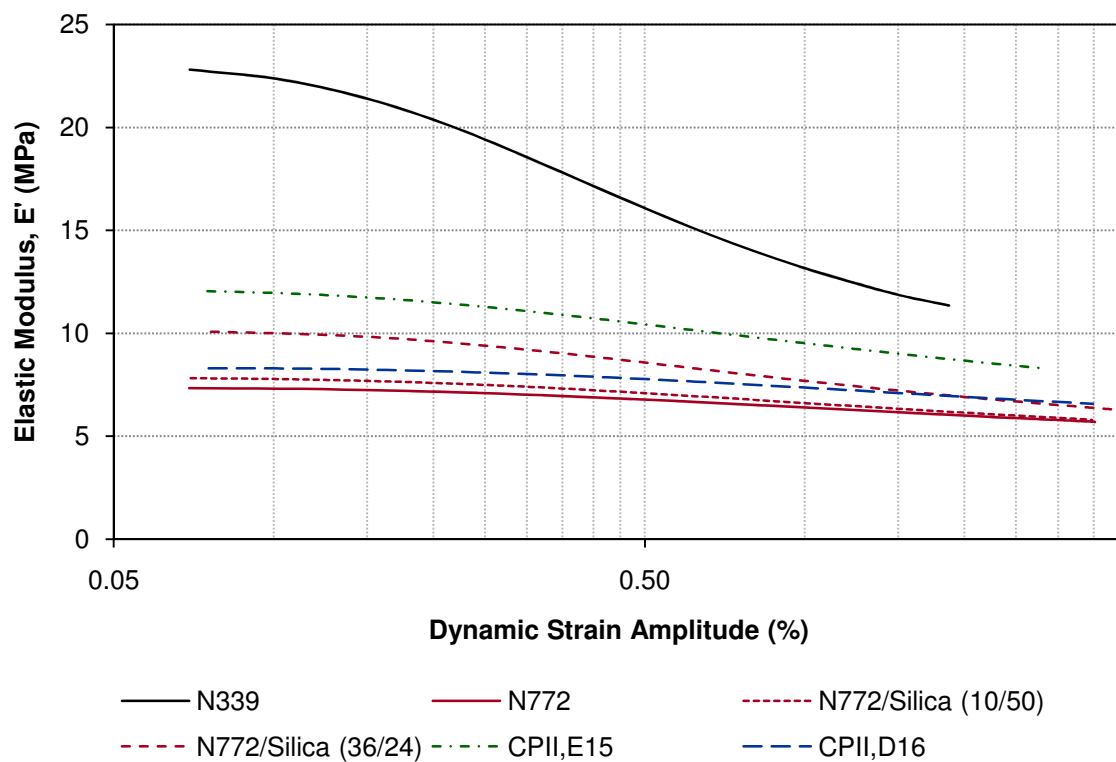


Figure 6.10. Elastic modulus plots against double strain amplitude of the various compounds containing different types of fillers

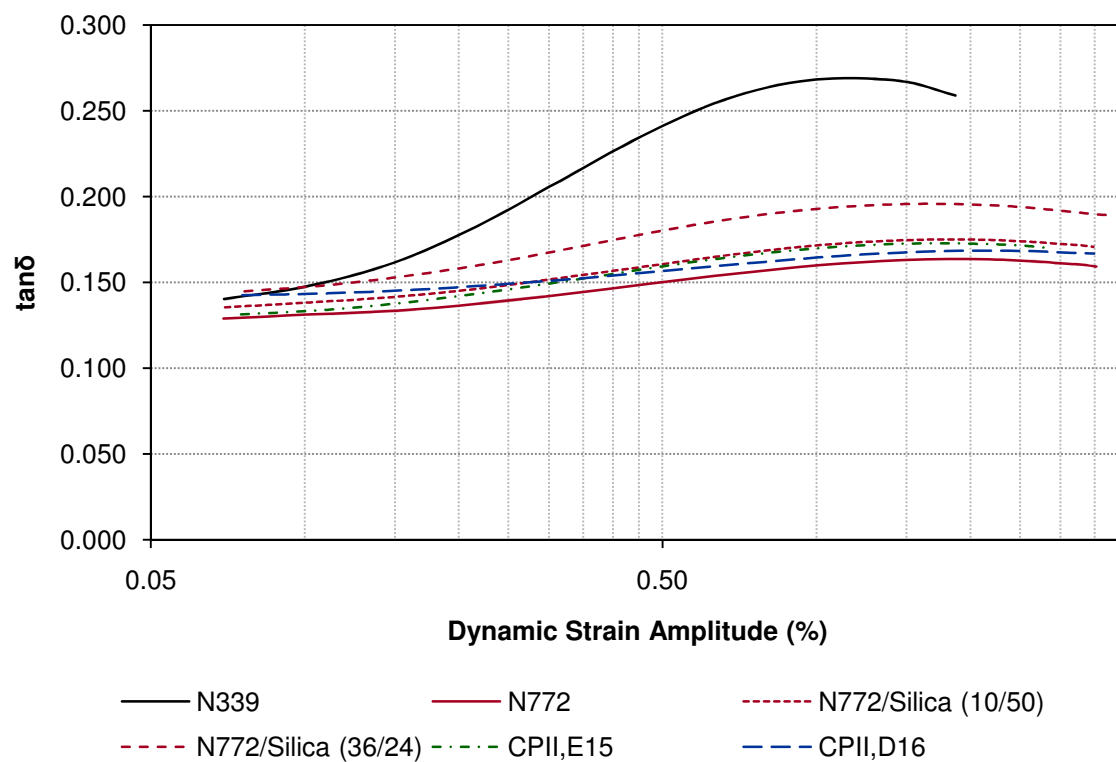


Figure 6.11. $\tan \delta$ plots against double strain amplitude of the various compounds containing different types of fillers

The vulcanisate filled with N339 is expected to show the highest Payne effect (% change of $E'_i = 50.2$) compared to the one filled with N772 (% change of $E'_i = 22.5$) as it has higher surface area and structure. Higher surface area leads to shorter inter-aggregate distance, and subsequently to a more developed filler network. In addition, stronger filler-polymer interaction is expected with increasing surface area, so more rubber becomes immobilised compared to lower surface area carbons and larger particles. These factors make the effective volume of the filler higher, thus the effect on increasing strain amplitude will be larger (Wang, 1998). In addition, the higher structure of N339 might contribute in the larger Payne effect observed. Wang (1998) explains that the effect of structure on the dynamic properties of the rubber is complex, as two opposing effects occur: (i) filler with higher structure implies shorter distances between aggregates due to higher effective volume (ii) the larger effective size of aggregates, however, reduces the diffusion rate of the filler in the polymer matrix – this does not enhance filler networking.

The viscous modulus, unlike the elastic modulus, increases with increase of DSA until it reaches a maximum and then drops. Viscous modulus is related to the energy loss of the rubber and is a function of the breakdown and reformation of the filler network (Wang, 1998). A stronger filler network will reach a higher value of E'' before it is broken, as seen by the high percentage of viscous modulus change of the compound with N339. In addition, $\tan\delta$, which is the ratio of viscous and elastic modulus, also shows a maximum value for the vulcanizate filled with N339.

Table 6.5. Dynamic properties of the rubber compounds

	% change of E'	% change of E''	% change of $\tan\delta$
CP _{II,E} 1	30.7	4.7	29.6
CP _{II,E} 2	31.2	4.6	30.5
CP _{II,E} 15	31.2	5.0	31.4
CP _{II,D} 16	20.6	3.0	18.1
CM _D ,800_210	16.4	2.1	13.5
CM _D ,1500_41a	19.1	2.5	16.3
N339	50.2	21.5	91.1
N772	22.5	8.4	26.8
N772/Silica (50/10)	25.9	8.1	29.0
N772/Silica (36/24)	37.3	6.0	35.2

The compounds filled with chars generated from sample E have closer values, as the range of conditions used was narrower than the conditions used in generating the chars from sample D (using microwave and conventional heating). Chars CP_{II,E}15 and CP_{II,D}16 which were generated using identical conditions, but different feedstock, display considerable differences. Similarly, differences are also observed between the compounds filled with only N772 and those with blends of N772 and silica. On increasing the silica content, the compounds with blends of N772 and silica show an increasing Payne effect. This is because silica forms a stronger filler network than carbon black, due to its being less compatible with rubber and it can also form hydrogen bonds (Fröhlich et al., 2005). Further, compounds with CP_{II,E}15 and the other fillers obtained from sample E, which had a high amount of silica and higher surface area, showed a larger Payne effect, as expected from a stronger filler-filler network. This implies that there might be some active Si–OH groups available in the char. As mentioned in Section 4.3.3.1 in reference to Figure 4.6, even though under the conditions the chars are generated, most –OH groups should have been removed through dehydration, some –OH groups in silica materials remain until heated to temperatures around 1000°C (Iler, 1979). Further, the heterogeneity between feedstock compositions is an issue that can affect the possibility of reusing chars in rubber formulations. In the current study, sample D was sourced externally from ground whole passenger car tyres and sample E was produced internally by combining a small amount of crumb from the UHPW system that originated from a small number of tyre treads to make a homogeneous sample. This resulted in significantly different compositions. It is envisaged that in an industrial scale operation, homogeneity of the compositions will be achieved from continuous mixing of sufficiently larger quantities of feedstock crumbs.

What is fascinating about rubber compounding is that the properties of a rubber compound can be altered through modifications. For example, samples from char CM_E1500_41 were used in a formulation with and without a coupling agent, TESPT (bis[3-(triethoxysilyl)propyl]tetrasulfide), commonly used in conjunction with silica. Even though the dispersion was not significantly improved, or the tensile strength (15.6 MPa to 15.5 MPa), the modulus at 100% and 300% increased from 1.62 to 2.32 MPa and from 5.67 to 8.48 MPa, respectively. This could again imply that there are some ‘unshielded’ silanol groups, Si–OH active in the chars. Carbon black could also react with the coupling agent, depending on the functional groups present in its surface. More investigation is needed to identify the active

surface groups on the chars to enable further modifications either to the chars themselves or of the formulation, to increase their reinforcing capabilities.

Ismail & Haw (2008) also observed an increase of the modulus at 100% and 300% when incorporating a coupling agent (maleated natural rubber) in their vulcanisates, using palm ash as a filler. Other examples of modifications of non-conventional fillers to improve their quality can be found in published research. Meon et al. (2004), for example, reports that montmorillonite modified with quaternary ammonium salts resulted in a more organophilic clay; this improved tensile strength and reduced hysteresis loss. Goodyear has replaced 10% of a conventional filler by an extracted and modified form of corn starch (Meon et al., 2004).

In addition, even the way the char is reduced in size can make a difference. One of the collaborators in the RµPERT consortium, who is involved in rubber industry, is positive that an appropriate method to grind the char, such as jet milling, can make its performance in rubber compounds even better.

Further, the mixing process and the sequence of adding ingredients can change the behaviour of a compound (Dick, 2001). Due to the limited amount of char in the current work, a small volume mixer was used; a higher volume mixer could promote better mixing and dispersion of the char.

6.5 Conclusions

End-of-life tyres are considered a problematic waste and the feasibility of recovering value through the use of chars obtained from the pyrolysis of waste tyres in rubber formulations has been investigated and demonstrated in this chapter.

Rubber compounds were prepared using chars generated from conventional and microwave-induced pyrolysis of tyre rubber as described in Chapters 4 and 5. The rubber compounds prepared were assessed for relevant physical and mechanical properties and found to be comparable to rubber compounds containing N772 as well as compounds with N772 and silica. The char filled compounds had hardness values of 56 – 61, tensile strength in the range of 16.3 – 18.6 MPa, modulus at 100% and 300% elongation between 1.49 – 2.02 MPa and 5.69 – 7.43 MPa respectively and elongation at break of between 605 and 702%. These compared to the values of the N772-filled compound which had Hardness = 58, TS = 18.9

MPa, $M_{100} = 1.74$ MPa, $M_{300} = 7.89$ MPa and Elongation at break = 625%. This places the optimum chars in the category of semi-reinforcing fillers.

It has also been suggested in this work that modifications to the rubber formulation and process conditions can result in better reinforcing properties. Promising results were obtained from char-filled rubber compounds formed with added coupling agent where the modulus at 100% and 300% increased from 1.62 to 2.32 MPa and from 5.67 to 8.48 MPa, respectively.

Overall, through a combination of pyrolysis optimisation and rubber compounding adjustment, the potential for reusing the tyre char in new tyres is evident.

7 Conclusions and recommendations for further research

7.1 Concluding discussion

End-of-life tyres are considered to be a significant problematic waste. The UK alone produces more than 450,000 tonnes of used tyres each year. By design, tyres are very robust and hence hard to degrade. Legislation banning landfill disposal of tyres (whole or shred) means that there must be 100% recovery of material from this substantial waste stream.

Various waste management options are currently applied to the handling of waste tyres. Latest UK statistics show that the generation of crumb is the most popular reuse route, accounting for more than 30% of waste tyres (EA, 2010). This crumb is subsequently used in numerous civil engineering applications including asphalt mixtures, carpet underlay etc. Other management options include the reuse of whole tyres both in the UK and abroad, which accounts for 20% of the amount of waste tyres generated. In the UK reuse can be in the form of noise barriers, while abroad a second life as a tyre in countries with less strict restrictions on the thickness of the tread occurs. In addition, tyres can be used for energy generation as a substitute fuel in incineration plants and cement kilns due to the inherently high calorific value. This route accounts for approximately 18% of waste tyres in the UK, 38% of waste tyres in Europe (ETRMA, 2012) and 40% of waste tyres in USA (RMA, 2011).

The continued development of additional management options, however, is driven by issues such as the increasingly high volume of waste tyres generated, the need to exploit the potential economic value of end-of-life tyre and need for more sustainable material management practices wherever possible. Pyrolysis of waste tyres, which is the heating of the rubber in the absence of oxygen to generate a carbonaceous solid, oil and gas, is a technology which provides a means for sustainable value recovery from waste tyres.

The primary aim of this research was to investigate end-of-life tyre pyrolysis using conventional and microwave-induced heating with a view to recovering value in the form of reusable residue for inclusion in rubber. The objectives of this research were to (i) review the management of waste tyres (ii) characterise samples of waste tyre crumb obtained from different sources and techniques (iii) investigate the pyrolysis of the crumb by thermal and

microwave methods and evaluate the residues, and (iv) investigate the feasibility of using the solid residue in rubber formulations.

A detailed review of the management practices and legislation for waste tyres was carried out and presented in Chapter 1, along with an introduction to tyres and microwave theory.

Following this review, the characterisation of samples of waste tyres in the form of granules was presented in Chapter 3. This characterisation was by CHNS analysis, calorific measurements and thermal analysis. Thermal analysis using 5°C/min heating rate showed that the main rubber degradation occurs between approximately 300 and 480°C, with DTG plots presenting two peaks associated with the degradation of natural and synthetic rubber respectively. The carbon content ranged from 60.59 to 85.65% and the calorific values from 32.1 to 36.4 MJ/kg. The results obtained confirmed compositions reported in the literature on the mix design of tyres and highlighted the significantly increased use of silica in tyre tread.

In Chapter 4, tyre crumb was pyrolysed by conventional means to examine the influential parameters on selected properties of the chars generated. These properties included the carbon content, the surface area and the pH. A Carbolite HTR 11/150 laboratory scale rotary furnace was used and the experiments were conducted under a nitrogen atmosphere. In the first set of experiments a Plackett-Burman screening test was employed to test the influence of seven parameters: temperature, heating rate, dwell time, particle size, nitrogen flow, rotation of the vessel and sample weight. The experiments generated chars with pH-values of 7.75 – 9.15, carbon content of 36.7 – 45.0% (outlier char CP_{I,C6} with a carbon content of 49.6% was excluded from the model as it was significantly under-pyrolysed) and surface areas ranging from 101.1 to 128.6 m²/g (CP_{I,C6} was 43.4 m²/g). These experiments identified the most important parameters to be temperature and heating rate.

In the second set of experiments reported in Chapter 4, a Box-Blehnken design was used to investigate the possibility of fitting a quadratic model of the responses with temperature, heating rate and dwell time as parameters. The dwell time was added to ensure that complete pyrolysis of the samples was achieved. The chars generated had pH-values of 7.80 – 8.60, carbon content of 50.21 – 53.61% and surface areas of 94.2 – 113.3 m²/g. The key parameter was found to be temperature. In addition, experiments performed under the same conditions but using different crumb samples highlighted again the difference in the chars properties; the pH-value, ash content and surface area of char originating from whole passenger tyre crumb

was 9.10, 19.54% and 82.3 m²/g respectively, compared to 8.07, 45.88% and 105.7 m²/g of char originating from tyre tread.

The investigation of microwave-induced pyrolysis was conducted and discussed in Chapter 5. Microwaves offer an attractive alternative to conventional heating, because whereas in conventional heating energy is transferred through convection, conduction and radiation, in microwave heating, energy is delivered directly to the material through interaction with the electromagnetic field. This interaction results in the volumetric heating of the material potentially causing a more efficient heating, faster reaction time and energy savings.

Though microwave technology is established in various applications, such as the food industry, there is limited research on its use for pyrolysis purposes. For this work, four different apparatus configurations were used. These were two modified domestic microwave ovens, a modified microwave synthesis apparatus (RotoSYNTH) and a custom-made rotary furnace manufactured by Cobham Microwave Ltd. in collaboration with Imperial College designed specifically for this project.

The use of the domestic microwave ovens highlighted the difficulty to control the creation of hot spots and uneven heating in static systems as the chamber experienced nodes and antinodes of the electromagnetic field. With RotoSYNTH, which is a rotary system, hot spots were also observed and the nature of microwaves means that the design of the reactor is important for efficient heating and prevention of hot spots.

One of the biggest challenges was the temperature measurement, as the use of thermocouples was prohibited inside the chamber. As a compromise, measurement by infrared sensor of the quartz vessel in contact with the tyre crumb was used for the monitoring of the pyrolysis process in the Cobham microwave configuration. The behaviour of tyre rubber under microwaves was related to the change of its dielectric properties with increasing temperature. This results in a more carbon concentrated material with increasing electron mobility via the transfer of the π bond electrons along the aromatic layers (Dodds, 2006).

Properties of completely pyrolysed chars (surface area, ash-content, pH-values) and oils (CHNS, individual components as identified by GC/MS) generated using Cobham microwave had similarities with chars and oils obtained from conventional pyrolysis.

Chars obtained from studies reported in Chapters 4 and 5 were successfully reused as replacements for semi-reinforcing fillers in rubber formulations. These rubber compounds

were assessed for relevant physical and mechanical properties and were found to be comparable to rubber compounds containing N772 as well as compounds with N772 and silica, and the detailed results presented in Chapter 6. Further, it was proposed that better reinforcing properties could be obtained through modifications to the formulations to accommodate the differences between the recovered char and traditional fillers.

Whereas the concept of pyrolysis is not new, the application of pyrolysis in the management of waste has yet to be applied in a commercially successful system. This is influenced by several factors including the economics of the system, feedstock availability and product quality. In terms of waste tyres, the feedstock is significant – pyrolysis can be of whole tyres, however microwave-induced pyrolysis is of shredded tyres. The shredding of tyres was considered energy intensive, and may still be, even with the introduction of robotic technologies like the UHPW system. The true energy intensity still needs to be investigated and quantified. However, microwave pyrolysis could potentially offer energy savings due to more efficient heating mechanisms compared to conventional heating systems. The key parameter is to optimize the design of the reactor so that uniform heating is achieved with minimal losses to the surroundings.

It may also be perceived that restrictions on the source (in terms of distance travelled) of the waste tyres for pyrolysis is a hindrance to the commercialisation of the process. This was premised on a consideration that the transportation of the tyres only adds more burdens to the system and that close proximity between the waste and the plant is of economic and environmental benefit. Current developments in environmental assessment using life cycle methodology have shown that the impacts from transportation are minimal in comparison to raw material and process impacts. It would be commercially advantageous to locate the pyrolysis plant close to power stations for the dual reasons of energy supply for pyrolysis and the collection and transfer of resulting syngas from pyrolysis to the power station for energy generation. The economics of the latter is further embedded in the fact there is therefore no requirement for gas treatment onsite, along with the relevant infrastructure – this is a facility that will be available at the power station.

In addition, one other determining factor in the economics is the quality of the pyrolysis outputs. The implementation of quality control mechanisms and purpose-driven research and development is imperative. The quality control requirement reflects the importance of ensuring the production of better quality, fit for purpose, carbonaceous material, which will

consequently have a better market value. A fuller understanding of the char properties will also enable modification of the rubber formulation to achieve the desired filler replacement.

The successful use of the char as a filler replacement represents a significant step in sustainable management of waste tyres through closed loop recycling.

7.2 Contribution to knowledge

The contributions to knowledge derived from the current work have been many and varied given the holistic approach used in this research, and are as follows:

- This is the first combined comparative study of the products and potential reuse opportunities of conventional thermal and microwave generated tyre pyrolysis chars;
- An in-depth study and demonstration of the key influential parameters for the pyrolysis of tyre crumb by conventional means has been completed;
- A similarly comprehensive study of the feasibility of using microwave technology for tyre crumb pyrolysis, using a new and bespoke microwave furnace design, has been undertaken. This has highlighted the key challenges and issues to be considered for further development of this application;
- The work has provided evidence that the characteristics of the outputs of tyre pyrolysis using both conventional and microwave heating exhibit similarities. This implies that potential differences arise mainly due to the reactor configuration and experimental conditions rather than from the different forms of heating;
- Confirmation that the solid residue from tyre crumb pyrolysis can be used as a semi-reinforcing filler in rubber compounds and demonstration that further modifications of the formulation recipe can increase its reinforcing ability.

7.3 Further work

The work presented in this thesis has shown that the recovery of value from waste tyres can be achieved by using the solid residue obtained from both conventional and microwave-induced pyrolysis as a replacement for semi-reinforcing fillers in rubber compounds. The benefits from using microwave technology over conventional heating need to be harnessed. From the results obtained in this work the following opportunities for future work have been identified:

- (i) Microwave Pyrolysis: Numerous advances have been made in microwave technology especially in the food industry, but its application in waste management is still limited. Most of the current published work has been from work using modified domestic microwaves. There is a need to develop suitably optimised microwave designs. The custom made microwave (Cobham system) used in this thesis was a prototype and it exhibited particular operational characteristics which indicate that further optimisation is recommended through microwave design for the following:
 - a. Real-time temperature measurements to enable better control of the reactions in the cavity, ideally in multiple locations within the chamber
 - b. Uniform heating of the material during pyrolysis. This can be achieved by rotation of the sample, though the design is crucial to prevent hot spot creation. As shown with the RotoSYNTH experiments, even this rotation needs to be optimised
 - c. Pyrolysis of high volumes of material which means using cavities which are well matched to the absorption properties of the feedstock, thus reducing losses to the surrounding
 - d. The current work involved the use of low heating rates (less than 30°C/min). The effect of higher heating rates on the properties and characteristics of the chars and the oils obtained from pyrolysis needs to be investigated further.
 - e. Design and optimisation of a continuous system instead of a batch system for large scale pyrolysis
- (ii) Char application in rubber compounds: The characteristics of the chars have to be further investigated, for example the influence of the inorganic components and surface activity. This will help understand what modifications are needed to either the char or the formulation recipe, or both, to improve the char interactions with the rubber. Different formulations should be examined to accommodate the differences between the waste tyre-derived char and the traditional fillers. More testing parameters, in addition to those used in this work, should be included to assess the char's performance (weathering effects, abrasion etc.).
- (iii) Environmental and economic evaluation: In line with true sustainability in practice, the conversion of waste tyres into a filler replacement, using microwave pyrolysis as a management method for the waste stream, needs to be assessed in

terms of the environmental implications and the economics. Life cycle assessment methodology is recommended as a suitable approach for this. It can be used to evaluate both energy and resource requirements of any system alongside the environmental impacts in defined categories.

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Appendix I

Table A. Classification of carbon blacks (Wang et al., 2000)

Group No.	Average N ₂ surface area (m ² /g)
0	> 150
1	121 - 150
2	100 - 120
3	70 - 99
4	50 - 69
5	40 - 49
6	33 - 39
7	21 - 32
8	11 - 20
9	0 - 10

Table B. Microwave pyrolysis yields from Chapter 5

i) Domestic microwave I yields

Time (min)	Char Yield (wt. %)	Standard Deviation
0.5	90.0	
1.0	57.8	8.0
1.5	51.8	
2.0	53.4	8.3
3.0	50.0	0.0
4.0	49.2	1.1
5.0	48.1	

ii) Domestic microwave II yields

Power (W)	Char Yield (wt. %)	Standard Deviation
250	45.5	0.6
440	45.6	0.4
600	46.0	0.6
850	46.3	0.2

iii) RotoSYNTH yields

50 g	Duration (min)	Char Yield (wt. %)	100 g	Duration (min)	Char Yield (wt. %)
300 W	180	96.4	300 W	120	52.9
600 W	60	45.5	750 W	50	44.0
750 W	50	44.7	1000 W	60	43.5
750 W	50	44.2	1200 W	30	44.1
1000 W	50	46.5			
1200 W	30	45.2			

iv) Cobham Microwave Part I yields

	Char Yield (wt. %)	Oil Yield (wt. %)	Gas Yield (wt. %)
CM _D 2000_40	41.2	47.5*	11.3*
CM _D 2000_33	41.4	52.3	6.3
CM _D 2000_27	41.6	52.7	5.7
CM _D 1500_60	41.5	52.3	6.2
CM _D 1500_53	40.9	52.4	6.7
CM _D 1500_41a	41.5	52.0	6.5
CM _D 1500_41b	41.1	53.1	5.8
CM _D 1500_41c	41.2	52.3	6.4
CM _D 1500_40	41.3	52.7	6.0
CM _D 1200_119	40.7	53.3	6.0
CM _D 1200_90	40.4	51.5	8.1
CM _D 1200_70	40.7	52.7	6.6
CM _D 1200_66.5	40.9	54.4	4.7
CM _D 1000_180	40.1	52.5	7.4
CM _D 1000_120	40.5	53.1	6.4
CM _D 1000_90	40.3	52.2	7.4
CM _D 800_210	39.8	54.6	5.6
CM _D 800_160	40.3	54.7	5.0
CM _D 800_97	40.5	53.7	5.9
CM _D 750_142	40.3	53.8	5.9
CM _D 600_265	39.9	53.6	6.5

* Oil leak experienced in the first experiment

Appendix II

Figure A. Proximate analysis plot of sample B (Chapter 3)

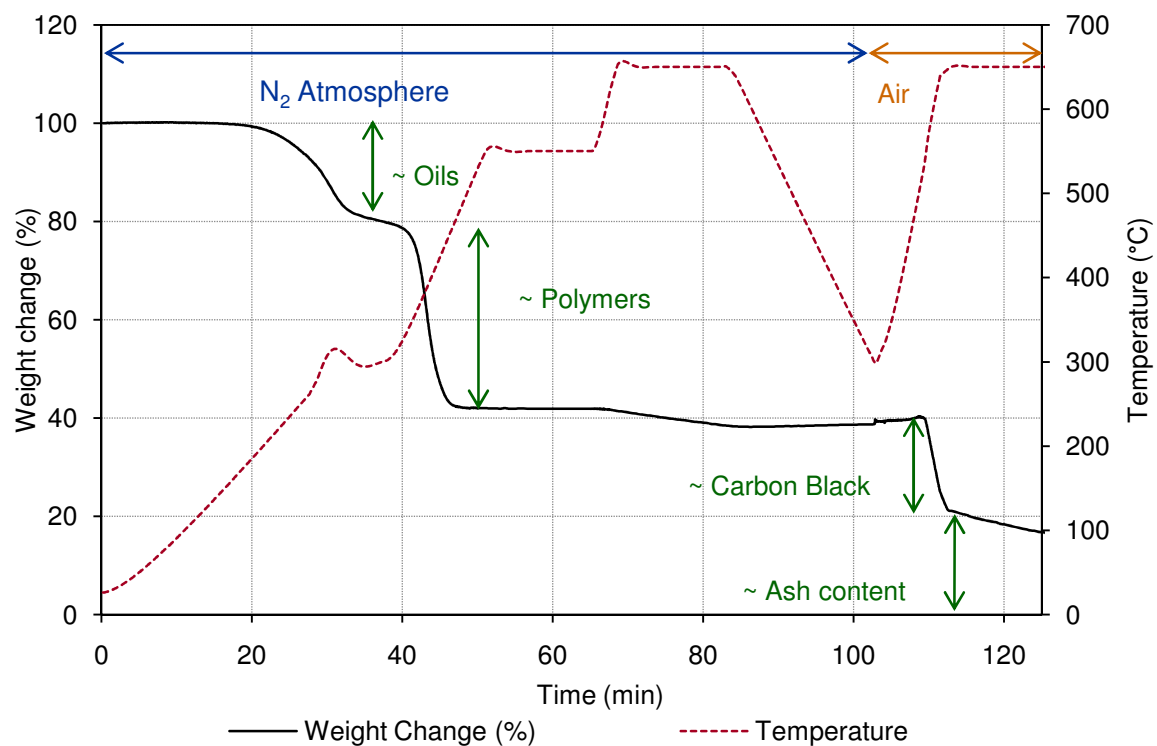
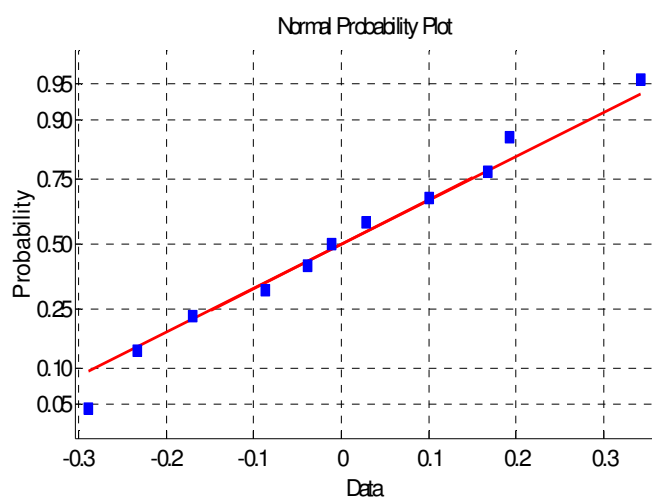


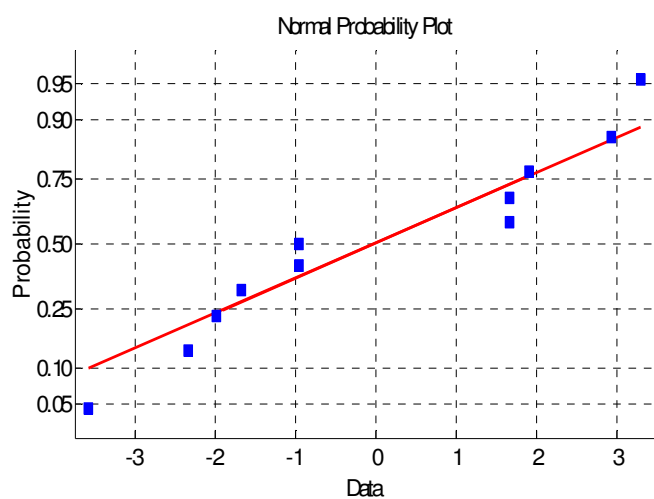
Figure B. Normal probability residuals plots (Chapter 4)

Part I

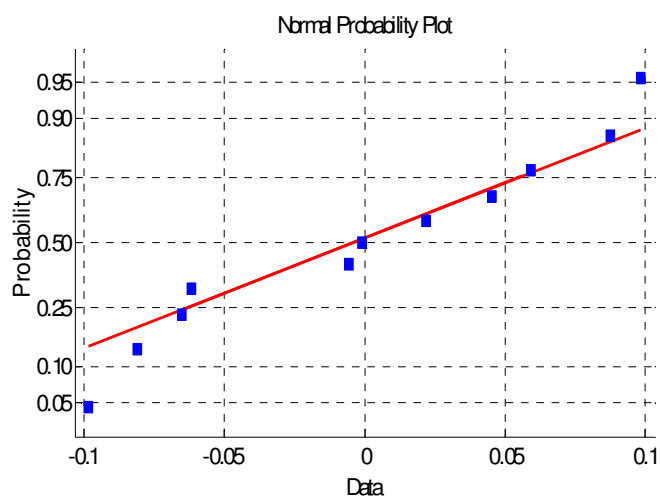
- Effect on Carbon Content



- Effect on Surface area

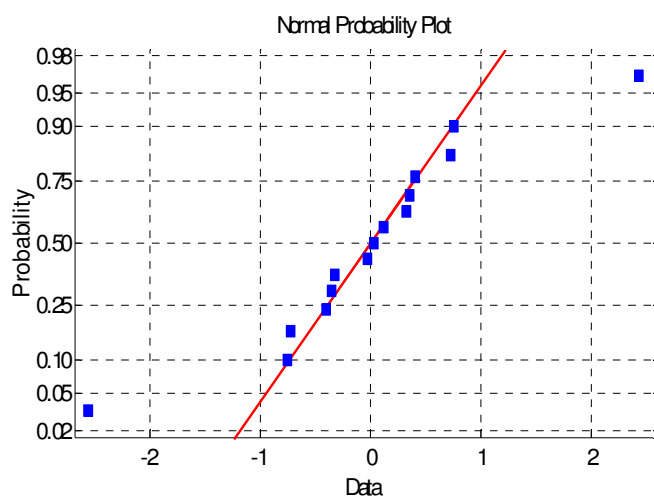


- Effect on pH-value

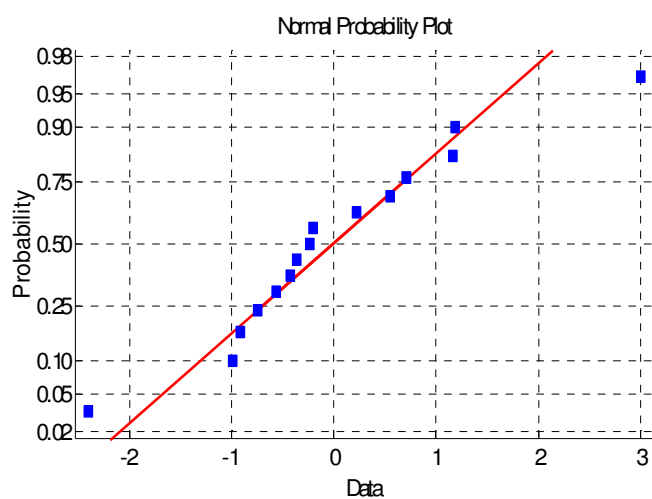


Part II

- Effect on Carbon content



- Effect on Surface area



- Effect on pH-value

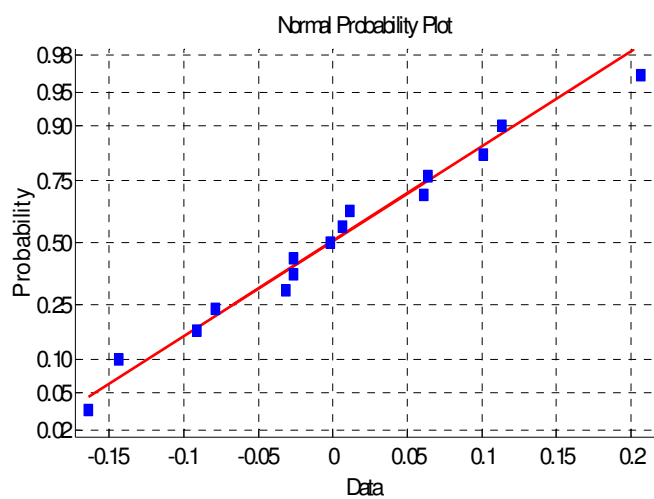


Figure C. Example plot of TG analysis of char pyrolysed for 3 min using domestic microwave I configuration (Chapter 5)

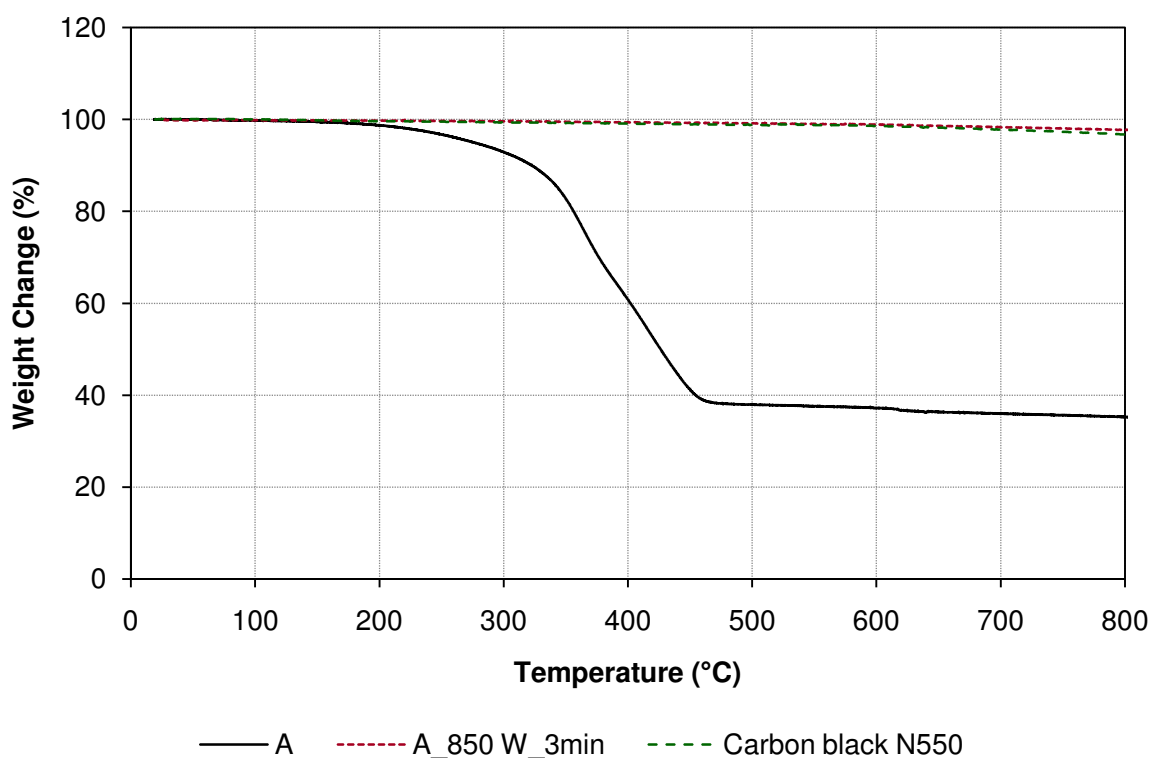


Figure C shows the thermal degradation profiles of sample A (raw rubber), of sample A after being exposed to microwaves at 850 W for 3 minutes and of a reference carbon black (N550 grade).

Appendix III

A. Mixing Process for compounds with and without coupling agent

The mixing process was completed in three stages. At the first stage the Brabender mixer was heated to 80°C and set at 60 rpm rotor speed counter mixing.

The following mixing sequence was used:

- 0 minutes: the polymer was added, followed by the char add-mix shown in the Table I below
- 1 min: ram raised ram lowered
- 2 min: ram raised, ram lowered. Speed reduced to 40rpm
- 3 min: ram raised, ram lowered
- 4 min: ram raised, ram lowered
- 5 min: ram raised, ram lowered

Table I. Rubber mixing formulation

<i>Ingredients</i>	A (phr)	B (phr)
Rubber (SBR)	100	100
Filler	60	60
Process Oil	10	10
ZnO	3.4	3.4
Stearic acid	2	2
Anti-oxidant (6PPD)	1.5	1.5
Coupling agent (TESPT)	-	8

The material was then removed and blended immediately on the ARTIS 13” 2-roll mill using a nip setting of 0.5. It was then allowed to rest for a minimum of 16 hours before conducting the second mixing stage. At the second stage the Brabender mixer was heated to 80°C and set at 60 rpm rotor speed counter mixing.

The following mixing sequence was used:

- 0 mins: Master batch added in strip format, ram lowered
- 1 min: ram raised, ram lowered. Speed then reduced to 40RPM
- 2 min: ram raised, ram lowered
- 3 min: ram raised, ram lowered
- 4 min: ram raised, ram lowered

On removal from the mixing chamber the first batches of compound were transferred to the ARTIS 13” 2-roll mill and passed through the nip once on a nip setting of 0.5. The second batch of each compound, once mixed was then added to the mill along with the first batch and the material passed through the nip of the mill 6 times. The nip was then increased to 1.0

and a sheet produced, this was then allowed to rest for a minimum of 16 hours before conducting the conversion mixing stage. The total batch weight of the two batches of each compound was then added to the nip of the ARTIS 13” 2-roll mill using a nip setting of 0.2, mill rolls were cooled to 18°C. The correct weight of each curative was then slowly added to the nip of the mill. The formulation details is shown in Table II below.

Table II. Rubber mixing formulation

<i>Ingredients</i>	A (phr)	B (phr)
Accelerator (TBBS)	1.5	1.5
Sulfur + mineral oil	1.37	1.37

Presentations

Oral Presentations

Reclaiming rubber fillers by microwave devulcanization of tyres. Presented at the 10th International Conference on Materials Chemistry (MC10), 4 – 7 July 2011, University of Manchester, UK

The RµPERT Project: Demonstration and application of a novel, state-of-the-art rotary microwave furnace for tyre devulcanization. Presented at the Microwave and Flow Chemistry Conference, 28 February – 2 March 2012, Lanzarote

Poster Presentations

Car Tyres: Where fools fear to retread? Producing the sustainable tyre. Presented at the SET for BRITAIN Exhibition in the Engineering Section held at the House of Commons on Monday 14th March 2011.

Back to Black: Closing the tyre recycling loop. Presented at the Department of Civil and Environmental Engineering Research Poster Presentation Day, Imperial College London on Wednesday 29th June 2011. Awarded Highly Commented.

Back to Black: Closing the tyre recycling loop. Presented at the Graduate Schools Poster competition on Friday 22nd July 2011. Awarded best poster title.

Recycling Carbon Fillers from Tyres by Microwave Pyrolysis. Presented at the conference “Medical Devices and Carbon Materials: Current Issues in Health and the Environment” on 22nd September 2011.