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Enhanced Waste Tyre Pyrolysis for the Production of Hydrocarbons and Petrochemicals

By:

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Declaration

I, Riki Strydom, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

28 August 2017

Signed Date

Abstract

Energy security, environmental and economic issues have spurred the interest in pyrolysis of scrap tyres for the production of fuels and energy in South Africa. However, the application of the process on a commercial scale is being hampered by the high cost required to upgrade the comparatively low quality pyrolytic products as well as the high energy input. Further insights into the mechanisms of thermal degradation of rubber will assist to improve on the process economics for production of liquid hydrocarbons fractions suitable for use as transportation fuels and chemicals. This study developed a correlation to predict the contents of waste tyres that will be converted into hydrocarbons during pyrolysis from the proximate analysis data. The mechanism/kinetics of thermal degradation behaviour of waste tyres is also studied, in order to locate the optimal temperature that will maximize the yield of liquid hydrocarbons and other recoverable materials.

Data from thermogravimetric analysis is used to determine the kinetic constants for the pyrolysis reaction over a temperature range of 500 °C - 750 °C. A relationship between the optimal temperatures and the volatile mater content depending on the desired products was obtained. This is necessary to eliminate thermal cracking of the pyrolytic oil into the non-condensable gas that will result from excessive temperature and the associated energy cost. Relationship to determine the kinetic equation constants is presented as a function of the volatile matter content. An inductor furnace batch reactor system is used to carried out the pyrolysis reaction, using Argon as the inert gas to provide the oxygen free environment required. The products are sent through a 2-stage condensers, the first operated at room temperature to collect the pyrolytic oil, and the second maintained at -5 ^{o}C to collect the condensable pyrolytic gases.

It was found that the total elemental carbon and hydrogen in a tyre from the proximate analysis can be accurately represented as $C = 6.163/\left(\frac{1}{FC} + \frac{2.341}{VM}\right)$ and $H = PC/-1.761 \times \left(\frac{VM}{FC}\right) + 16.114$ respectively. It was found that thermal degradation of waste tyres during pyrolysis occurs at specific (but wide) range of temperatures, which depends on the chemical composition of the scrap tyre and the desired product mix. An empirical relationship to obtain the optimal temperature at which more than 90% of the volatile matter in the waste tyre has been converted into hydrocarbons using the ratio of total elemental carbon to hydrogen was determined to be, $T_{90} = -54.452 * \left(\frac{C}{H}\right) + 1156.3$. Aside from maximizing the pyrolytic oil yield of waste tyres, the model gives a good indication of when to stop the ramp-up of temperature during pyrolysis saving a significant amount of time and energy.

This thesis is dedicated to my parents.

For their endless love, support and encouragement

Acknowledgements

Number one on my list, I wish to thank my parents for all their love and support throughout my life. Thank you both for giving me the strength to reach for the stars and chase my dreams.

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I would like to give a special thanks to Mrs H Small, Mrs E. Alberts and Mr A. Bester for the coffee and chat giving me their words of encouragement when I was feeling down and did not know how to proceed plus giving me that kick when needed.

To all my friends, thank you all for sticking with me. Your friendship means a great deal to me.

Thank you, Lord, for always being there for me and lighting my way.

This phrase has always been in the back of my mind and helped me on my journey:

Ad astra per aspera

(A rough road leads to the stars)

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Introduction

1.1 Overview

It is estimated that approximately 1.5 billion tyres are decommissioned as End of Life Tyres (ELT) each year globally (Williams 2013). This figure includes passenger car tyres which account for 85% of the total while the remaining 15% is composed of truck tyres and other categories. Figure 1 presents the global generation of ELTs (also refers to waste or scrap tyres (WBCSD 2010) in 2010. The same pattern is not expected to be markedly different from this presently.

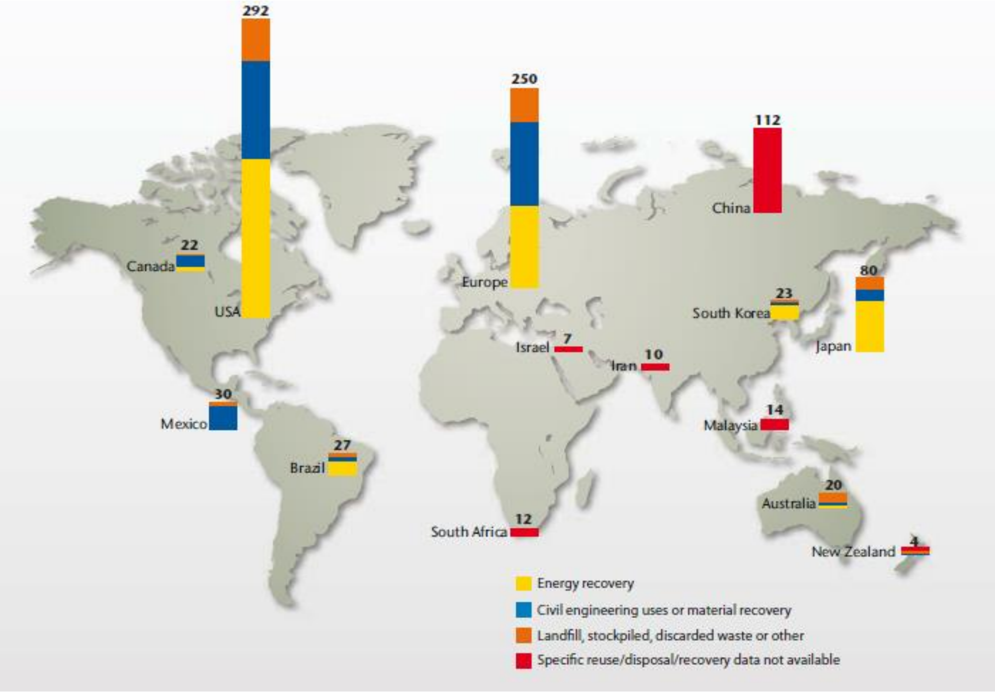

Figure 1: World Map of Waste Tyre Production (WBCSD, 2010)

It was estimated that worldwide, about 4 billion scrap tyres are currently stockpiled in landfills (WBCSD, 2010) with 1.5 billion added every year (López et al., 2013; Önenç et al., 2012). Latest South African statistics show that 60 million waste tyres are stockpiled and scattered throughout the country in 2013 with 11 million being added annually (REDISA 2013). This would imply that in 10 years, 170 million waste tyres will be around if current disposal ways are not drastically increased. It needs not be over-emphasised then that the current scrap (or waste) tyres disposal and management method in South Africa as elsewhere on the globe is grossly inadequate with overwhelming growing grave environmental and public health (Kordoghli, Paraschiv, Tazerout *et al.* 2015) and even economic consequences. Hence safer and sustainable ways for disposal of ELTs are attracting increasing interest worldwide (Saleh and Gupta 2014).

The statistics show that the number of motor vehicles worldwide is increasing at an incredible rate which in turn elevates the waste tyre problem to an alarming level. From an economic standpoint, no feasible way to effectively recycle the waste tyres has been found (Rathsack, Riedewald and Sousa-Gallagher 2015). Currently, re-treading of these used tyres to extend their lifespan is widespread (Sienkiewicz et al., 2012). However, when it is no longer practical to retread, the prevailing disposal method is landfilling (Downard, Singh, Bullard *et al.* 2015). However landfilling as a disposal method is also the most hazardous to the environment as well as a health risk (Karmacharya, Gupta, Tyagi *et al.* 2016, Shirule and Husain 2015).

Waste tyres pose an extreme fire risk which is especially difficult and time consuming to extinguish. Untreated landfill tyre fires have been known to smoulder for years. An additional problem with tyre fires is the harmful emissions released to the atmosphere, soil and water (Lung 2009). In some environments the storage of waste tyres provides ideal breeding ground for insects and various bacteria (Kalverkamp and Pehlken 2016). These dumps have been linked to outbreaks of West Nile fever, malaria and dengue fever among other fatal diseases (Lung 2009). To prevent fire risk and infestations, waste tyres are shredded and buried (Karmacharya, Gupta, Tyagi *et al.* 2016). Even then a two-fold problem arises. The process is very energy intensive and the tyres potentially valuable energy is lost.

Therefore, around the world, countries are trying to curb discarding ELTs in landfills, however it still remains the prevalent method of disposal (Martínez, Puy, Murillo *et al.*

2013). In the European Union, tyres are banned from landfills while the United States have restrictions requiring tyres be shredded or monofilled (WBCSD 2010). Hence there is a pressing need to develop commercially viable and environmental safe technologies to combat the vast and growing amount of waste tyres being currently stockpiled in a number of landfills across the world. The lack of any environmental or economically feasible solutions to deal with the waste tyre disposal poses a serious dilemma. A cost effective, environmentally sound and sustainable management of scrap tyres has remained a daunting task (Kannan, Diabat and Shankar 2014, Williams 2013).

A steady decline in world fossil fuel reserves has sparked interest in alternate energy sources. A growing need for new sustainable energy solutions has led to the growing investigation thereof. Ironically, end users of fossil transportation fuels are the increasing number of motor vehicles worldwide which in turn elevates the waste tyre problem. Due to tyres its high energy content, waste tyres landfills are seen as stockpiles of potentially valuable energy resources that can be converted to fuels, chemicals among others (Choi, Oh and Kim 2016). A dual solution will be achieved by utilizing the vast and growing stockpile of waste tyres currently to meet the growing global energy demand. It will serve as an alternate energy source and as well as a sustainable and environmentally friendly waste tyres disposal means. It is known that rubber has a gross calorific value higher than that of coal (Rathsack, Riedewald and Sousa-Gallagher 2015) leading to an investigation into converting the waste tyres to a viable energy source.

Gaining in popularity is pyrolysis which would convert waste tyres into valuable chemicals and/or alternative fuels for compression ignition engines (Hita, Arabiourrutia, Olazar *et al.* 2016). South African is currently bedevilled by an energy crisis with the power outage first witnessed in 2007 becoming a permanent feature and pose a serious threat to the much needed economic growth. Therefore, the growing commitment to and investment in the development of innovative technologies for waste tyres recycling and processing in South is impelled by environmental as well as economic factors. The unsustainability and the public health concern of the present landfilling disposal method and the country dependency on imported crude to meet the growing demands for transportation fuels and energy has led to the growing investment in the development of commercial processes for the conversion of scrap tyres to fuels and energy in South Africa.

The Integrated Industry Waste Management Plan (IIWMP) approved on 28 November 2011 among others created the Recycling and Economic Development Initiative of South Africa (REDISA), an organization charged to implement the plans set out in the IIWMP and is expected to develop a sustainable South African tyre recycling and processing industry. New regulations are being implemented in South Africa by REDISA in conjunction with the Department of Environmental Affairs to curb illegal dumping of waste tyres. The regulations dictate that all tyre manufacturers and importers must register and pay a levy for every kilogram tyre brought into circulation. These funds will then be allocated to the collection and safe disposal of the waste tyres. Another portion of the funds will be used for research and development purposes to create recycling processes to solve the dilemma (REDISA 2013).

It was realised that waste tyres can serve a source of fuels and chemicals. By taking this approach, waste tyres to fuel process may be employed to develop sustainable energy processes which have the added benefit of job creation in the South African economy. In order to achieve the goals set out in the IIWMP with respect to the development of home-grown technologies and expertise in the management of waste tyres, it is necessary to develop processes, technologies and expertise in waste tyre processing. Current efforts are geared towards using this hitherto waste for the production of fuels, chemicals and innovative products. The main challenge is to develop innovative technologies for the production of fuels for transportation, agricultural machineries and industrial (heating) applications that are economically viable on a large scale. Such technology must be suitable for the South African environment, and provide opportunities for human capital development through skills development and technology transfer and ultimately facilitate job opportunities and wealth creations. Hence the plant must be cost effective, energy efficient and with minimal environmental footprints.

1.2 Waste Tyre Recycling Methods

There exist numerous types of disposal routes for waste tyres. Some are environmentally friendly and safe with the benefit of energy recovery when processed in the correct context while others are impacting our daily lives in an adverse way. In Europe, ELT recovery and treatment have taken centre stage by setting a target of 95% recycle/recovery by 2015. Figure 2shows the improvement of waste tyre management and utilization as of 2010 (European Tyre & Rubber manufacturers' association 2011).

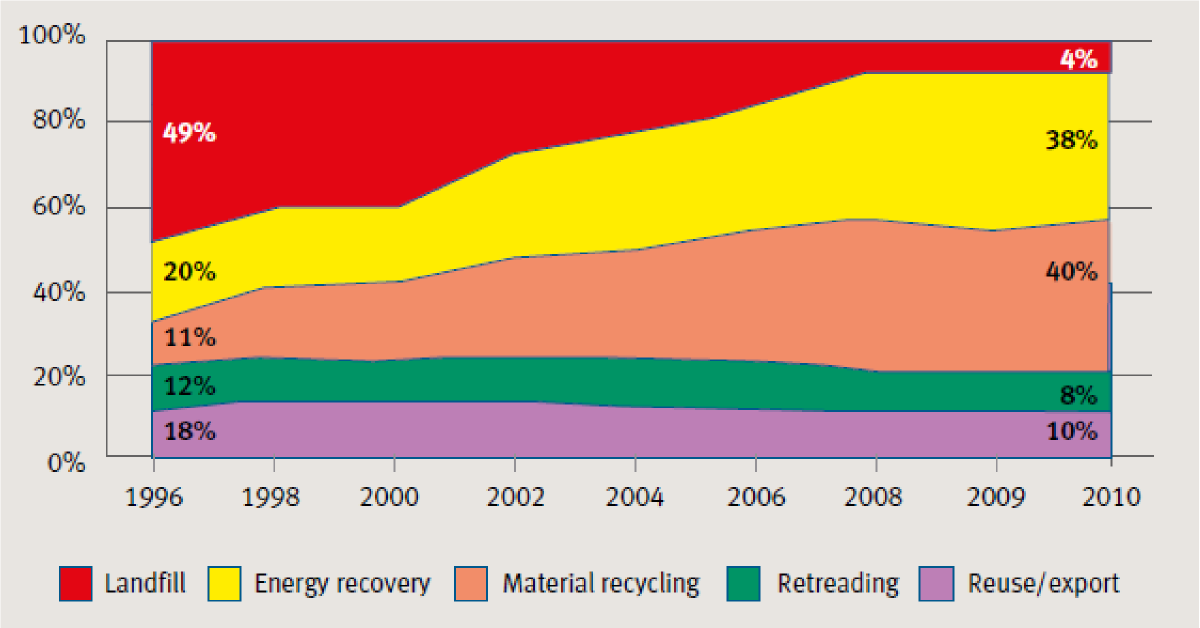

Figure 2: Summary of the evolution of waste tyre treatment

1.2.1 Waste Tyres as Fuels

Due to the fact that waste tyres have a much higher calorific value than coal it is possible to use tyre as a fuel substitute. (İlkılıç and Aydın 2011). Cement plants being energy intensive are the main consumers of Tyre-derived Fuels (TDFs). Other industries making use of TDFs are thermal power stations and the paper and pulp industries. Advantages of using TDFs include cheaper stock costs than coal and significantly reduced CO_2 emissions, thus it provides savings on carbon taxes (Portland Cement Association 2008).

1.2.2 Retreading of Worn-out Tyres

Retreading, recapping or remoulding is a process of increasing the life span of a worn tyre. The process involves the removing of the old tread by high speed mechanical buffeting (The Tire Retread & Repair Information Bureau 2013). Once clean the new tread can be applied to the casing by Mold Cure or Pre Cure methods. Retreading tyres consumes two-thirds less energy and releases one third less greenhouse gasses compared to the production of new tyres making it both an economical and environmentally friendly option of recycling tyres (The Tire Retread & Repair Information Bureau 2013).

1.2.3 Materials Recovery

Once retreading is no longer a possible option to recycle tyres, material recovery is sought. Tyres are mechanically separated into their rubber, steel and textile parts as far possible. The steel and textile can be recycled while the rubber is shredded or powderized depending on the final application. The rubber is used extensively for civil engineering applications and can be moulded into new rubber products such as dustbins, furniture, wheelbarrows etc. An added advantage of material recover is that the physical volume of the tyre that cannot be used and needs to be discarded is reduced by a factor of four (ChemRisk LLC 2009).

1.2.4 Devulcanization

Devulcanization is a relatively old concept but has gotten renewed interest during the past decade due to the inadequacy of present tyre management approaches. As the name implies, the process of devulcanization modifies the structure of vulcanized rubber by severing its monosulfidic, disulfidic, and polysulfidic crosslinks (carbon-sulfur or sulfur-sulfur bonds). This devulcanized rubber material can then be revulcanized in other products ideally as a virgin rubber substitute. Very few processing plants are producing devulcanized rubber in a commercial capacity, likely reasons may include low quality product and high production costs (CalRecovery Inc. 2004).

1.2.5 Reverse Polymerization

Environmental Waste International (EWI) developed a microwave-based process known as Reverse Polymerization (Environmental Waste International Inc. 2015). During this process, the tyres are bombarded with microwave energy that is absorbed by the organic material increasing the bonds stored energy until they break. Thus complex organic compounds are broken into simpler compound with lower molecular weights. Solid tyres sublimate into gaseous hydrocarbon vapours that can be condensed. As with pyrolysis this process is done in the absence of oxygen. Advantages of using this process include:

- Lower operating temperatures: 150 - 350°C
- A high degree of control can be exerted on the microwave energy input

- Microwave energy heats the tyre uniformly whereas pyrolysis heat from the outside inward (Environmental Waste International n.d.)

1.2.6 Thermo-chemical Conversion

Waste tyres with a gross calorific value of 3.3 $\times 10^4$ kJ/kg similar to that of coal, cheaper cost compare to fossil fuels and reduced CO_2 emission has attracted interest as feedstock in Wastes-to-Energy (WTE) plants. The high energy content is recovered for instance via thermo-chemical conversion process as fuels and chemicals. Pyrolysis the thermal distillation or decomposition of organic matters into oils, gases, and char (Kordoghli, Paraschiv, Tazerout *et al.* 2015), is receiving the most attention as a way of converting the waste tyre into fuels. The decomposition occurs by the application of heat in the absence of oxygen, or under conditions where the oxygen concentration is too low for combustion or gasification reactions to occur (Zabaniotou, Antoniou and Bruton 2014).

The resulting products are liquid hydrocarbon fuels, combustible non-condensable gases at atmospheric conditions) and solid char remains mostly comprising of carbon black. The products distribution depends on the reaction conditions including temperature, pressure, space time, the heating, use of catalysts and so on (Choi, Jung, Oh *et al.* 2014, Hu, Fang, Liu *et al.* 2014, Raj, Kennedy and Pillai 2013, Williams 2013). Figure 3 shows a simplified diagram of the pyrolysis of waste tyres (Martínez, Puy, Murillo *et al.* 2013).

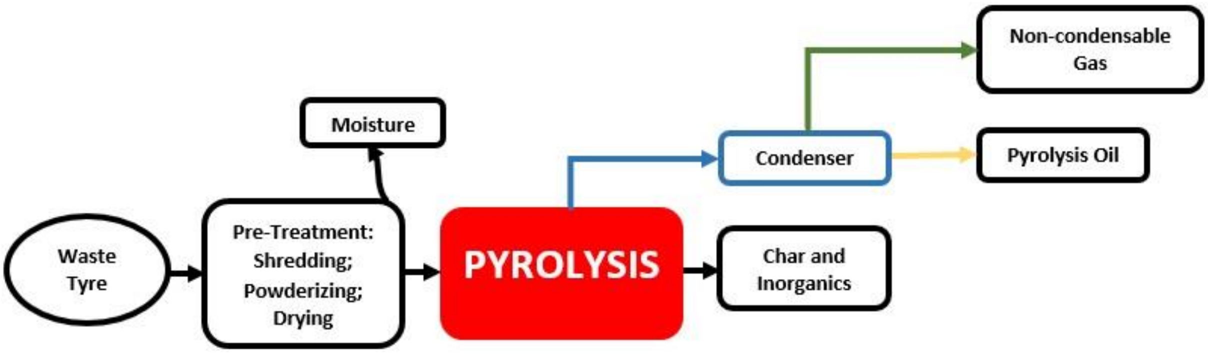

Figure 3: Waste Tyre Pyrolysis Block Flow Diagram

Pyrolysis oils can be used directly or as a blend with other heavy oils for industrial heating or as feedstock in petrochemical processes. It can as well be upgraded into transportation fuels by lowering the sulphur content to acceptable level using conventional refining process. The non-condensable gases on the other hand can be used as fuel gas or electricity generation. Further processing using conventional refining processes (for instance hydrotreating for sulphur removal) can produce diesel ranges fractions suitable as transportation fuels and chemicals as feedstock for petrochemical processes.

Despite extensive research efforts, the expected wide spread application of pyrolysis on a commercial scale is still being hampered by economics majorly due to the cost associated with improving the products comparatively low quality as well as the process high energy demand. To be widely marketable the sulphur and other impurities present in the oils and gas stream must be lowered requiring added unit operation. There is also the issue of the gaseous pollutants emission from the plant. Thus in order to make waste tyre pyrolysis an attractive alternate, a robust design is needed to deal with all these factors. Most studies focus on the optimization of certain process parameters that target specific products or yields of waste tyre pyrolysis with little emphasis on commercial viability and large scale operation.

Current research into waste tyre pyrolysis seeks to maximize oil yield while changing different process conditions, reactor set-ups, catalysts and heating units such as microwaves and open flames. However, during waste tyre pyrolysis a vast range of process variables have been identified to affect both the product yields and quality to varying degrees.

1.3 Statement of Research Problem

Pyrolysis of scrap tyres are typically conducted at elevated temperatures (700 – 800 ^{o}C) to ensure maximum thermal conversion of its polymeric compounds content to hydrocarbons. However, scrap tyres have a vast range of chemical constituents which are not factored in for their influence on the pyrolytic process. It is widely accepted that that thermal degradation of scrap tyres occurs at specific (but wide) range of temperatures, depending on the chemical composition of scrap tyre. It is therefore necessary to develop a correlation that can be used to accurately predict the chemical compositions of scrap tyres and hence locate an optimal pyrolysis temperature to maximize oil yields and other materials recovery. It will also minimize energy input into the process, and hence improve the process economics among other benefits.

A number of correlations have been reported to predict the elemental compositions of biomass and coal from proximate analysis. No such correlation are however available in the open literatures for scrap tyres. This study carried out a detail elucidation of the physical and chemical properties of different scrap tyres to develop simple models for the elemental composition from the proximate analysis. It further investigated how the elemental composition affects the thermal degradation behaviour and the selectivity to pyrolytic oil and other recoverable materials. Also, the mechanisms involved in the thermal breakdown of scrap tyres to find the kinetics rate laws parameters are herein presented and discussed.

1.4 Aims and Objectives of the Research

The main thrust of this project is to investigate the mechanism of thermal degradation of waste tyres as influenced by the chemical composition in order to identify factors that influences the products distribution from waste tyre pyrolysis. These include hydrocarbon gases and oil and other recoverable materials, particularly the carbon black.

To realise this aim, the study focus on the following objectives,

a) Analysis of waste tyres chemical compositions to develop a model to predict the elemental composition of waste tyres from proximate analyse.
b) Preliminary investigation into the mechanism of thermal degradation of waste tyres which influences the pyrolytic process conditions and oil yield to develop reaction rate kinetics.
c) Determine the production distributions as a function of process conditions in terms of liquid products yields
d) To analyse the chemical compositions of the oil and recoverable materials from the pyrolysis reaction to determine appropriate end use and applications and/or unit operations required for its upgrading.

1.5 Research Questions

a) Can a detailed chemical compositional analysis of scrap tyres be accurately predicted from the proximate analysis results?

b) What is the optimum pyrolysis temperature such that just enough energy is supplied to convert only the volatile polymeric compounds in the tyre and hence recover maximum carbon black?

c) Does the pyrolysis temperature influence the products distribution of the hydrocarbon compounds in the product?

d) Is there significant change in the selectivity towards liquid hydrocarbons at the optimum temperature located when waste lube oil is added to the powdered tyre?

1.6 Scope of Study

Various forms of pyrolysis processes have previously been investigated such microwave, catalytic and co-pyrolysis process to produce transportation fuel grade hydrocarbons from scrap tyres. In this study the focus is on the analyses of the liquid hydrocarbons in the pyrolytic oil using an inductor furnace for the pyrolysis of scrap tyres. The intention is to improve on the yield of C_{5+} hydrocarbons while minimizing the pyrolytic gases formation.

1.7 Research Design and Methodology

A thorough literature review will be compiled on the current waste tyre problem and how it effects RSA in terms of pileup and health reasons. This will lead to further investigations into the current waste tyre disposal methods and patents which will demonstrate that which is lacking to enhance the performance of waste tyre pyrolysis. This was vitally important as it will demonstrate how this thesis will contribute to knowledge and effective industrial implementations.

Additional literature reviews on the chemical and physical properties of waste tyre will provide information needed with regards to the analyses needed to assess waste tyre feedstock and pyrolysis products. Typical testing of waste tyres includes:

- Caloric Value measurements – calorific value/energy content
- Ultimate and Proximate Analysis – chemical composition
- Thermogravimetric analysis – thermal degradation behaviour of the tyres
- Gas Chromatography – pyrolysis products analysis for instance to determine the hydrocarbons type and yield.

The research will be conducted using five waste tyres of different compositions distinguished by their brand names (which will not be included for ethical reasons). These preliminary analyses results help to understand the characteristics of the tyres which influence their thermal degradation. Mathematical modelling is developed to permit a highly accurate prediction of the various tyres thermal degradation behaviour and their chemical properties.

Once all the degradation behaviours of the tyre is fully investigated to find the optimum pyrolysis temperature, a batch reactor is used to carried out the pyrolysis at the optimum temperature and 1 atm. The products obtained are categorized in terms of their hydrocarbon content. Chemical analysis of the hydrocarbon products is then used to recommend the most feasible use of the pyrolysis oil and recoverable materials.

1.8 Significance of the Research

In South Africa, there is an urgent need to find commercially viable and environmental safe ways to manage the vast amount of waste tyres currently stockpiled. The pyrolysis of these waste tyres to produce fuels will greatly assist in lessening the country's dependence on fossil fuels. The ultimate goal will be to provide a foundation to set up a working waste tyre pyrolysis plant which will not only supply valuable chemicals, but will also contribute to the establishment of a new industry for job creation. This research will provide a huge step forward in optimizing current pyrolysis technology that may be able to completely solve the waste tyre dilemma and the world's fossil fuel demand by laying the foundation for tyres thermal properties to effectively degrade into usable products.

It is expected to successfully model the total elemental compositions of waste tyres with respect to its proximate analysis. As the cost of performing ultimate analysis is double that of proximate analysis the model would drastically lower operational and investigative costs to perform these analyses. Further insight into the waste tyre degradation mechanisms would help to improve performance of waste tyre pyrolysis in terms of optimized pyrolysis temperature, oil yield and recoverable materials. By investigating different tyre compositions the variation in oil quality can be used to recommend end uses such as alternate fuels or other valuable chemicals.

1.9 Thesis Layout

Chapter 1 gives an introduction to the work of this thesis. Chapter 2 presents a thorough review of past works done on waste tyre properties, waste tyre thermal kinetics and degradation and waste tyre pyrolysis and its resulting products. Chapter 3 describes the materials and experimental methods used in this research. Chapter 4 follows on Chapter 3 through the results obtained from performing the experiments detailed before. Chapter 5 discusses the results obtained from the experiments of the waste tyre and makes certain correlations there from.

2

Survey of Literatures

2.1 Physiochemical Characterisation of Waste Tyre

The main components in vehicles tyres are natural rubber (NR) and synthetic rubber (SR) which includes styrene butadiene copolymer (SBR) and butyl rubber (BR) together with carbon black (CB), textile, steel and a small amount of other additives determined by the individual manufacturers (Kar 2011, Lah, Klinar and Likozar 2013). NR is harvested from the *Hevea* tree (Rubber tree) which has distinctive elastic characteristics that makes it crucial for tyre manufacturing while SR is synthesized from petroleum based products. Both NR and SR have the general chemical formula C_xH_y and are considered thermoplastics. CB is used to strengthen the rubber components as well as aid in their abrasion resistance, it is produced by the partial combustion of fossil Hydrocarbons (HC's). The textile and steel are included to reinforce the tyre together with the other additives to control the various physical properties. Individual component quantities cannot be quantified as tyres are insoluble in organic solvents (Unapumnuk, Lu and Keener 2006).

One of the final steps is tyre manufacturing is the vulcanization process. This process is an irreversible reaction that creates crosslinks (bridges) between the individual molecular chains of the polymer in turn forming a three-dimensional network. These bonds are insoluble and have superior mechanical properties thus making the decomposition of tyres challenging. The most popular vulcanization process involves the addition of sulphur together with ZnO to control the process and enhance the final products physical properties. This becomes problematic for the pyrolysis oil and gas products.

The characterization of waste tyres in terms of analysis and energy content is determined with the ultimate and proximate analysis. The fixed carbon (FC) from the proximate analysis originates from the CB used during the tyre manufacturing. In contrast to the carbon content of the ultimate analysis in which carbon is lost to the HC's by way of the volatiles (Murillo, Aylón, Navarro *et al.* 2006). It was established that the volatile component of tyre arises from the polymeric compounds in NR and SR and should correspond to the quantity of pyrolysis oil and gas obtained upon completion of the process (Aylón, Fernández-Colino, Murillo *et al.* 2010). Thus, the remaining char coincides with the non-volatile matter of which the fixed carbon is in the majority.

A collection of reported ultimate and proximate analysis for waste tyre data (steel free) is compiled in Table 1. High hydrogen content of up to 8.4wt% can be observed as well as varying degrees of sulphur due to the extent of the vulcanization processes, while volatile matter (VM) varies from 34.90 to 66.00wt%. These differences can be attributed to the tyre brands and will affect the pyrolysis products yields, compositions and gross calorific values (GCV).

2.1.1 Prediction of Total Carbon and Hydrogen Content

The elemental composition is one of the most important properties of any fuel for its utilization. To experimentally determine the ultimate analysis of any biomass requires specialized equipment and highly trained analysts to perform accurate measurements making this a very costly process. However, the proximate analysis can easily be performed by any capable scientist and using an ordinary muffle furnace (Majumder, Jain, Banerjee *et al.* 2008, Parikh, Channiwala and Ghosal 2007, Shen, Zhu, Liu *et al.* 2010). Therefore, to save costs and man-hours certain correlations are developed to determine the elemental composition of biomass from the proximate analysis of that substance. Various published works are available that reported models to predict the ultimate analysis contents from the proximate analysis for biomass and coal. It is of vital importance that correlations like these are highly accurate and versatile to prevent any unnecessary complications that may arise as a result of the prediction along the processing routes.

Table 1: Ultimate and Proximate analysis of tyres reported in recent literature (dry).

Ultimate Analysis [%]					**Proximate Analysis [%]**				**CV [MJ\kg]**	**Reference**
C	**H**	**N**	**S**	**O**	**VM**	**FC**	**Ash**	**M**		
86.4	8.0	0.5	1.7	3.4	62.2	29.4	7.1	1.3	40	(Williams and Brindle 2003)
74.3	7.2	0.9	1.71	15.89^{d}	58.2	21.3	18.9	1.6	30.5	(Önenç, Brebu, Vasile *et al.* 2012)
86.0	8.4	0.5	1.9	3.2a	66.0	29.1	4.9	0.4	38.3	(López, Centeno, Alguacil *et al.* 2011)
74.3	7.2	0.9	1.71	15.89^{d}	58.2	21.3	18.9	1.6	30.5	(Ucar, Karagoz, Ozkan *et al.* 2005)
88.64	8.26	0.43	1.43	nr	67.3	31.14	3.83	0.94	ui	(Mastral, Murillo, Callén *et al.* 2001)
84.05	7.99	0.23	1.41	6.32d	66.7	27.4	4.4	1.5	37.7	(Siva, Onenc, Uçar *et al.* 2013)
88.64	8.26	0.43	1.43	nr	67.3	31.14	3.83	0.94	ui	(Mastral, Murillo, Callen *et al.* 2000)
86.7	8.1	0.4	1.4	1.3	61.9	29.5	8.0	0.7	36.2	(González, Encinar and Canito 2001)
78.6	7.1	0.3	1.8	4.8	67.5	25.2	5.3	2.1	37.3	(Leung, Yin, Zhao *et al.* 2002)
89.5	7.3	0.3	1.9	0.9^{d}	61.9	29.9	7.1	1.1	37.35	(Díez, Martínez, Calvo *et al.* 2004)
77.6	7.0	0.43	1.4	7.7	71.5	28.5	8.3	0.2	36	(Singh, Wu and Williams 2012)
82.8	7.6	0.5	1.3	4.5	68.7	27.2	3.3	0.8	36.46	(Dai, Yin, Wu *et al.* 2001)
85.16	7.27	0.38	2.3	0.54	61.3	33.47	5.22	1.16	ui	(Galvagno, Casu, Casabianca *et al.* 2002)
89.4	7.0	0.2	2.0	nr	65.5	29.4	3.7	0.9	nr	(Conesa, Martin-Gullón and Font 2005)
77.3	6.2	0.6	1.8	7.1^{d}	67.7	25.5	6.8	nr	nr	(Portofino, Donatelli, Iovane *et al.* 2013)

67.08	6.12	0.17	2.05	25.58[d]	59.69	19.45	19.13	1.72	27.37	(Kar 2011) low
83.92	6.83	0.78	0.92	nr	64.97	30.08	4.16	0.75	38.6	(Zhang, Wang, Ma *et al.* 2008)
82.52	6.95	0.47	1.7	8.37[d]	65.45	24.08	9.63	0.84	37.46	(Banar, Akyildiz, Özkan *et al.* 2012)
86.39	6.91	0.46	0.12	1.42	64.91	29.54	4.7	0.85	16.6?	(Raj, Kennedy and Pillai 2013)
81.84	7.6	0.39	1.28	nr	68.98	24.42	6.6	nr	37.04	(Huang and Tang 2009)
75.5	6.75	0.81	15.5	15.5	59.50	20.85	18.12	1.53	29.18	(Islam, Joardder, Hasan *et al.* 2011)
87.9	7.4	0.3	1.1	nr	63.6	31.8	3.8	0.8	38.61	(Martínez, Murillo, García *et al.* 2013)

nr – not reported, d – by difference, ui – unit inconsistency

Parikh, Channiwala and Ghosal (2007) developed prediction algorithms for ultimate analysis carbon and hydrogen contents by factoring in the proximate analysis fixed carbon and volatile matter contents:

$$C = 0.637 * FC + 0.455 * VM \tag{1}$$

$$H = 0.052 * FC + 0.062 * VM \tag{2}$$

Eq. **Error! Reference source not found.** and (2) were derived using about 200 data points that Parikh, Channiwala and Ghosal (2007) generated from controlled thermal degradation of various types of biomass material samples and other published data. These correlations were then validated using 50 published data points. Parikh, Channiwala and Ghosal (2007) calculated an average absolute error limit with respect to the experimentally determined results of 3.21% and 4.79% for the carbon and hydrogen content respectively. The work shows that the relationship of total elemental carbon and hydrogen to volatile matter and fixed carbon is a linear function.

In addition to factoring in the fixed carbon and volatile matter contents to the correlation Shen, Zhu, Liu *et al.* (2010) included the effect of ash content on the carbon and hydrogen predictions. The correlations were determined using 66 data points obtained from published literature:

$$C = 0.635 \times FC + 0.460 \times VM - 0.095 \times A \tag{3}$$

$$H = 0.059 \times FC + 0.069 \times VM + 0.010 \times A \tag{4}$$

Shen, Zhu, Liu *et al.* (2010) reported no substantial difference in the fixed carbon and volatile matter factors when compared to the correlations of Parikh, Channiwala and Ghosal (2007). It is suggested by Shen, Zhu, Liu *et al.* (2010) that the fixed carbon and volatile matter content are different because of the ash content differences on a dry basis. Thus the ash content is incorporated into the correlation. By validating the correlations with 20 published data points average absolute errors of 3.17% and 4.47% were obtained for the carbon and hydrogen content respectively.

Vista User Group, Electric Power Research Institute and Black & Veatch (2014) developed a correlation for approximating the elemental composition of coal from its proximate analysis:

$$C = \frac{\left(DMMFFC + 0.9 \times \ (DMMFVOL - 14)\right) \times \ (VM + FC)}{100} \tag{5}$$

$$H = \frac{\left(\left[\left(DMMFVOL \times 7.35/(DMMFVOL + 10)\right) - 0.013\right] \times \ (VM + FC)\right)}{100} \tag{6}$$

where:

DMMFFC is the dry mineral-matter-free fixed carbon [wt%]

DMMVOL is the dry mineral-matter-free volatile matter [wt%]

DMMFFC and DMMVOL are calculated as follow:

$$DMMFFC = \frac{FC}{(FC + VM)} \times 100 \tag{7}$$

$$DMMVOL = \frac{VOL}{(FC + VM)} \times 100 \tag{8}$$

Vista User Group, Electric Power Research Institute and Black & Veatch (2014) stated that these correlations yield reasonable approximations for predicting the carbon and hydrogen contents. However, it is stated that the correlations have been shown to work best using coal specifically bituminous coals from the eastern United States.

2.2 Thermal Degradation Behaviour of Waste Tyres

To be able to successfully and efficiently carry out waste tyre pyrolysis the mechanisms involved in the breakdown of waste tyres must first be fully understood. The initial steps of waste tyre degradation that facilitate the yield of hydrocarbons can be investigated using Thermogravimetric Analysis (TGA). Using this technique, the mass of the waste tyre as it is subject to increasing temperature over a period of time in an inert atmosphere can be accurately monitored (ASTM 2008). The thermogravimetric curve (TG curve) shows the waste tyre weight loss versus temperature, while the derivative thermogravimetric analysis (DTG curve) is the derivative of the TG with respect to temperature.

Thermogravimetric analysis falls into two analysis categories namely Isothermal TGA and Dynamic (non-isothermal) TGA. (Al-Salem, Lettiere and Baeyens 2009 By definition, Isothermal TGA is the investigation of a materials thermal decomposition rate at a set or pre-determined temperature. Isothermal TGA requires a fast heating rate to prevent reactions occurring before the set temperature and small sample sizes. These prerequisites keep the sample temperature profile constant by overcoming mass and heat transfer barriers. In contrast Dynamic TGA heats the sample from room temperature at a pre-determined or set heating rate to a target temperature which is typically when the sample mass is unchanging (Al-Salem, Lettiere and Baeyens 2009).

A tyre's physical characteristics makes shredding and powderizing to a size small enough to achieve a uniform temperature profile difficult requiring significant input of energy. Sample weight loss is entirely dependent on time during isothermal TGA while temperature is the prevailing factor in dynamic TGA. For these reasons dynamic TGA and dynamic pyrolysis is considered a superior technique in terms of reactor and process designs.

2.3 Mechanisms of Waste Tyres Thermal Degradation

The dynamic DTG of a waste tyre performed at a heating rate of 15K/min by González, Encinar and Canito (2001) is presented **Error! Reference source not found.** Figure 4. When DTG is used to investigate the decomposition of waste tyre 2 – 3 regions/stages of chemical processes can be identified. As of yet researchers have failed to come to an agreement as to whether the DTG of waste tyres can be divided into two or three regions. Haydary, Jelemenský, Gašparovič *et al.* (2012) considers tyre pyrolysis a two stage chemical process. During the first stage the decomposition of NR occurs as well as the release of the volatile additives and compounds of lower molecular weights. Thereafter stage two sees the decomposition of the SBR and BR polymer chains. Haydary, Jelemenský, Gašparovič *et al.* (2012) notes that over a certain temperature region both processes can run concurrently.

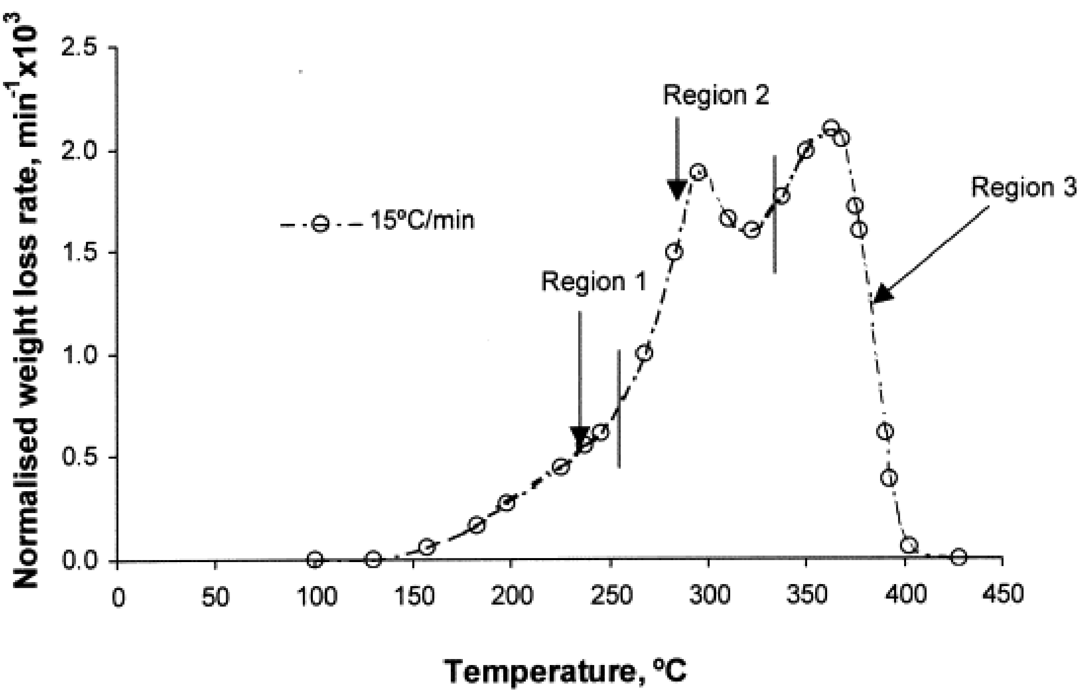

Figure 4: Differential Thermogravimetric curve by González, Encinar and Canito (2001)

The consensus among researchers is a three stage pyrolysis process states that the first stage is the volatilization of the processing oil and evaporation of moistures in the tyre. Stage two is degradation of NR while stage three is the SBR and BR (Seidelt, Müller-Hagedorn and Bockburn 2006). González, Encinar and Canito (2001) suggests that the three regions may be due to three non-interacting groups of volatiles contained in scrap tyres. The decomposition process then evolves by means of first orders reactions that run parallel with each other. González further found that the dual weight loss peaks for dynamic DTG are dependent on the process heating rates whereby at higher rates the peaks may coincide (40 – 50 K min^{-1}). For isothermal DTG singular peaks are obtained and shift towards shorter times at higher process temperatures.

To gain a greater insight into the complexities of waste tyre pyrolysis some researchers tend to investigate the effect the core components of tyres have on the TGA/DTG. According to Jitkarnka, Chusaksri, Supaphol *et al.* (2007) the regions identified in TGA can be attributed to the decomposition of the individual tyre constituents (NR, BR and SBR). By performing TGA on each component they exhibit two weight loss peaks over the temperature range which corresponds to its primary and secondary products. Carbon black, ZnO and sulphur was found to have no effect on the primary peaks, however a slight shift of the secondary peaks is seen whereby the NR peak forms a shoulder while shifting to higher temperatures and the BR peak shifts to lower temperatures.

These results are in accordance with work done by Seidelt, Müller-Hagedorn and Bockburn (2006) who tested similar experimental variations. Fernández-Berridi, González, Mugica *et al.* (2006) performed high resolution TGA on various blends of NR and SB. **Figure 5** shows one such experiment with a 40/60 ratio of NR/SBR. The maximum decomposition of NR is identified at 350°C whereas the SBR peak is found at 424°C.

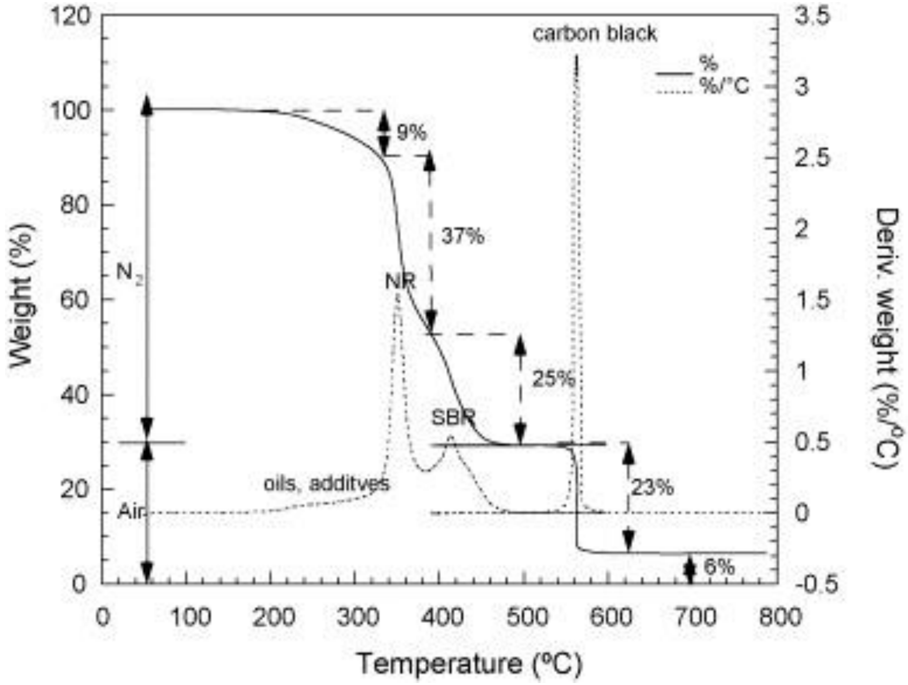

Figure 5: Experimental results of TGA and DTGA by Fernández-Berridi, González, Mugica *et al.* (2006)

To date no definitive differences in styrene and butadiene rubber can be determined using TGA due to the inability of discerning individual weight loss peaks when combined. Fernández-Berridi, González, Mugica *et al.* (2006) also found that an increase in SBR content increases the overall thermal stability as the NR degradation peak shifts to a higher temperature region on the DTG concurs with Jitkarnka, Chusaksri, Supaphol *et al.* (2007) work.

Today it is generally acknowledged that TGA/DTG can be used as a precursor to pyrolysis as it identifies the volatilization of the tyres individual components. Due to the nature of non-interaction of these components a model for tyre pyrolysis can effectively be built that can predict optimum temperature profiles for controlling the final products or product phases.

2.4 Thermal Degradation Kinetics

The degradation of polymers by heating or burning thereof yields complicated reaction mechanisms which include the scission of the chains, chain stripping, cross-linking of chains and the formation of coke and ash. To gain a clearer picture of the kinetic parameters that relates to useful engineering purposes, this simple reaction for waste tyres is assumed:

$$waste\ tyres \overset{k}{\rightarrow} pyrolytic\ products$$

The rate of reaction for conversion of waste tyres can be expressed using the Arrhenius equation (Fogler, 2006). Eq. (9) and Eq. (9) thus form the basis of the mathematical modelling which is to follow.

$$\frac{dX}{dt} = A\, exp\left(-\frac{E}{RT}\right) f(X) \tag{9}$$

$$X = \frac{W_0 - W_t}{W_0 - W_f} \tag{10}$$

where:

t is the time [min]

A is the pre-exponential factor [min^{-1}]

E is the activation energy [kJ/mol]

T is the reaction temperature [K]

R is the universal gas constant [8.314 J/mol.K]

X is the mass loss of a single reaction

W_0 is the sample original mass

W_t is the mass of the sample at a given time

W_f is the final sample mass

The function incorporated into Eq. (9) assumes that the nth order of the unreacted waste tyre material is expressed as:

$$f(X) = (1 - X)^n \tag{11}$$

The rate at which waste tyres are converted can be expressed in terms of the rate constant k:

$$\frac{dX}{dt} = k(1 - X)^n \tag{12}$$

$$\text{and } \; k = A\exp\left(-\frac{E}{RT}\right) \tag{13}$$

Therefore:

$$\frac{dX}{dt} = A\exp\left(-\frac{E}{RT}\right)(1 - X)^n \tag{14}$$

Once the thermogravimetric analysis of the waste tyres has been performed the kinetic parameters for the reaction in the above equations can be calculated. After taking the natural logarithm of Eq. (9) and employing simple mathematical manipulation the following equation is determined:

$$\ln\left(\frac{dX}{dT}\right) = -\frac{E}{R}\left(\frac{1}{T}\right) + n\ln[A\,f(1 - X)^n] \tag{15}$$

A fixed conversion yields $n\ln[A\,f(1 - X)^n]$ in Eq. (15) as a constant. This implies that by plotting ln $\left(\frac{dX}{dT}\right)$ versus $\left(\frac{1}{T}\right)$ from the thermogravimetric data a straight line is found. The slope of this straight line will yield $-\frac{E}{R}$ and its intercept corresponding to $n\ln[A\,f(1 - X)^n]$. Thus assuming first order reaction kinetics for a fixed conversion the activation energy and pre-exponential factor can be accurately determined (Aguado, Olazar, Vélez *et al.* 2005, Al-Salem, Lettiere and Baeyens 2009, Islam, Haniu and Fardoushi 2009, Lah, Klinar and Likozar 2013).

2.5 Waste Tyre Pyrolysis

2.5.1 Temperature effect on volatiles

As the pyrolysis of waste tyres is a highly endothermic process the governing variable that is used to initiate and sustain the process is temperature. Temperature thus forms a vital part in the effect of conversion, product distribution and quality. Numerous authors have found that the conversion of tyres to its hydrocarbon counterparts is at an optimum/critical temperature of around 500°C operating at atmospheric pressure. Table 2 shows some examples of the product distribution at this temperature. Lower temperatures simply soften the waste tyres and leave it in a sticky solid state.

Ramping the temperature above the waste tyre degradation point influences the oil/gas yield ratio. None more evident than the work of López, Olazar, Aguando *et al.* (2010) that shows gas yield increases at the expense of the oil yield as seen in **Figure 6**.

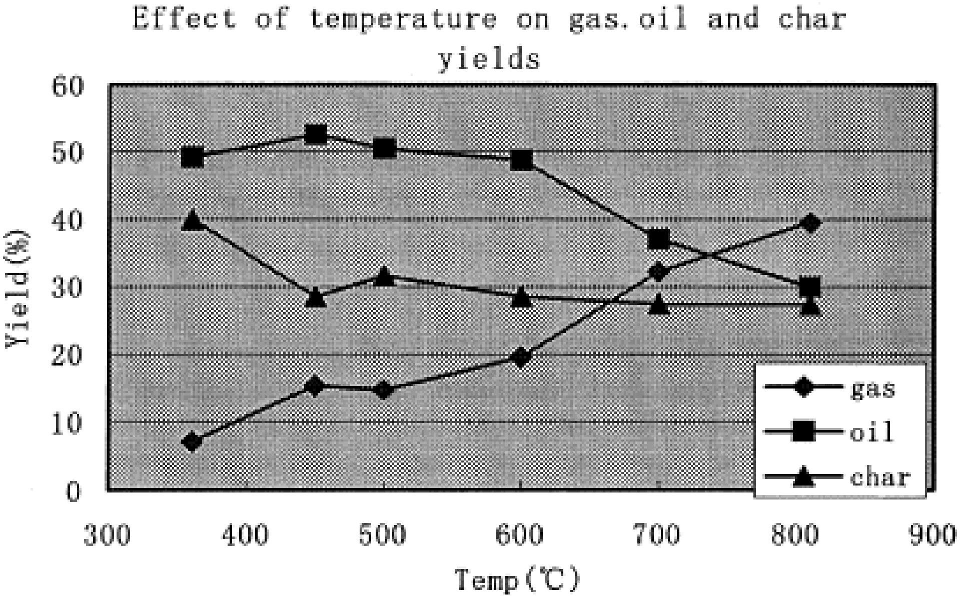

Figure 6: Waste tyre pyrolysis product distribution (López, Olazar, Aguando et al. (2010)

The higher the operating temperature the greater the effect of thermal cracking (secondary reaction) becomes noticeable as the heavier hydrocarbons are broken into smaller molecular chains (Díez, Martínez, Calvo *et al.* (2004); Aydin and Ilkiliç (2012); Aylón, Fernández-Colino, Murillo *et al.* (2010);(Banar, Akyildiz, Özkan *et al.* 2012)). Berrueco, Esperanza, Mastral *et al.* (2005) showed that solid yield continues to increase up to 500°C thereafter remained almost constant. Meanwhile gas fraction shows an upward trend while the oil decreased over the entire temperature range which supports the notion of thermal cracking of the oil. The critical pyrolysis temperature was 425°C according to experimentation by Kar (2011). A maximum oil yield of 60.02wt% at 425°C was obtained and steadily decreased to 54.12wt% at 500°C while the gas followed an inverse trend from 2.99 – 20.22wt% over the entire temperature range. Raj, Kennedy and Pillai (2013) found that at a lower temperature of 440°C accompanied with slow feed rate the maximum oil yield can be achieved, any higher temperatures shows thermal cracking.

In contrast some authors found no effect of the temperature increase on the yield of gas and oil. Ucar, Karagoz, Ozkan *et al.* (2005) compared the pyrolysis of passenger car tyres (PCT) and truck tyres (TT) at 550, 650 and 800°C. They reported that there is no significant effect on the product distribution by increasing the operating temperature. This was supported by Lasergoiti, Caballero, Marco *et al.* (2004) who carried out experiments over the temperature range 300 – 700°C. The authors found no effect of temperature above 500°C and suggest that tyre decomposition is complete which contradicts Zhang, Wang, Ma *et al.* (2008) work which shows increased oil at elevated temperatures.

By controlling the pyrolysis temperature, the volatiles released should be close to the measured proximate analysis values. The consulted literature however shows a slight increase in char formation. This is attributed to the secondary repolymerization reactions of the polymer-derived products which forms additional carbonaceous materials (Zhang, Wang, Ma *et al.* 2008). By locating the optimum process operating temperature will facilitate in enhancing the selectivity of the product distribution and in turn speeding up the overall conversion time.

Table 2: Reported Works on the Effect of Temperature on Product Distribution

Product Yield [wt%]			**Temp [°C]**	**Reactor**	**Experimental**	**Ref.**
Char	**Oil**	**Gas**				
33.9 - 35.8	44.5 - 55.0	1.8 - 6.8	425 - 600	Conical Spouted Bed	Continuous process	(López, Olazar, Aguando *et al.* 2010)
40	46.1	13.9	550	Tubular	Distillation plant operated at batch scale	(López, Centeno, Alguacil *et al.* 2011)
42	47.4	7.4	550	Fixed Bed	Tyre polymer type compared to pyrolysis products	(Ucar, Karagoz, Ozkan *et al.* 2005)
47.88	40.26	11.86	500	Not reported	Reducing sulphur by pyrolysis with catalyst	(Aydin and Ilkiliç 2012)
35.2	62	2.8	420	Fixed Bed	Vary temperature, particle size and carrier gas flow rate to find optimum conditions	(Barbooti, Mahamed, Hussain *et al.* 2004)
37.6	55.6	6.8	550	Fixed Bed	Determine composition and properties of products while Temperature and Heating rate vary	(González, Encinar and Canito 2001)
36.1	52	11.9	500	Quartz Fixed Bed	Two stage process. Evolved gasses passed through zeolite catalyst to investigate its effect on the products	(Shen, Wu, Wang *et al.* 2006)
52.7	39.9	3.6	500	Static-bed batch	Influence of temperature on global yield	(Berrueco, Esperanza, Mastral *et al.* 2005)
33	56	10	550	Continuous system	Commercial process	(Roy, Chaala and Darmstadt 1999)
26.5	44.5	29	400	Fluidized Bed	Vary feed rate, particle size and temperature to maximize pyrolysis oil	(Raj, Kennedy and Pillai 2013)
35.1	31.1	33.8	400	Fixed Bed	Pyrolysis of tyre derived fuel by varying temperature	(Banar, Akyildiz, Özkan *et al.* 2012)

2.5.2 Catalytic Pyrolysis

The use of catalysts in waste tyre pyrolysis is predominantly conducted for the enhanced selectivity of the product yields and/or the upgrading of the pyrolytic oil to valuable chemicals. The advantage of using catalysts is that greater control can be exerted on the final composition of the oil and gas yields than with temperature alone by varying the catalyst morphology and chemical properties. USY produced 12 wt% catalyst coke and ZSM-5 only 6 wt% in relation to the catalyst/tyre ratio of 0.5 and 1.0 respectively (Boxiong, Chunfei, Binbin *et al.* 2007). Increasing the catalyst/tyre ratio generally improves the catalytic activity, however these experiments shows that USY has a higher degree of cracking activity and forms more catalyst coke compared to ZSM-5. This is a result of larger pore sizes of USY allowing larger hydrocarbon chains to be cracked and form aromatics which are inclined to generate this coking because of their hydrogen transfer abilities and cyclization reactions.

Table 3 shows a review of different catalysts that can be used and their influence on tyre pyrolysis. Zeolites, Ultrastable Y-type (USY) and ZSM-5, are the most commonly used for waste tyre pyrolysis because of their flexibility in terms of pore size and surface acidity, which can be altered by varying the Silica and Alumina ratios as shown by Williams and Brindle (2003). The oil produced from ZSM-5 compared to Y-type had a lower aromatics concentration due to its smaller pore size though still considerable higher that without catalyst. An acidity change in 2 different Y-types found that the oil yielded higher aromatic hydrocarbon concentrations when the catalyst acidity was higher. It was also reported in this study and others similar that the gas yield increased at the expense of the oil in the catalysts presence (Kar 2011, Olazar, Arabiourrutia, López *et al.* 2008, Williams and Besler 2002). This is explained by Olazar et al. (2008) due to the strong acid sites on the catalyst and the composition of the liquid yield making it suitable for this transfomation as it is not limited to the shape selectivity of the smaller pores.

Olazar, Arabiourrutia, López *et al.* (2008) performed pyrolysis *in situ* with HZSM-5 and HY zeolites and found that HZSM-5 lowers the waste tyre degradation temperature from 773K to 723K thus enabling operational energy conservation. Both catalysts were compared in such a way that the acidic differences were not to influence the results. HY zeolite formed heavier structures such as tar and aromatic C_{10}^{-} while HZSM-5 modified the non-aromatic C_{10}^{-} fraction.

Table 3: Some investigations into catalytic pyrolysis of waste tyres

Catalyst	Operating Conditions	Results	Ref.
Y-Type, ZSM-5	Evolved gasses passes through secondary catalyst loaded reactor at 500°C. 2 Y-types of different acidities and large pore sizes while ZSM-5 with a smaller pore size and lower acidity was used.	Char yield remains constant throughout with slight coke formation, gas increases at the expense on oil. Catalysts reduced the mean MW of the oils, Y-type having the greater effect due to their larger pore sizes.	(Williams and Brindle 2003)
Perlite	Reactor loaded with varying perlite/tyre ratio at 425°C	Catalytic pyrolysis increased the oil yield by 8.48% then falls with increased catalyst ratio (0.1-0.25). Gas yield constant then increases from ratio 0.1-0.25.	(Kar 2011)
HZSM-5, HY, HBeta	In situ catalytic and thermal pyrolysis by varying residence time 5 - 200s	50°C pyrolysis temperature reduction was found by using catalyst in situ as well as producing more gasses and light aromatic $C10^{-}$. Product yield for all catalyst are similar although the distribution differs	(Olazar, Arabiourrutia, López *et al.* 2008)
Mordenite	ITQ-21 and ITQ-41 used as zeolite additives of HMOR. Pyrolysis carried out at 500C and evolved gasses passed through upper reactor zone of 350^{0}C loaded with varying quantities of catalyst	Gas increased at the expense of oil. Higher HMOR-to-tyre ratios yields less asphaltenes and more saturated HC. Addition of ITQ decreased the catalyst cracking activity and gasoline, while ITQ-21 increased kerosene and ITQ-24 having the opposite effect.	(Dũng, Mhodmonthin, Wongkasemjit *et al.* 2009)
MgO, $CaCO_3$	Fixed amount of catalyst/tyre mixture pyrolyzed at 300-400C. Effect of time on pyrolysis at 350C investigated.	CaCO3 yields less liquid, but more gas than MgO. Oil from MgO contains 40% gasoline fraction and 60% diesel , CaCO3 yields 10% and 90% respectively.	(Shah, Jan and Mabood 2008)
$Ca(OH)_2$	Catalyst ratio was increased at constant 500C	Sulphur content was decreased significantly with 5% catalyst, however remained almost constant from 10% up.	(İlkiliç and Aydin 2011)
Silica MCM-41, 2%Ru/MCM-41	Pyrolysis carried out at 500C and evolved gasses passed through upper reactor zone of 350C loaded with catalyst	Oil yield decreased for both catalysts. 4 times higher olefins yield with catalyst than without. Catalytic oils have more single ring aromatics and less poly/polar-aromatics.	(Dũng, Klaewkla, Wongkasemjit *et al.* 2009)
USY	Evolved gasses passes through secondary catalyst loaded reactor while several parameters were tested.	Increased catalyst/tyre ratio and temperature drastically increased gas and light naphtha.	(Shen, Wu, Wang *et al.* 2006)
ZSM-5	Tyre pyrolyzed with catalyst and waste lubricating oil at 430C until no more liquid is produced.	LBO enhances the ZSM-5 catalytic effect by providing a more homogeneous condition. Oil yield increased substantially while gasses decreased. Light oils also increased with a decrease in heavy components.	(Qu, Zhou, Wang *et al.* 2006)
NaOH, NaCO3	Catalyst mixed with tyre was pyrolysed at varying temperatures under vacuum.	NaOH lower the pyrolysis temperature and increased oil yield.	(Zhang, Wang, Ma *et al.* 2008)

Boxiong, Chunfei, Binbin *et al.* (2007) and Williams and Besler (2002) investigated the influence of catalyst bed temperature of USY and ZSM-5 zeolites at the catalyst/tyre ratio on the product yields and compositions. In comparison with ZSM-5, the USY yield of oil was 32.6 wt% to 40.4 wt% at a catalyst temperature of 400°C and continues to decrease with the increase of temperature (Boxiong, Chunfei, Binbin *et al.* 2007). The gas shows a dramatic change of 15.1 – 20 wt% for ZSM-5 and 16.3 – 21.8 wt% for USY at a catalyst temperature increase 430 – 600°C while the uncatalysed gas yield is 6.1 wt% (Williams and Besler 2002). USY produced 12 wt% catalyst coke and ZSM-5 only 6 wt% in relation to the catalyst/tyre ratio of 0.5 and 1.0 respectively (Boxiong, Chunfei, Binbin *et al.* 2007). Increasing the catalyst/tyre ratio generally improves the catalytic activity, however these experiments shows that USY has a higher degree of cracking activity and forms more catalyst coke compared to ZSM-5. This is a result of larger pore sizes of USY allowing larger hydrocarbon chains to be cracked and form aromatics which are inclined to generate this coking because of their hydrogen transfer abilities and cyclization reactions.

2.6 Waste Tyre Pyrolysis Products

2.6.1 Pyrolysis Oil

The preferred product produced from waste tyre pyrolysis is the condensable gas which forms the pyrolysis oil or pyrolytic oil. This oil is a complex mixture of hydrocarbons including a high concentration of aromatic compounds. The primary utilization of the pyrolysis oil is as an alternate fuel due to its favourable hydrocarbon composition. The gross calorific value is a key property in determining the viability of using pyrolysis oil as an alternate fuel. In literature the gross calorific value of waste tyre pyrolysis oil is reported to be in the range of 37.4 – 44 MJ/kg (de Marco Rodriguez, Laresgoiti, Cabrero *et al.* 2001, Díez, Martínez, Calvo *et al.* 2004, Islam, Tushar and Haniu 2008, Quek and Balasubramanian 2013, Roy, Chaala and Darmstadt 1999). Thus the pyrolysis oil has higher calorific values than that of the raw waste tyre from which it has been recovered from. Compared with commercially available diesel the gross calorific values are similar to that of pyrolysis oil, which is slightly lower, whereas the calorific value of commercial diesel is measured higher than 44 MJ/kg. Further encouraging signs of the possibility of using pyrolysis oil as an alternate fuel to diesel can be observed in its similar distillation curves, density and viscosity(Antoniou and Zabaniotou 2013, Quek and Balasubramanian 2013).

Studies using pyrolytic oil as a fuel substitute in internal combustion engines show no adverse effects to the engine and favourable results in terms of its functionality and emissions. Specifically, Murugan, Ramaswamy and Nagarajan (2008) tested the performance of distilled desulfurized waste tyre pyrolysis oil and commercial diesel blends (20% and 90% pyrolytic oil ratio) as fuels for combustion in a four stroke cylinder air cooled diesel engine lacking any additional engine modifications. It was determined that the engine is capable of running satisfactory with a blend of up to 90% pyrolytic oil to diesel according to Murugan, Ramaswamy and Nagarajan (2008), while operating a four stroke single cylinder injection diesel engine Doğan, Çelik and Özdalyan (2012) determined that up to 90% pyrolytic oil to diesel blends is possible. It was further determined by Doğan, Çelik and Özdalyan (2012) that the pyrolytic oil content in the fuel blends used has no significant impact on the engines power, torque output, fuel consumption or brake thermal efficiency when compared to the commercial diesel used for the blends.

İlkılıç and Aydın (2011) used calcium hydroxide ($Ca(OH)_2$) catalyst in the pyrolysis of waste tyres to reduce the amount of sulphur in the pyrolytic oil and then blend with commercial diesel (5%, 10%, 15%, 25%, 35%, 50% and 75%). Results of İlkılıç and Aydın (2011) in a four stroke single cylinder air cooled diesel engine show effective engine operations with blends of 5%, 10%, 15%, 25% and 35% pyrolytic oils to diesel whereas 50%, 75% and 100% emits high CO, HC, SO_2 and smoke. In addition Murugan, Ramaswamy and Nagarajan (2009) also noticed oil sticking on the nozzle stem and sac when using blends of pyrolytic oil and diesel in steps of 20% from 20% to 70% in a single cylinder water cooled direct injection diesel engine. Murugan, Ramaswamy and Nagarajan (2009) reported reliable operation of the engine was achieved up to a 70% blend of pyrolytic oil. Murugan, Ramaswamy and Nagarajan (2008) found that the brake thermal efficiency of an engine fuelled with a pyrolytic oil blend increased with an increase in blended concentration.

These higher blends also yielded higher emissions of NO_x, HC, CO and smoke due to the high aromatic contents and increased ignition delays (Murugan, Ramaswamy and Nagarajan 2008). In terms of emissions Williams, Bottrill and Cunliffe (1998) combusted pyrolytic oil externally in an 19.3kW ceramic-lined, oil-fired, spray burner furnace. Williams, Bottrill and Cunliffe (1998) reported successful combustion of the pyrolytic oil with no detectable emissions of polycyclic aromatic hydrocarbons while combustion took place in 6 Vol% excess of oxygen. By comparison Williams, Bottrill and Cunliffe (1998) determined that the NO_x and SO_2 emissions of pyrolytic oil are higher than that of commercially available diesel (Martínez, Rodríguez-Fernández, Sánchez-Valdepeñas *et al.* 2014). These higher emissions are attributed to the higher concentrations of sulphur and nitrogen in the pyrolytic oils which range from 0.11 – 3.6wt% and 0.22 – 2.05wt% respectively (Antoniou and Zabaniotou 2013, Banar, Akyildiz, Özkan *et al.* 2012, de Marco, Caballero, Cabrero *et al.* 2007, Díez, Martínez, Calvo *et al.* 2004, Kar 2011, López, Olazar, Aguando *et al.* 2010, Ucar, Karagoz, Ozkan *et al.* 2005, Unapumnuk, Lu and Keener 2006, Williams, Bottrill and Cunliffe 1998).

Since the pyrolytic oils contain small concentrations of oxygen and high H/C atomic ratios in the form of aliphatic and aromatic compounds it may be used in various other applications not only as an alternate fuel. These high concentrations are as a result of the aromatic structure of tyres and the cylcization of the olefinic structures coupled with dehydrogenation and Diels-Alder reactions(Antoniou and Zabaniotou 2013). It has been reported that the total aromatic content in pyrolytic oil ranges from about 15.22 – 74.8% (Antoniou and Zabaniotou 2013, Cunliffe and Williams 1998, Dũng, Wongkasemjit and Jitkarnka 2009, Kar 2011, Lasergoiti, Caballero, Marco *et al.* 2004, Roy, Chaala and Darmstadt 1999, Stelmachowski 2009, Ucar, Karagoz, Ozkan *et al.* 2005). Depending on the pyrolysis process variables and waste tyre feedstock, the pyrolysis may be modified to target specific reactions which may yield pyrolytic oils with defined properties (Martínez, Puy, Murillo *et al.* 2013). In fact de Marco Rodriguez, Laresgoiti, Cabrero *et al.* (2001) and Lasergoiti, Caballero, Marco *et al.* (2004) researched the effect of temperature on the yield of aromatics in pyrolytic oil which seemed to increase with an increase in reaction temperatures.

Williams and Brindle (2003) demonstrated the ability of drastically increasing the concentrations of single ring aromatic content by utilizing different zeolite catalysts (ZSM-5 and Y-Type) with varying properties. Another major factor influencing the pyrolytic oil composition is the starting material. Ucar, Karagoz, Ozkan *et al.* (2005) reported that passenger car tyres contains approximately 41% aromatics while truck tyres contains considerably less aromatics at approximately 15%. These high concentrations of aromatics in the pyrolytic oils leads researchers to suggest using the pyrolytic oils as a source of valuable chemical such as benzene, toluene, xylene and limonene(Jitkarnka, Chusaksri, Supaphol *et al.* 2007, Pakdel, Pantea and Roy 2001, Quek and

Balasubramanian 2013, Stanciulescu and Ikura 2006, Stanciulescu and Ikura 2007, Witpathomwong, Longloilert, Wongkasemjit *et al.* 2011).

2.6.2 Non-condensable Gas

The gaseous product captured after the pyrolytic oil recovery is called the pyrolytic gas or pyrogas which is not condensable at atmospheric conditions. As with the pyrolytic oil, the pyrolytic gas is depended on similar factors which influences its composition and yield. This gas is typically comprised of paraffins and olefins with carbon numbers of $C_1 - C_5$. The gross composition of this pyrolytic gas generally includes Hydrogen, Carbon Monoxide, Carbon Dioxide, Methane, Ethene, Ethane, Propene, Propane, Butene, Butane and a variety of lower concentrations of sulphur and nitrogen based compounds(Antoniou and Zabaniotou 2013, Berrueco, Esperanza, Mastral *et al.* 2005, Fernández, Barriocanal and Alvarez 2012, López, Centeno, Alguacil *et al.* 2011, López, Centeno, Alguacil *et al.* 2013, Zhang, Wang, Ma *et al.* 2008, Zolezzi, Nicolella, Ferrara *et al.* 2004). Although the pyrolysis of waste tyres occurs in an inert environment some oxides are still formed. These oxides present in the pyrolytic gas is as a result of the additives required in the production of tyres such as iron oxides and zinc oxides.

The gross calorific values of the pyrolytic gas has been measured in the range of 34.6 – 84.0 MJ/m^3 (Aylón, Murillo, Fernández-Colino *et al.* 2007, de Marco Rodriguez, Laresgoiti, Cabrero *et al.* 2001, Díez, Martínez, Calvo *et al.* 2004, Honus, Juchelkova, Campen *et al.* 2014). One of the foremost expenditures in waste tyre pyrolysis is the high energy requirements needed to heat the reactor vessels to relevant temperatures for pyrolysis to take place. It has been suggested by Galvagno, Casu, Casabianca *et al.* (2002) to use the pyrolytic gas in situ with the intention of reducing plant management costs. According to Aylón, Murillo, Fernández-Colino *et al.* (2007) the high calorific values of the pyrolytic gas makes its combustion ideal for the energy requirements of the pyrolysis as well as that of other energetic systems.

Aylón, Murillo, Fernández-Colino *et al.* (2007) also investigated the application of using the pyrolytic gas as an energy source in terms of the emissions in order to meet the policies set out in the Waste Incineration Objective (European Commission 2000). It has been reported by Aylón, Murillo, Fernández-Colino *et al.* (2007) that the combustion of the pyrolytic gas meets the Legislation and may be considered acceptable if appropriately managed. The biggest concern in the combustion of pyrolytic gas is the production Sulphur Dioxide (SO_2) (Aylón, Murillo, Fernández-Colino *et al.* 2007). The concept of using catalysts to reduce sulphuric compounds in the pyrolytic gas has been widely explored and found effective to varying degrees. Leung, Yin, Zhao *et al.* (2002) determined that calcined dolomite and limestone can be effectively used to absorb the Hydrogen Sulphide, however its lifetime is extremely limited.

Hu, Fang, Liu *et al.* (2014) found that when the reactor temperature was raised from 733 – 973 K caused a considerable amount of sulphur to be released by the cracking of organic polymers. Not only did Hu, Fang, Liu *et al.* (2014) find a substantial increase in the H_2S content in the pyrolytic gas, other sulphuric gasses were also formed such as COS, SO_2 and CH_3SH. Ucar, Karagoz, Ozkan *et al.* (2005) reported the sulphur distribution in the pyrolytic gas is more than double in passenger car tyres than it is in truck tyres. Ucar, Karagoz, Ozkan *et al.* (2005) speculates that this discrepancy might be due to the differences in the ash contents of passenger car tyres and truck tyres.

2.6.3 Char

Once the pyrolysis of waste tyre has reached completion a solid deposit remains, excluding the reinforcing steel wires, which contains carbon black and inorganic ash. This carbon-rich deposit is aptly named tyre char or pyrolytic carbon black. As mentioned the pyrolytic char contains carbon black, this is due to the fact that carbon black forms part of the original tyre material. Being a non-pyrolysable material carbon black remains as part of the char after waste tyre pyrolysis has occurred. Additionally, the inorganic ash content in the pyrolytic char originates from the inorganic content of the original tyre material.

The composition of the tyre char varies with changes in the pyrolysis process and the original tyres composition. Typically the pyrolysis of waste tyres yields pyrolytic carbon black in the range of 31.4 – 52.9 wt% (Ariyadejwanich, Tanthapanichakoon, Nakagawa *et al.* 2003, Aylón, Murillo, Fernández-Colino *et al.* 2007, Choi, Jung, Oh *et al.* 2014, Fernández, Barriocanal and Alvarez 2012, Islam, Tushar and Haniu 2008, Laresgoiti, de Marco, Torres *et al.* 2000, Martínez, Murillo, García *et al.* 2013, Unapumnuk, Keener, Lu *et al.* 2008). The second major component which forms part of the pyrolytic char is the inorganic ash content in the range of 5 – 40wt% (Choi, Jung, Oh *et al.* 2014). High ash contents in chars are attributed to the additive metals used in tyre manufacturing according to Williams (2013). This pyrolytic carbon black is generally more than the total fixed carbon and ash content used in the manufacturing process of the original tyre. The repolymerization reactions of the polymeric compounds during pyrolysis accounts for some secondary carbonaceous materials to be formed and is used to explain this weight increase (Aranda, Murillo, García *et al.* 2007, Murillo, Navarro, López *et al.* 2004, Zhang, Wang, Ma *et al.* 2008). Consequently a fraction of the organic vapours released are converted into coke though the dealkylation and dehydrogenation reactions or absorbed onto the pyrolytic chars' surface (Roy, Chaala and Darmstadt 1999, Zhang, Wang, Ma *et al.* 2008). Senneca, Salatino and Chirone (1999) gives this as the reason pyrolytic char has much coarser particles than that of the original tyre carbon black.

While in contrast Helleur, Popovic, Ikura *et al.* (2001) shows through TEM investigations that the physical shapes and sizes of pyrolytic carbon black is similar to that of the standard carbon black used in tyre production. Choi, Jung, Oh *et al.* 2014 also confirms that the pyrolytic chars have textural properties similar to that of commercially available carbon blacks. A maximum activated char surface area of 437m2/g was obtained by Choi, Jung, Oh *et al.* (2014). Foremost in the utilization of pyrolytic carbon black is the production of activated carbon as discussed in various review articles (Antoniou and Zabaniotou 2013, Mui, Ko and McKay 2004, Saleh and Gupta 2014, Williams 2013). The activation of pyrolytic carbon black has been accomplished by using three different chemical treatments/Activation agents:

- Carbon Dioxide (Fung, Cheung and McKay 2012, Murillo, Navarro, López *et al.* 2004)
- Steam (Ariyadejwanich, Tanthapanichakoon, Nakagawa *et al.* 2003)
- Potassium Hydroxide/Nitrogen (Sun, Brady, Rood *et al.* 1997, Teng, Lin and Hsu 2000)

In terms of pressure, when pyrolysis was completes at 10 kPa Pantea, Darmstadt, Kaliaguine *et al.* (2003) measured a pyrolytic carbon black yield of 36.4 wt% (9% steel) whereas at atmospheric pressure (100 kPa) a 4.0% increase was observed.

3

Materials and Methods

3.1 Source of Waste Tyres

Waste passenger car tyres were obtained from a local dealership whereby 5 different brands were selected of which 2 are local and 3 international brands. The different tyres are denoted as follow:

- Local 1
- Local 2
- International 1
- International 2
- International 3

3.2 Waste Tyre Size Reduction and Powderization

Tyres needed to be powderized in order attain a constant heat transfer through the material during pyrolysis. Initially manual grinding with a scrapper was tested, however due to the tyre's tough physical characteristics powder production was minimal and this method was deemed impractical. Upon further experimentation a handheld grinder was fitted with a cylindrical attachment which has sharp groves etched on an inclined plane and wrapped helically around its axis. This technique showed a significant improvement in achieving tyre powderization with a limiting factor of the material overheating leading to carbonization. By grinding and stopping at intervals the carbonization of the tyre can be limited.

3.3 Thermal Degradation Behaviour

The Thermogravimetric Analysis (TGA) approach was used to study the degradation behaviour of waste tyres with temperature. The TGA were performed using a Perkin Elmer TGA 7 by measuring the weight change in relation with increasing temperature. The program used to determine the TGA of the tyres is:

- Heat the sample in N_2 from 20°C-920°C at 20°C/min
- Hold at 920°C for 15 min in N_2
- Hold at 920°C for 15 min in O_2

By using the thermogravimetric data from the analysis the differential thermogravimetric curves were obtained by differentiation. Figure 5 illustrates the thermogravimetric conditions and what is achieved at the appropriate temperature intervals. ASTM D6370 - 99 Standard Test Method for Rubber-Compositional Analysis by Thermogravimetry (TGA) was followed to ensure results conformed to quality control standards.

3.4 Calorific Value Measurements

The calorific value of the waste tyre powder was measured using an e-2k Bomb Calorimeter by following the ASTM D5468 – 02 Standard Test Method for Gross Calorific and Ash Value of Waste materials. Test method stated 0.5g of sample was to be loaded into the reactor vessel and pressurized with UN1072 Industrial grade compressed oxygen to 3000 kPa. Results were achieved intermittently, upon inspection the fire wire was completely destroyed and the vessel interior coated in a black carbonaceous residue indicating a faulty combustion. By consulting with the manufacturer it was reasoned that the sample mass was too high for the calorimeter to handle. Sample test weight was reduced to 0.25g and retested with no complications. Equipment software compensated for the weight discrepancy to the calorific value. For a good statistical average 3 tests were performed per sample.

3.5 Proximate Analysis

A quick method for determining outputs during pyrolysis of waste tyres is to perform proximate analysis on the raw material. In proximate analysis the fixed carbon, volatile matter, moisture and ash content is measured. 1g of sample was inserted in a moisture balance and heated to 100°C until the sample weight remained constant thus proving all moisture was removed from the sample. The fixed carbon, volatile matter and ash content were measured using the standard practice of ASTM D3172-07 Standard Practice for Proximate Analysis of Coal and Coke. For a good statistical average 3 tests were performed per sample.

3.6 Ultimate Analysis

In this study the elemental composition of the waste tyres were analysed by Ultimate Analysis which determined the carbon, hydrogen, sulphur and nitrogen content. ASTM D3176-09 Standard Practice for Ultimate Analysis of Coal and Coke was used in this investigation as a standard practice. For a good statistical average three tests were performed per sample. The analyses were conducted on PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. The percentage composition of carbon, hydrogen, nitrogen and sulphur was determined first while the oxygen content was determined after.

For CHNS determination, the 1 g of the sample is put into the quartz tube maintained at a temperature of 1000 °C with oxygen as the carrier gas. The gases produced measured using an online gas chromatography (Hewlett-Packard 5890) fitted with a Thermal Conduction Detector (TCD) and connected to a Hewlett-Packard 5971 mass spectrometer. To determine the oxygen content, the same procedure is used as above however the column raised to the maximum temperature of 1100 °C and used as the carrier gas.

3.7 Pyrolysis Experimental Set-up and Sampling Procedure

A simplified process flow diagram of the bench scale pyrolysis set-up is shown in **Figure 7**.

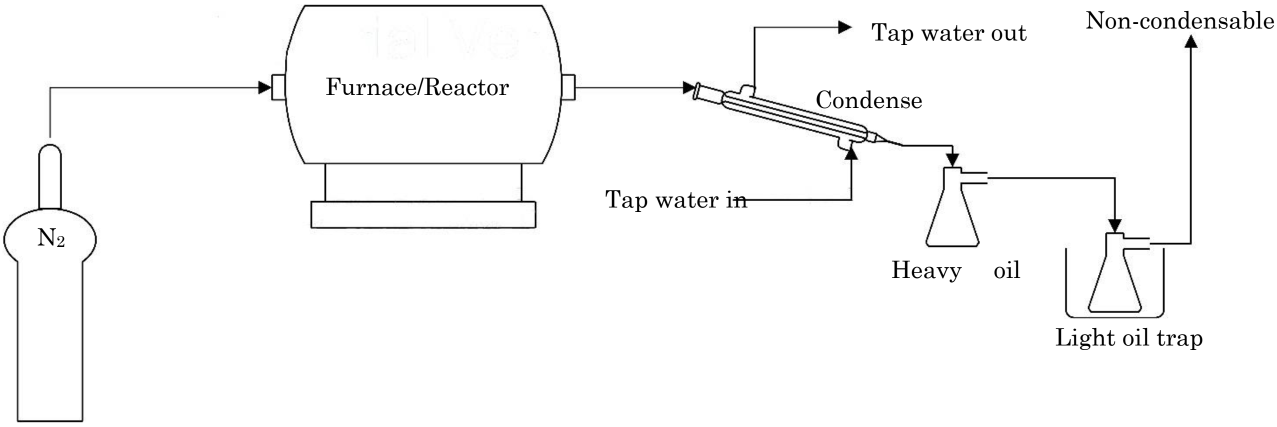

Figure 7: Schematic diagram of laboratory pyrolysis setup

The reactor vessel was manufactured from copper tubing of Ø 25mm x 300mm. The tubing ends were fitted with tapers and a stainless steel mesh at the joints to prevent large particulates from escaping with the carrier gas. Approximately 10g of powderized tyre was loaded into the reactor and heated to 550 °C at a heating rate of 10 °C/min and at atmospheric pressure. Nitrogen was used to create an inert reaction environment and as carrier gas. During waste tyre pyrolysis the gaseous product that formed was continuously transported through the tube of a glass shell and tube condenser whereby counter-current running tap water in the shell was used as coolant. The condensed oil product was collected in a 250 ml Buchner flask. The remaining non-condensable gas was passed through a further 250 ml Buchner flask which was connected to a bath where a yellow wax like substance was found sticking to the walls of the flask. The final gaseous part of the product was vented to the atmosphere through a fume hood.

The process was stopped after approximately 30 minutes or when no more oil was observed to be condensing. The char and light oil weight (first condensation step) was measured and stored for analysis. Due to the minimal product and its waxy nature the heavy oil (second condensation step) was difficult or in some cases not possible to collect and measure. Following sample collection the system was thoroughly cleaned before the next waste tyre experiment was started.

3.8 Product Analyses

This analysis of the pyrolytic oil was performed using an Agilient Technologies 6890N Network GC System. The oil samples were diluted with n-hexane in a ratio of 1ml of oil to 9ml hexane. A sample standard was made up of the following hydrocarbons in 0.05% solution of hexane:

C8	n-Octane
C9	n-Nonan
C10	n-Decane
C11	n-Undecane
C12	n-Dodecane
C13	n-Tridecane
C14	n-etradecane
C15	n-entadecane

This is used to identify the hydrocarbons present in the pyrolytic oil. The focus was on the liquid hydrocarbons formed from the condensable gases.

3.9 Char Analysis

In this study Scanning Electron Microscopy (SEM) was performed on the powdered tyres samples as well as the pyrolytic char obtained after the completion of pyrolysis has been achieved. A FEI Nova NanoSEM 230 was used for these analyses and testing done by a trained professional. Imaging and Energy Dispersive X-Ray (EDX) of all samples were performed according to ASTM E986 - 04(2010) Standard Practice for Scanning Electron Microscope Beam Size Characterization and ASTM E1508 - 12a Standard Guide for Quantitative Analysis by Energy-Dispersive Spectroscopy respectively.

4

Results and Discussions

4.1 Waste Tyre Compositions

Waste tyre properties are important parameters that effect from the way a tyre degrades to the final composition of the volatile products of pyrolysis. For example, the volatile matter is the maximum pyrolyzable content of a waste tyre that consists of the polymeric compounds originating from the natural and styrene rubber. The fixed carbon should theoretically correspond to the char remaining after pyrolysis which originates from the carbon black used in the tyres manufacture. Thus understanding the effect individual tyre components have on physical and chemical characteristics are important when scaling processes to industrial levels. This section focusses on understanding proximate analysis, ultimate analysis and gross calorific values of five different types of waste tyres rubber. These waste tyre properties are then compared with what is reported in literature. Summarized in **Table 4** and **Table 5** are the proximate and ultimate analysis results respectively of the five tyre samples used in this study. **Table 6** shows the average calorific values that were measured for each tyre.

Reported results in Table 4 demonstrates that the volatile matter of tyres A and E are in range of other reported results while tyres C, D and E are below 58 wt%. This is marginally lower than that reported by the authors investigated which ranges from 58.2–71.5 wt%. The fixed carbon content of tyres A and E are significantly less than that of tyres B, C and D. Observations while grinding tyres B, C and D to powder confirm the higher fixed carbon content by smoking fairly early on in the process indicating carbonization of the tyres. Based on these factors it may be suggested that the carbon black content of tyres A and E are lower than that of the other tyres.

Table 4: Proximate Analysis results of waste tyre samples (dry)

	Weight Percentage			
	Moisture	**Ash**	**Volatile Matter**	**Fixed Carbon**
Tyre A	1.2	16	67.9	14.7
Tyre B	1.1	3.7	61.8	33.4
Tyre C	1.1	3.2	56.3	39.4
Tyre D	1	4.6	57	37.4
Tyre E	1.5	16.8	57.7	24

Table 5: Ultimate Analysis results of waste tyre samples (dry)

	Weight Percentage			
	S	**C**	**H**	**N**
Tyre A	1.8	71.7	9.22	0.17
Tyre B	1.74	83.3	8.03	0.01
Tyre C	1.48	85.5	7.46	0.11
Tyre D	1.23	86.3	7.37	0.12
Tyre E	1.9	71.3	7.21	<0.01

Table 6: Average gross calorific values of waste tyre samples

	Gross Calorific Value [MJ/kg]
Tyre A	37.6
Tyre B	39.9
Tyre C	41.9
Tyre D	42.5
Tyre E	34.6

The elemental analysis results of the tyres in **Table 5** concur with the above suggestion that of lower carbon black content in tyres A and E when examining the carbon to hydrogen ratios (C/H). Tyres B, C and D fall into the range reported in other published findings of 9.633– 13.211 respectively (Berrueco, Esperanza, Mastral *et al.* 2005, López, Centeno, Alguacil *et al.* 2011). Whereas Tyres A and E have an elemental carbon to hydrogen ratio in a somewhat lower range. The lower C/H ratio accompanied with the high volatile matter content suggests the total carbon black content is lower than that of other reported results in Table 1. Excluding the varying volatile matter content and fixed carbon content differences of Tyres A and E and Tyres B, C and D the remaining ultimate and proximate analysis variables are in the ranges of results reported by the other investigations.

The main discernible differences in the tyres are noticed in the proximate analysis results of fixed carbon, volatile matter and ash contents. The volatile matter content and fixed carbon can be attributed to different tyres rubber compositions and ratios as well as the quantity of carbon black used in the manufacturing of the tyres as discussed in both of the above paragraphs. A substantial difference in the ash content of Tyres A and E and Tyres B, C and D are detected. This may be due to the differences in oxygen content. Ash contents reported by Islam, Joardder, Hasan et al. (2011), Kar (2011) and Önenç, Brebu, Vasile et al. (2012) are 18.12 wt%, 19.13 wt% and 18.9 wt% respectively while have an Oxygen content of 15.5 wt%, 24.58 wt% and 15.89 wt% respectively. This validates the trend observed for Tyres A and E also having a higher ash content with respect to a higher oxygen content. Aside from the oxygen content differences Tyres A and E also shows a higher Silicone contents that Tyres B, C and D as per scanning electron microscopy energy –dispersive X-Ray spectroscopy.

The gross calorific values (GCV) of all the tyres are reported in Table 6. The calorific values are in the range reported by other authors as in with the exception of tyre D which is slightly higher. Tyres A and E show calorific values in the lower section of the reported range, this may be explained by the similarly higher oxygen content of the tyres. Tyres B, C and D with the higher calorific values follows the same trend with lower oxygen content. This variance is validated in Table 1 by showing the same tendencies of higher tyre oxygen content yielding lower gross calorific values.

4.1.1 Models for the Prediction Chemical Properties of Tyre

By taking into accounts that both sets of analysis: ultimate and proximate, establishes the presence of carbon and hydrogen although in different manifestations, leads to the logical conclusion that a relationship exists between them. In this context it can be stated that the total elemental carbon and hydrogen contents are proportional to the volatile matter and fixed carbon contents of a material.

In this sub section the five tyres proximate and ultimate analysis are investigated by modelling the experimental results to find correlations between the tyres. The correlations will be used to build predictive algorithms for calculating the tyre total elemental carbon and hydrogen contents from proximate analysis data. Validation of the predictive correlation was accomplished by collecting an additional 58 data points from published authors.

4.1.1.1 Carbon content prediction

Figure 8 depicts how the ratio of $\frac{Carbon}{Fixed\ Carbon}$ interacts with $\frac{Carbon}{Volatle\ Matter}$ for the 5 experimental tyres. As seen a linear relationship is observed between the ratios which leads to a trend line to be fitted to the data with the following equation:

$$\frac{C}{FC} = -2.431 * \frac{C}{VM} + 5.899 \tag{16}$$

A good fit of R^2 = 91.41% for Eq. (16) to the data of Figure 8**Error! Reference source not found.** was found and deemed statistically significant. By mathematically manipulating Eq. 16 so the total elemental carbon becomes the subject of the equation for ease of calculations yields:

$$C = \frac{5.899}{\frac{1}{FC} + \frac{2.341}{VM}} \tag{17}$$

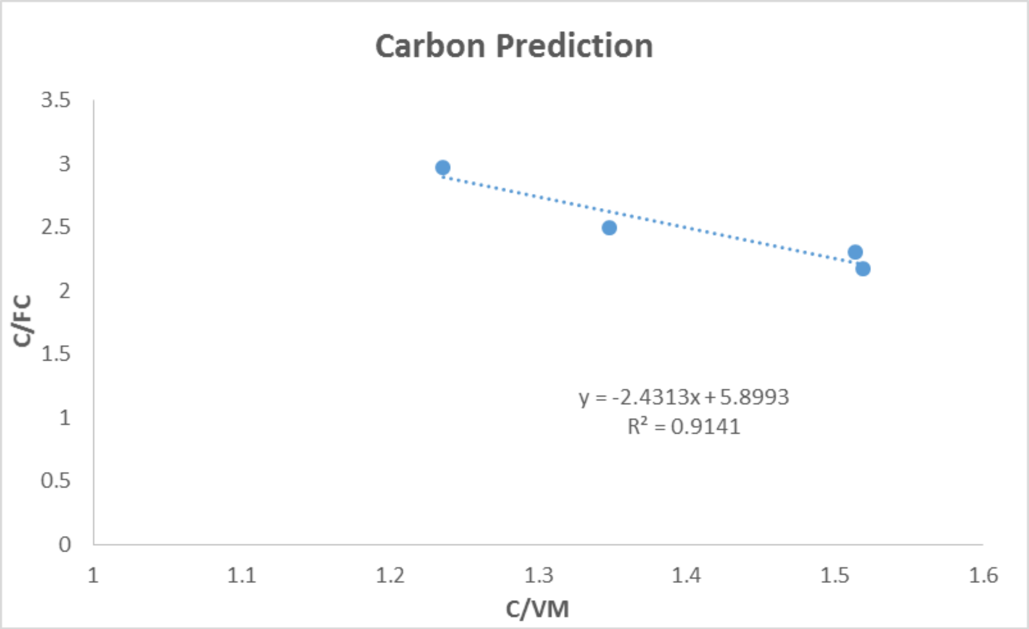

Figure 8: Linear relationship of total elemental carbon content

Figure 9 shows subtle differences in the predicted and experimental total elemental carbon content. The gradient of this straight line data fit appears correct however the variations in the data points are as a result of the model's intercept.

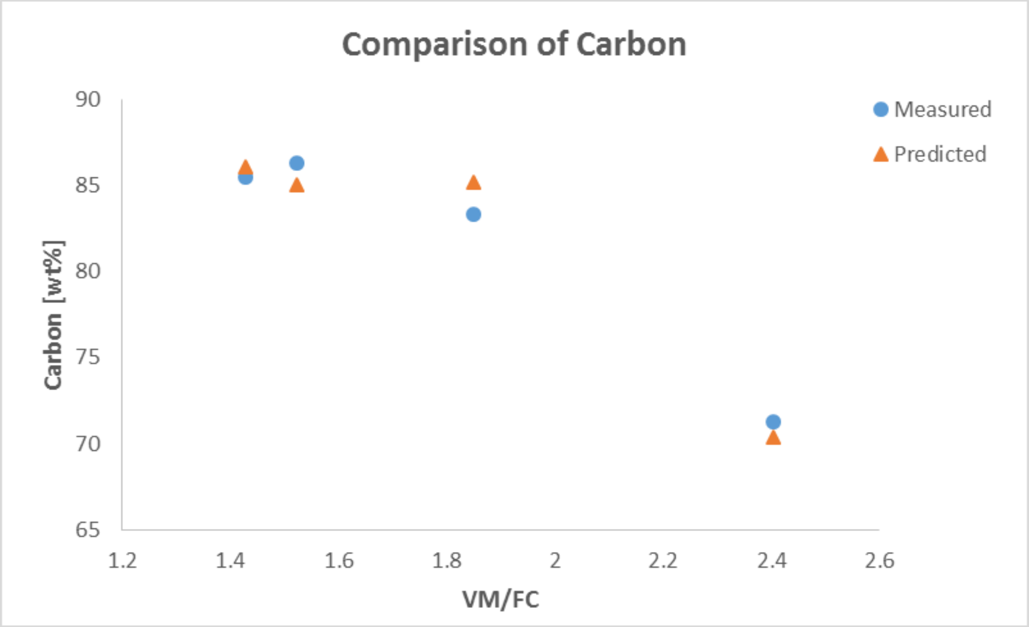

Figure 9: Comparison of the Experimental vs the Predicted total elemental carbon content

To corroborate this claim the total elemental carbon contents as stated in literature has been predicted used in Eq. (17) and presented in Figure 10. In order to test this generalized correlation to the fullest extent possible, care was taken to select data points that casts the widest possible range of ultimate and proximate analysis results of waste tyres. For this reason, the published data from was used as additional data points. Figure 10 substantiates the claim that the straight-line model of Eq. (17) has the correct gradient as the predicted and measured data points are above each other. These differences of the predicted versus experimental total elemental carbon content is thus as a result of the straight-line intercept. To correct this discrepancy, the model needs to be shifted with respect to the y-axis.

Statistical analysis of the measured vs predicted total elemental carbon content yields an average absolute error and average bias error of 5.331% and -4.275% respectively. The average bias error shows a statistically significant divergence with respect to the prediction algorithm. To lower this error regression analysis is used to alter the trend line intercept on the y-axis as suggested above. The adjusted equation for total elemental carbon prediction of tyres is as follow:

$$C = \frac{6.163}{\frac{1}{FC} + \frac{2.341}{VM}} \tag{18}$$

The range of data used for the correlation between the ultimate and proximate analysis includes:

56.3 wt% ≤ Volatile Matter ≤ 67.9 wt %

14.7 wt% ≤ Fixed Carbon ≤ 39.4 wt%

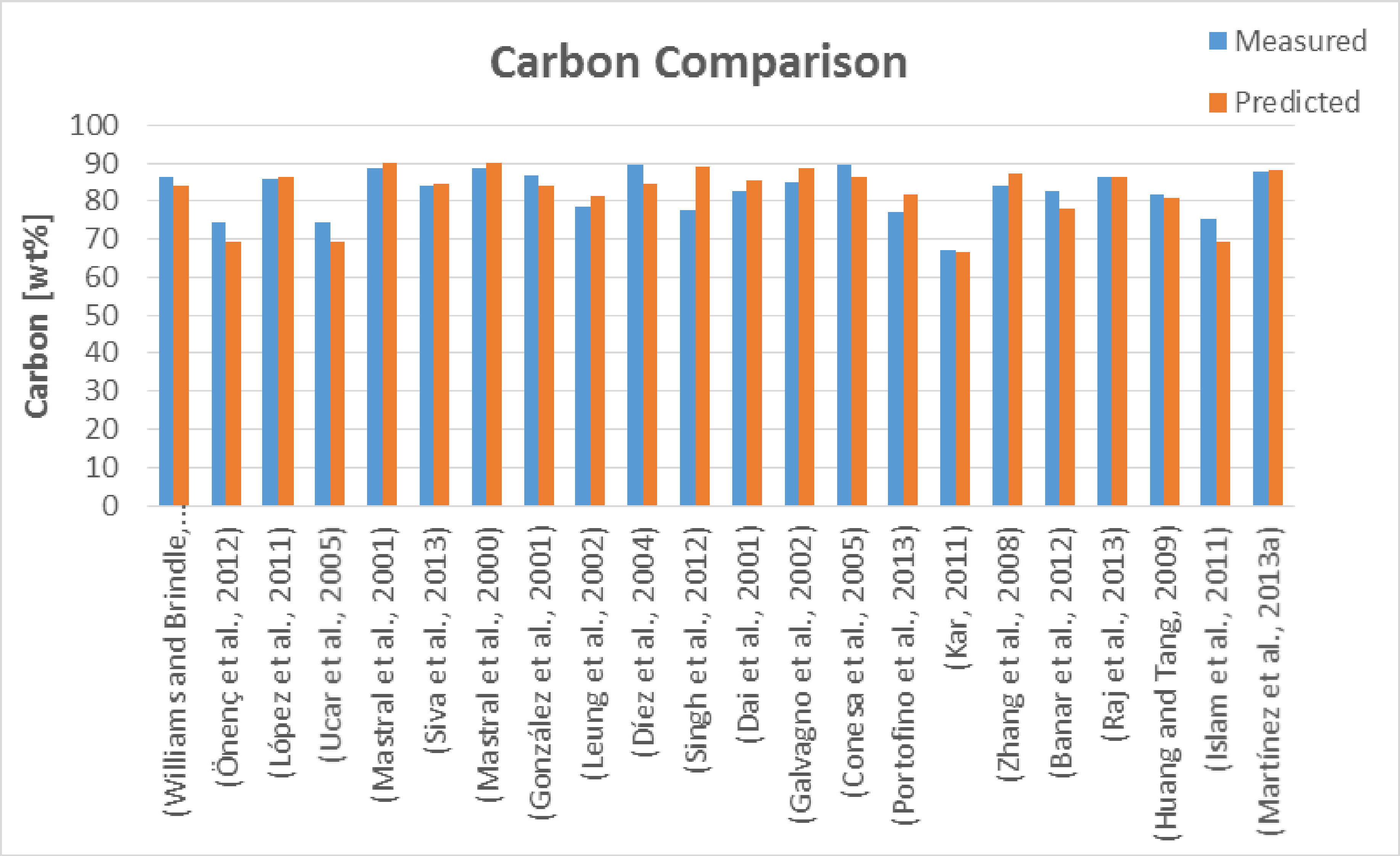

Figure 10: Graphical representation of the Carbon contents

Table 7 shows how the predicted carbon content using Eq. (18) compares to the measured carbon content of the ultimate analysis. However, this cannot be accepted as a true representation of the model, because the correlation was initiated by die experimental data. Therefore, it is necessary to further substantiate this claim with additional verification and analyses.

Table 7: Summary of experimental waste tyre Carbon prediction using Eq. (18)

Sample	Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
Tyre A	71.7	59.352	17.222	-17.222
Tyre B	83.3	88.953	6.786	6.786
Tyre C	85.5	89.882	5.125	5.125
Tyre D	86.3	88.811	2.909	2.909
Tyre E	71.3	73.538	3.139	3.139

For this reason the published data from Table 1 was applied to Eq. (18). The predicted carbon content is compared to their published ultimate analysis results in **Table 18**. An average absolute error and average bias error for the prediction of total carbon content was calculated at 3.761% and -0.002% respectively. The average bias error shows no statistically significant deviation from the true value and deems the algorithm for predicted total carbon from the measured carbon content acceptable. Due to the accuracy of the prediction algorithm the range of data that may be used in the prediction algorithm does not need to be in the range stated as data from Table is in the range of:

$$58.2 \text{ wt\%} \leq \text{Volatile Matter} \leq 71.5 \text{ wt \%}$$

$$19.5 \text{ wt\%} \leq \text{Fixed Carbon} \leq 33.8 \text{ wt\%}$$

This confirms that the volatile matter content in Table 1 is considerably higher than the five experimental tyres used and still yields statistically acceptable results.

Further validation of the total elemental predicted carbon contents is accomplished by applying Eq. (18) to additional ultimate and proximate analysis results summarized by other published authors. **Table 16** and **Table 17** shows the data that Martínez, Puy, Murillo *et al.* (2013) and Lung (2009) summarized from other published works. These summarized data points were used to determine the accuracy of the total elemental carbon prediction algorithm.

The average absolute errors and average bias errors for total elemental carbon prediction for the Martínez, Puy, Murillo *et al.* (2013) data is 3.584% and 1.211% respectively while Lung (2009) yields are 4.131% and 0.316% respectively. These averages show a very good data fit for the total elemental carbon prediction. **Figure 11** and **Figure 12** shows the graphics differences in the data.

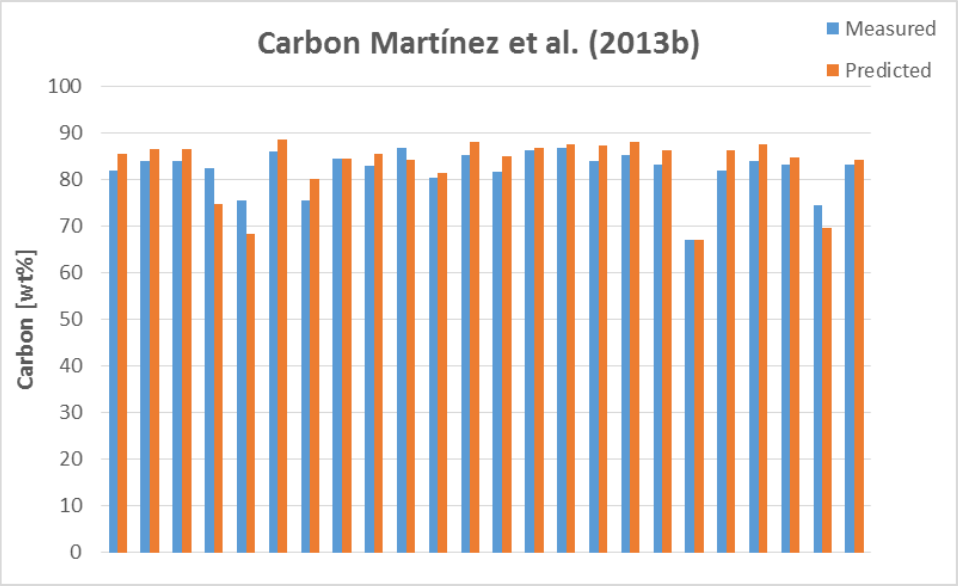

Figure 11: Comparison of carbon for Martínez, Puy, Murillo *et al.* (2013)

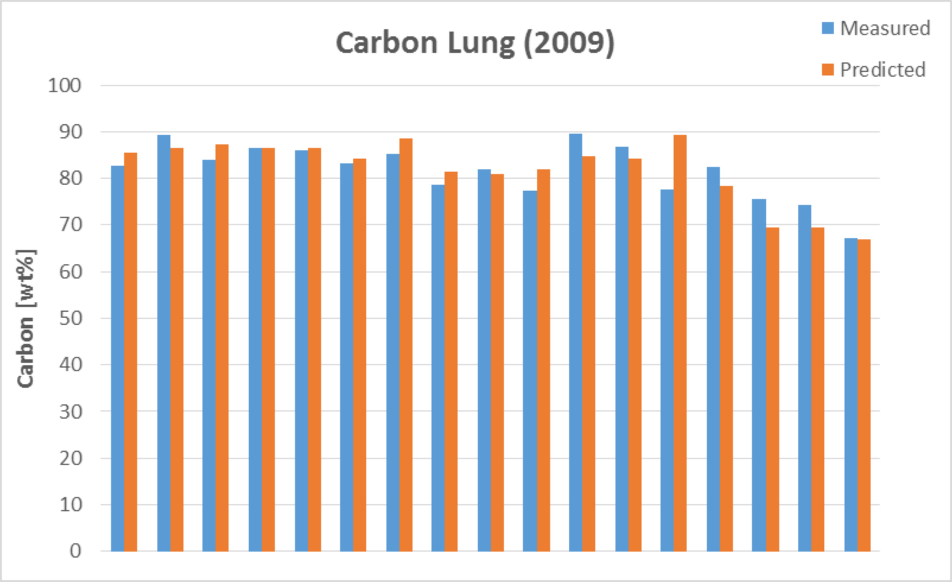

Figure 12: Comparison of carbon for Lung (2009)

4.1.1.2 Hydrogen content prediction

The total hydrogen content correlation makes use of the predicted carbon content from the previous section. Consequently, the total carbon content was predicted and then used in the modelling calculations below to determine the total elemental hydrogen content. Figure 13 shows the relationship between the ratio of $\frac{Predicted\ Carbon}{Hydrogen}$ $(\frac{PC}{H})$ versus the ratio of proximate analysis, $\frac{Volatile\ Matter}{Fixed\ Carbon}$ $(\frac{VM}{FC})$.

A straight trend line is fitted to the data with the following equation:

$$\frac{PC}{H} = -1.997 * \left(\frac{VM}{FC}\right) + 14.943 \tag{19}$$

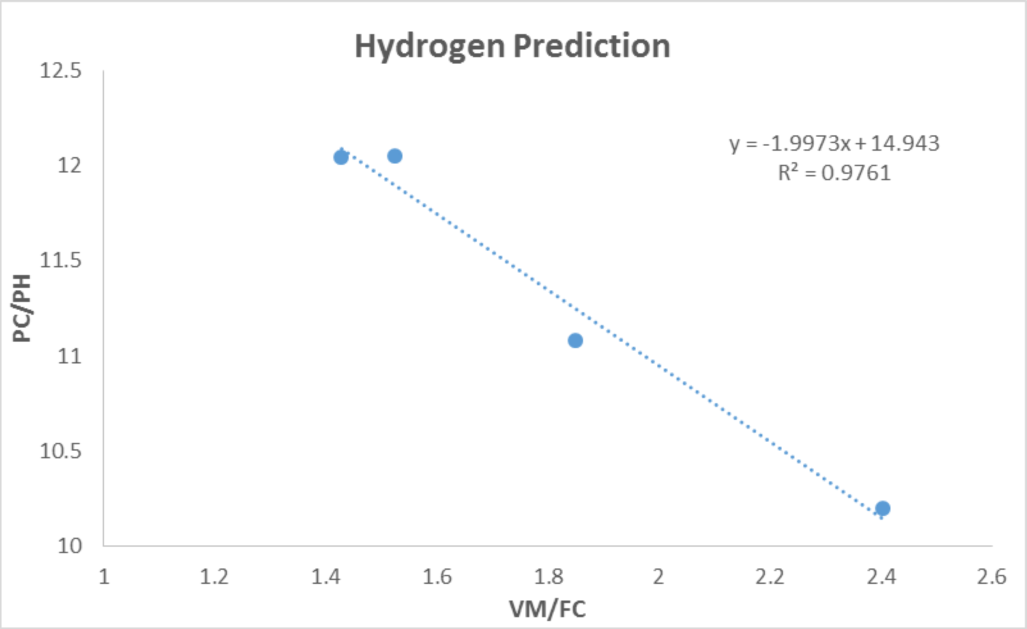

Figure 13: Linear relationship of total elemental hydrogen content using the predicted carbon

A good fit of R^2 = 97.61% for Eq. (19) to the data of Figure 13 was found and deemed statistically acceptable. Predicted total carbon (PC) content was used in Eq. (19) to calculate a predicted total hydrogen content and compare to the experimentally determined total hydrogen content from the ultimate analysis. By mathematically manipulating Eq. (19) so the total elemental hydrogen becomes the subject of the equation for ease of calculations yields:

$$H = \frac{PC}{-1.997 * \left(\frac{VM}{FC}\right) + 14.943} \tag{20}$$

Figure 14 shows slight differences in the measured and predicted ratios of the $\frac{Carbon}{Hydrogen}$. The prediction of the total hydrogen content appears correct in terms of the slope of the data and the intercept of the y-axis. To corroborate this claim total elemental hydrogen contents for Table 1 has been predicted using Eq. (20).

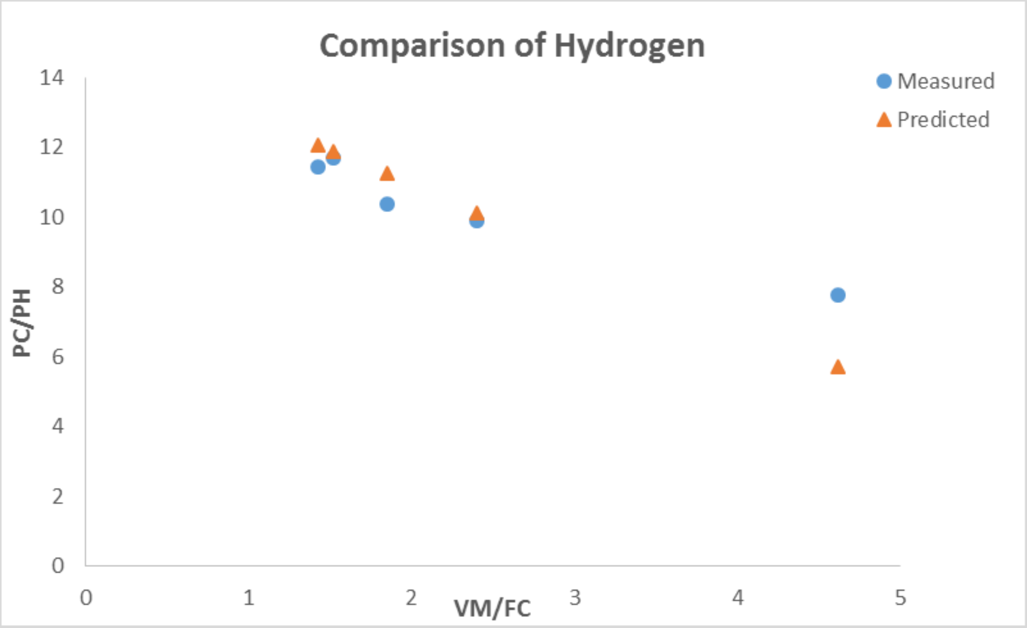

Figure 14: Comparison of the Experimental vs the Predicted (Carbon/Hydrogen) ratio

In order to test this generalized correlation to the fullest extent possible, care was taken to select data points that casts the widest possible range of ultimate and proximate analysis results of waste tyres. For this reason the published data from Table 1 was used as additional data points. **Figure 15** substantiates the claim that the straight line model of Eq. (19) has the correct gradient as the predicted and measured data points are above each other. These differences of the predicted versus experimental total elemental hydrogen content is thus as a result of the straight line intercept. To correct this discrepancy the model needs to be shifted with respect to the y-axis.

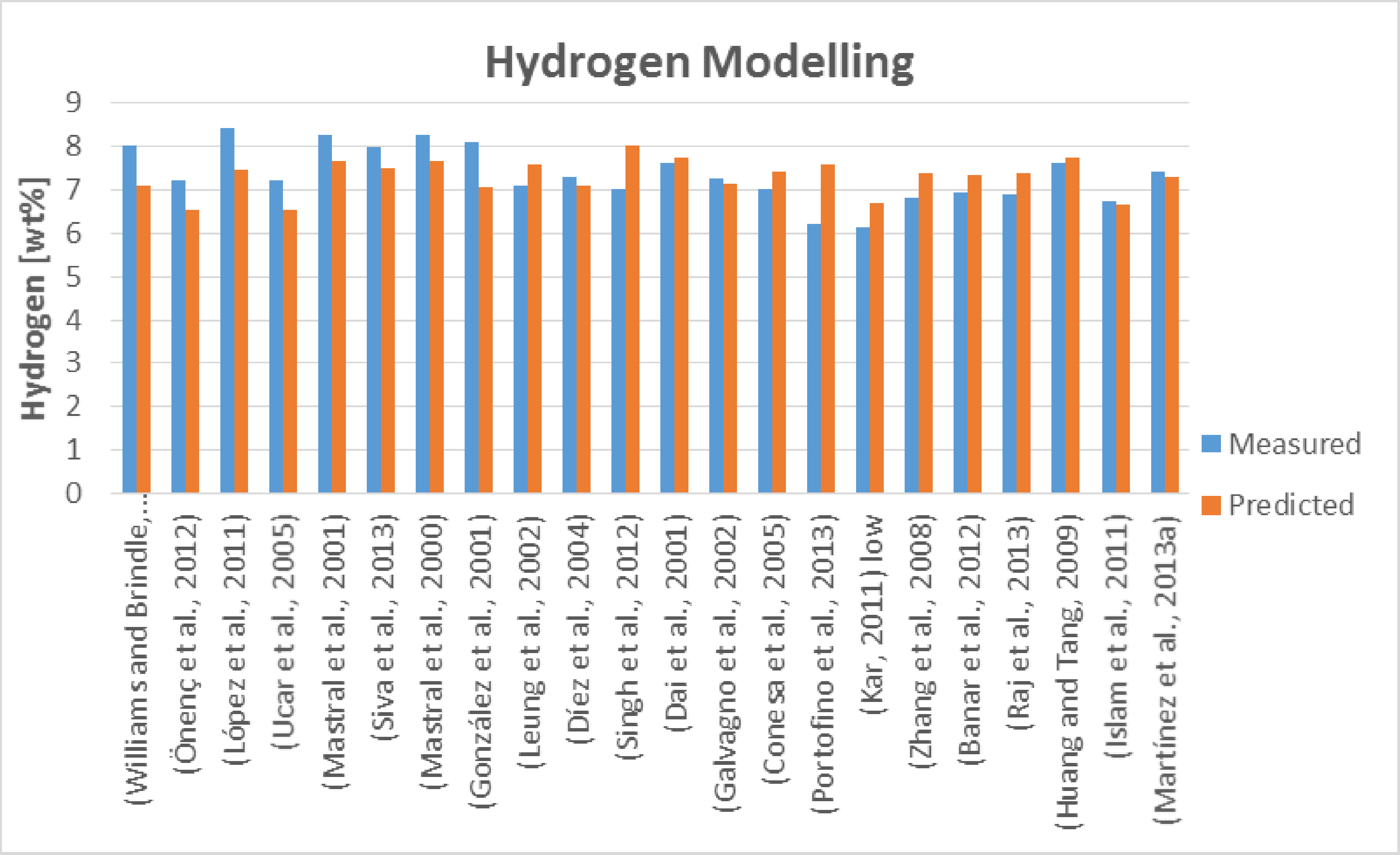

Figure 15: Graphical representation of the modelling of Hydrogen content from literature

Statistical analysis of the measured vs predicted total elemental carbon content yields an average absolute error and average bias error of 12.180% and 11.632% respectively. The average bias error shows a statistically significant divergence with respect to the prediction algorithm. To lower this error regression analysis is used to alter the trend line intercept on the y-axis as suggested above. The adjusted equation for total elemental carbon prediction of tyres is as follow:

$$H = \frac{PC}{-1.761 * \left(\frac{VM}{FC}\right) + 16.114} \tag{21}$$

The range of data used for the correlation between the ultimate and proximate analysis includes:

56.3 wt% ≤ Volatile Matter ≤ 67.9 wt %

14.7 wt% ≤ Fixed Carbon ≤ 39.4 wt%

Table 8 shows how the predicted carbon content using Eq. (19) compares to the measured carbon content of the ultimate analysis. However this cannot be accepted as a true representation of the model, because the correlation was initiated by the experimentally measured data. Therefore it is necessary to further substantiate this claim with additional verification.

Table 8: Summary of the experimental waste tyre Hydrogen prediction using Eq.(21)

Sample	Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
Tyre A	9.22	8.616	6.547	-6.547
Tyre B	8.03	7.163	10.797	-10.797
Tyre C	7.46	6.778	9.136	-9.136
Tyre D	7.37	6.795	7.801	-7.801
Tyre E	7.21	6.501	9.835	-9.835

For this reason the published data from Table 1 was applied to Eq. (21). The predicted hydrogen content is compared to its published ultimate analysis results as seen in **Table 21**. An average absolute error and average bias error for the prediction of total carbon content was calculated at 7.520% and 0.004% respectively. The average bias error shows a no statistically significant deviation from the true value and deems the algorithm for predicted total hydrogen from the measured hydrogen content acceptable. Due to the accuracy of the prediction algorithm the range of data that may be used in the prediction algorithm does not need to be in the range stated as data from Table 1 is in the range of:

$$58.2 \text{ wt\%} \leq \text{Volatile Matter} \leq 71.5 \text{ wt \%}$$

$$19.5 \text{ wt\%} \leq \text{Fixed Carbon} \leq 33.8 \text{ wt\%}$$

This shows that the volatile matter content in Table 1 is considerably higher than the five experimental tyres used.

Further validation of the total elemental predicted hydrogen contents is accomplished by applying Eq. (21) to additional ultimate and proximate analysis results summarized by other published authors. **Table 16** and **Table 17** shows the data that Martínez, Puy, Murillo *et al.* (2013) and Lung (2009) summarized from other published works. These summarized data points were used to determine the accuracy of the total elemental carbon prediction algorithm.

The average absolute errors and average bias errors for total elemental carbon prediction for the Martínez, Puy, Murillo et al. (2013) data is 6.680% and 1.711% respectively while Lung (2009) yields are 7.411% and 2.340% respectively. These averages show a very good data fit for the total elemental carbon prediction. Figure 17 and Figure 18 shows the graphics differences in the data.

4.1.2 Comparison with other published equations

Since no published correlations could be found for the prediction of total elemental carbon and hydrogen of waste tyres the validation of the derived correlations have been establish by comparing to other published correlations. However, it needs to be noted that the published correlations are only valid for the materials for which it has been originally derived. Hence, this section is of purely of academic to cover all basis of investigation.

To compare Eq. (18) and (21) prediction algorithms with existing ones, three equations have been selected from literature as discussed in 2.1.1 Prediction. **Figure 18** and **Figure: 19** shows the total elemental carbon and hydrogen values calculated from these different correlations for the five experimental tyres used in the present work. The average absolute error of Parikh, Channiwala and Ghosal (2007), Shen, Zhu, Liu *et al.* (2010) and

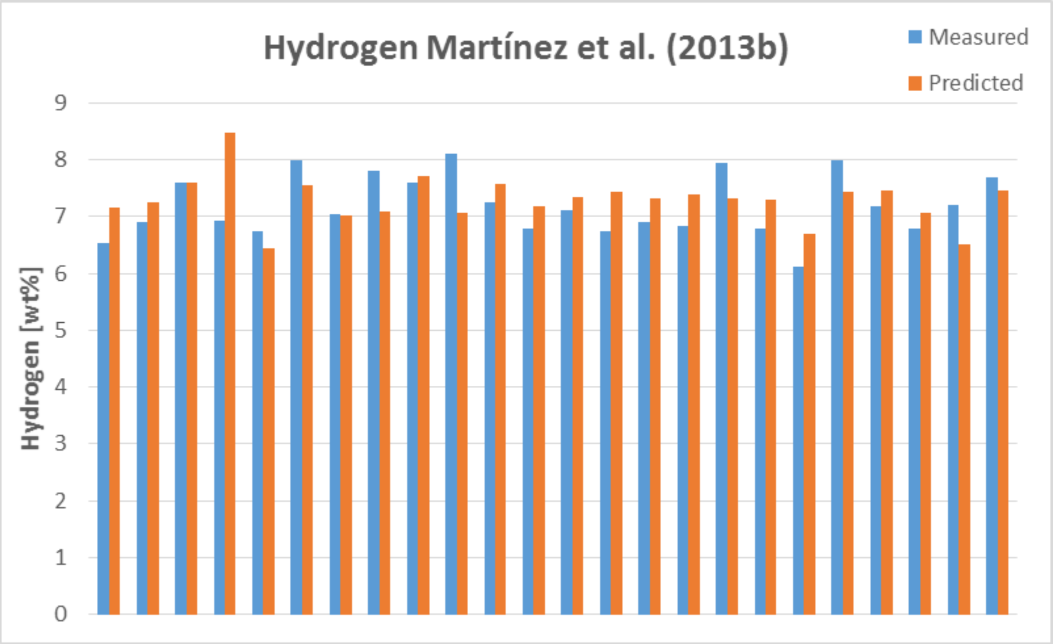

Figure 16: Comparison of hydrogen for Martínez et al. (2013b)

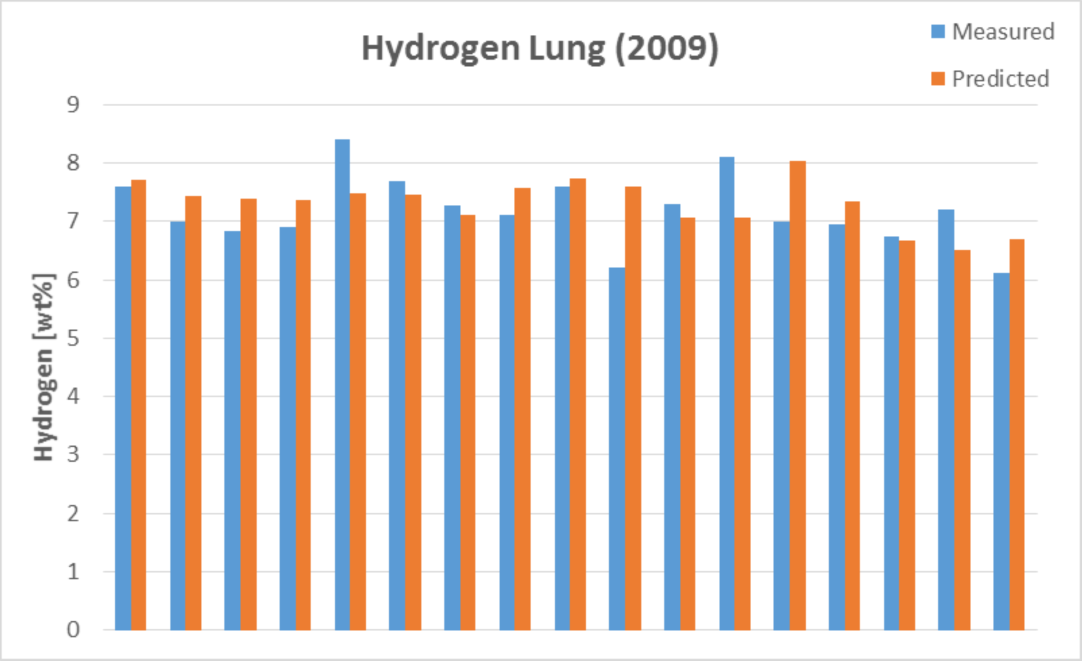

Figure 17: Comparison of hydrogen for Lung (2009)

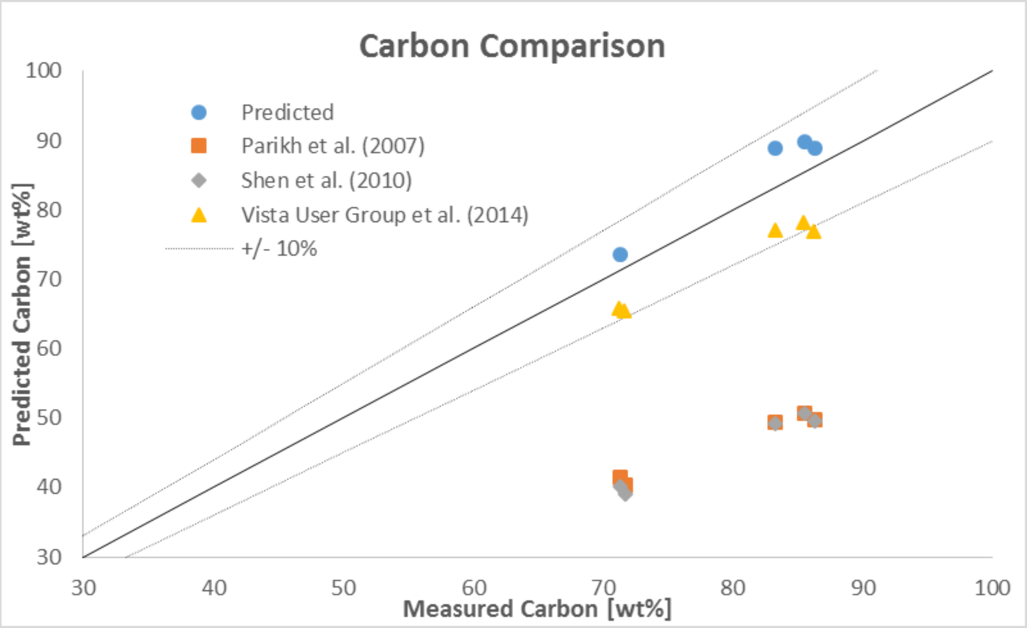

Figure 18: Comparing carbon from Eq.(18) to published correlations

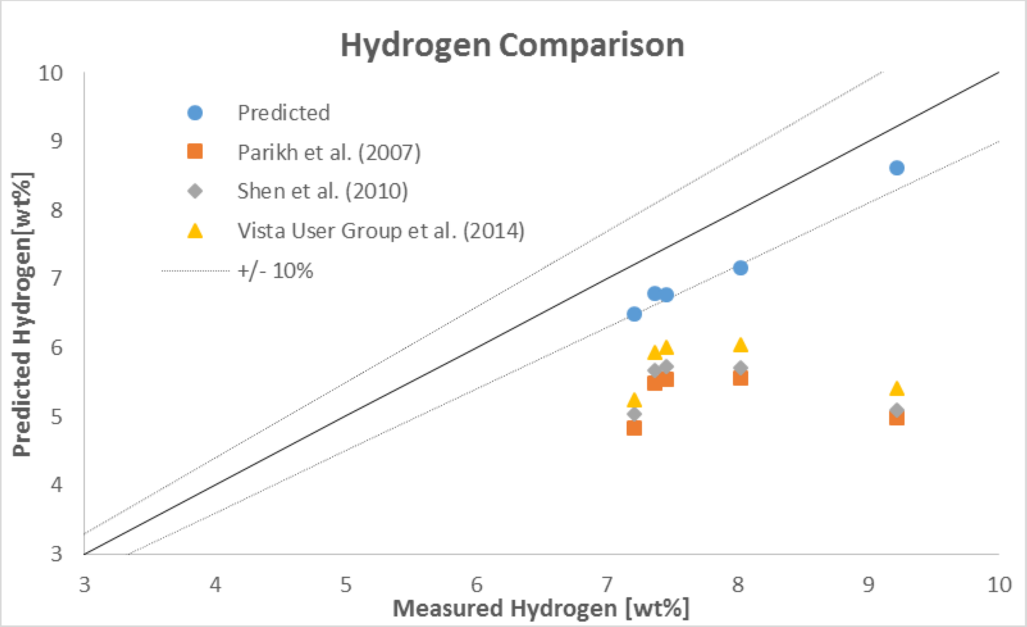

Figure: 19 Comparing hydrogen from Eq. (21) to published correlations

Vista User Group, Electric Power Research Institute and Black & Veatch (2014) for total elemental carbon content are in the order of 41.864, 42.684 and 8.804% respectively, while the average bias error for the same correlations are calculated at -41.864, -42.684 and -

8.804% respectively. It is observed that the only predicted data to fall within the ±10% range is that of Vista User Group et al. (2014) while both other correlations are considerably lower.

The average absolute error of Parikh, Channiwala and Ghosal (2007), Shen, Zhu, Liu *et al.* (2010) and Vista User Group, Electric Power Research Institute and Black & Veatch (2014) for total elemental hydrogen content are in the order of 32.237, 29.933 and 26.446% respectively, while the average bias error for the same correlations are calculated at -32.237, -29.933 and -26.446% respectively. The current predictive algorithm shows its data within the ±10% range while all the other correlations are outside the error range.

The most remarkable aspect of comparing the prediction algorithms is the data ranges at which the author's states as its operational range. Parikh, Channiwala and Ghosal (2007) and Shen, Zhu, Liu *et al.* (2010) report that their individual prediction algorithms are functional for: $4.7 \leq$ Fixed Carbon $\leq 38.4\%$, $57.2 \leq$ Volatile Matter $\leq 90.6\%$ and $9.2 \leq$ Fixed Carbon $\leq 32.79\%$, $57.2 \leq$ Volatile Matter $\leq 90.6\%$ respectively. These ranges are considerably larger than the ranges of the present works algorithms. Thus their predictions should yield smaller deviations when compared to the measured values and consequently have lower average absolute errors and average bias errors than those seen in **Table 9**. Theoretically by taking into account only fixed carbon, volatile matter and ash content, these predictions should also be accurate for the prediction of waste tyre total elemental carbon and hydrogen. However as stated by Parikh, Channiwala and Ghosal (2007) and Shen, Zhu, Liu *et al.* (2010) theses correlations were developed for biomass.

By comparing the functionality of the published algorithms to present correlations its validity is established. The low average absolute errors and average bias errors of the present correlations merits its acceptance in predicting the total elemental carbon and hydrogen of waste tyres.

Table 9: Average Prediction Errors

Algorithm	**Carbon**		**Hydrogen**	
	Average Absolute Error [%]	**Average Bias Error [%]**	**Average Absolute Error [%]**	**Average Bias Error [%]**
Present	7.036	0.148	-8.823	8.823
Parikh, Channiwala and Ghosal (2007)	41.864	-41.864	32.237	-32.237
Shen, Zhu, Liu *et al.* (2010)	42.684	-42.684	29.933	-29.933
Vista User Group, Electric Power Research Institute and Black & Veatch (2014)	8.804	-8.804	26.446	-26.446

4.2 Mass Loss Kinetics

In this section the thermal degradation behaviours of the five experimental waste tyres were investigated. By comparing the chemical characteristics of the experimental waste tyres to these thermal degradation behaviours certain relationships can be modelled that would yield preliminary results prior to testing and aid in increasing the waste tyre pyrolysis performance.

4.2.1 Analyses of the TGA Curves

The results of the dynamic thermogravimetric analysis of the five tyres used are shown in Figure 20. When delving into the information provided by thermogravimetric analysis in **Figure 20** it is clear that the mass losses of the tyres are insignificant before 200°C. Even though the mass losses of the tyres only start at approximately 200°C, the rate at which mass loss occurs remains low up onto around 10% mass loss of the original tyre weight. Thereafter the mass loss of the tyres proceeds at a much more rapid pace than before, before reaching the final temperature at which pyrolysis takes place. This final temperature is defined as the temperature at which the mass loss stagnates and no drastic changes are achieved when elevating the temperature even further. This phenomenon is seen in **Figure 20** where the graph of each waste tyre appears to reach a plateau. These final pyrolysis temperatures for the experimental tyres range from 570 – 620 °C which can be more accurately determine for each individual tyre by investigating the derivative thermogravimetric (DTG) curves as in section 4.2.2 Physical Appearance of the DTG Curves.

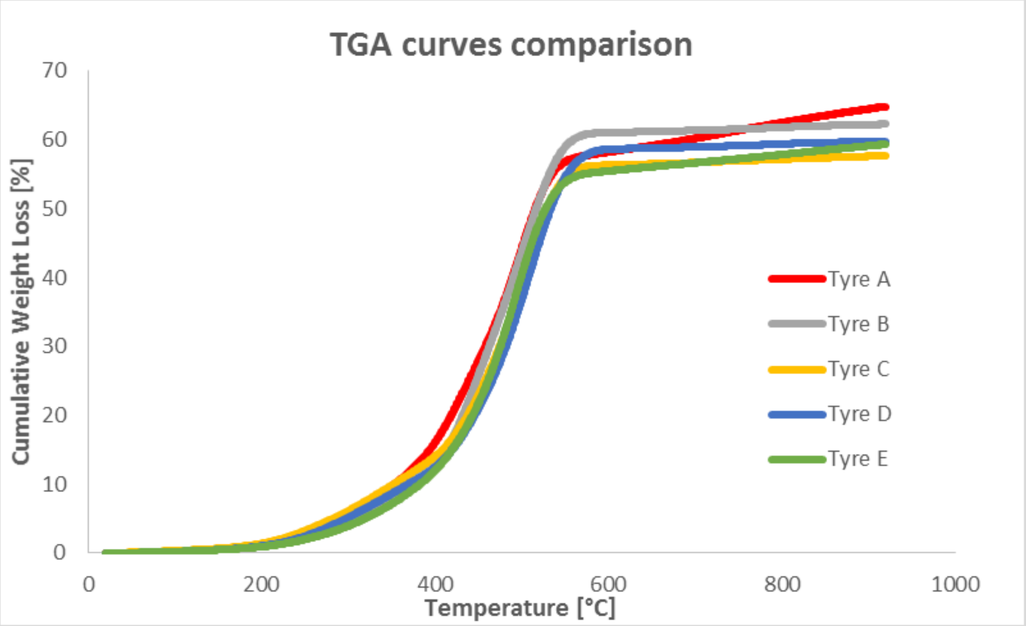

Figure 20: Cumulative Weight Loss of the five experimental tyres

From the thermogravimetric analysis curves the remaining residue, that is the char yield, of each waste tyre can be approximated which corresponds the sum of the fixed carbon and ash contents measured during proximate analysis. This approximation is solely dependent on the user’s discretion when investigating the slope. Table 10 shows the approximated char remaining once pyrolysis has reached its peak. This char content is considerably higher than the sum of measured total of fixed carbon and ash contents from the proximate analysis except in tyres D which is approximately the same. As the fixed carbon content remains unchanged during pyrolysis it stands to reason that the difference in the TGA residue and sum of fixed carbon and ash contents can be attributed to the formation of coke/char.

However upon closer observation of Tyres A and E, once the final pyrolysis temperature is reached slight inclines to their respective plateaus is seen in contrast to those of Tyres B, C and D. Ultimate analysis of Tyres A and E show much higher total elemental oxygen contents and consequently higher ash contents according to their respective proximate analysis when compared to Tyres B, C and D. Due to the standard test method used for the thermogravimetric analysis of the tyres the final analysis temperature is 920 °C, at this temperature the graph for Tyres A and E still shows some formation of ash and consequently char/coke. Thus the higher TGA residue yield implies that char is also produced during the pyrolysis process that has a high vaporization temperature.

Table 10: TGA vs Proximate Analysis

Sample	TGA Residue [wt%]	Fixed Carbon + Ash [wt%]
Tyre A	42.236	30.700
Tyre B	38.995	37.100
Tyre C	43.723	42.600
Tyre D	41.333	42.000
Tyre E	44.648	40.800

4.2.2 Physical Appearance of the DTG Curves

The results of the differential thermogravimetric (DTG) analysis curves of Figure 22 the mass loss of the five tyres used performed at a constant heating rate of 20°C/min. The physical appearance of the differential thermogravimetric analysis curves concurs with the curves published by other researchers.

No prominent initial mass loss peaks are distinguishable for the tyre samples. However, the differential thermogravimetric curves of pyrolysis for Tyres A and B shows steps. These steps are the initial mass loss peaks and can thus be divided into different regions. Tyres C, D and E exhibits only one mass loss peaks at approximately the same point as the second mass loss peaks of Tyres A and B. This phenomenon of dual mass loss peaks merging to a single peak is a trend observed by various researchers. Tyres A and B are in the final stages of merging the peaks as per the steps observed instead of individual peaks. At high heating rates the mass loss peaks tends to shift to higher temperatures while the peaks at lower temperatures has a tendency to merge with its higher temperature counterpart.

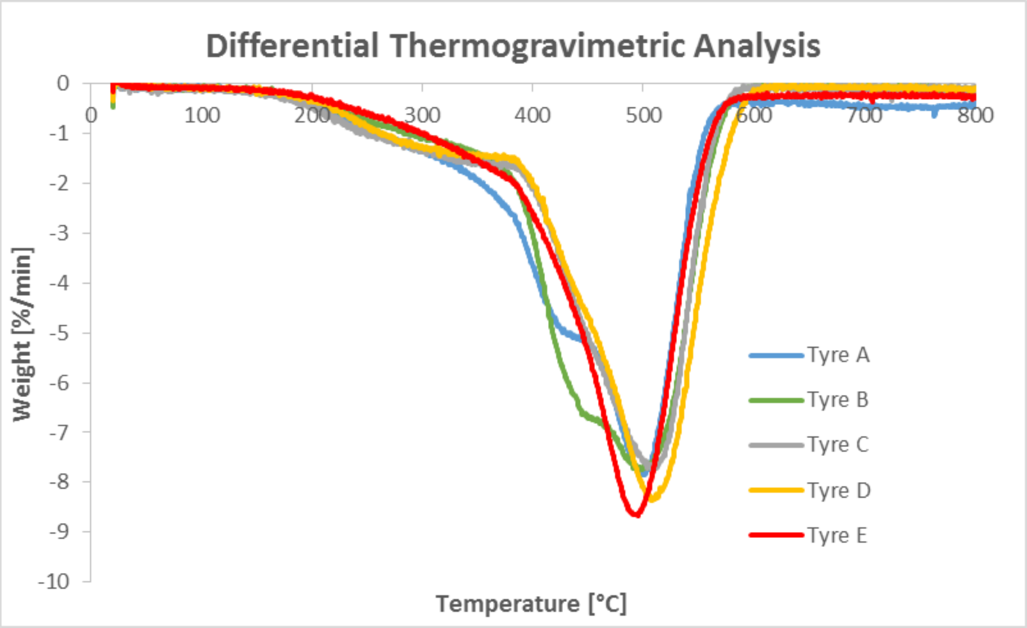

Figure 21: Differential thermogravimetric analysis of the five tyres

Table 11 shows these mass loss peak temperatures. As previously mentioned in section 4.2.1 the final pyrolysis temperature can accurately be determined from the differential thermogravimetric curves of the tyres. This temperature is read off of the graph when the differential thermogravimetric curves returns to zero after the final mass loss peak.

Table 11: Temperatures of the Mass Loss peaks

Sample	**Temperature [°C]**	
	Mass Loss Peak 1	**Mass Loss Peak 2**
Tyre A	437	498
Tyre B	454	502
Tyre C	-	505
Tyre D	-	504
Tyre E	-	495

By using this method the final temperature and the calculated conversion at which no volatiles are present in the tyres are shown in Table 12.

Table 12: Final Pyrolysis Temperatures

Sample	Temperature [°C]	Conversion [%]
Tyre A	570	84.6
Tyre B	590	96.9
Tyre C	591	95.6
Tyre D	610	97.2
Tyre E	590	89.6

On average the conversion at which waste tyre pyrolysis reaches completion is obtained to be approximately 90%. **Figure 22** originates by plotting the 90% conversion temperature (T90) of each experimental waste tyres against their respective total elemental carbon to hydrogen ratio.

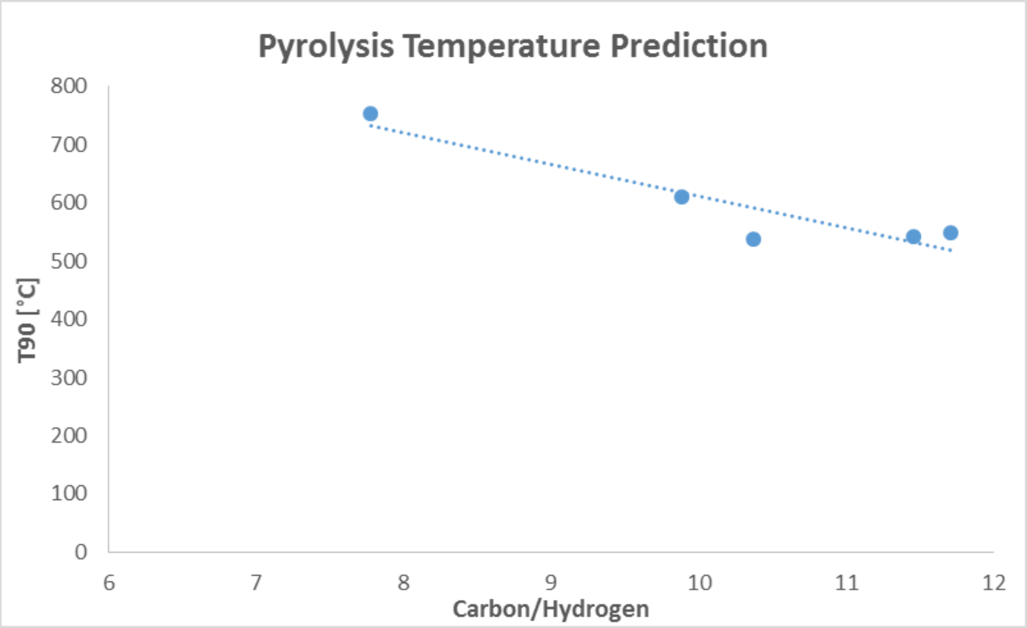

Figure 22: Prediction of the final waste tyre pyrolysis temperature

The plot indicates a good linear correlation of $R^2 = 0.87$ between the waste tyre's 90% conversion temperature and the total elemental carbon to hydrogen ratio. Based on this evidence, the temperature at which a waste tyre reaches the completion of pyrolysis process can be predicted using the ratio of its total elemental carbon to hydrogen using the following empirical relationship:

$$T90 = -54.452 * \left(\frac{C}{H}\right) + 1156.3 \tag{22}$$

where $\left(\frac{C}{H}\right)$ is the total elemental carbon to hydrogen ratio of the individual waste tyre used in the pyrolysis process.

The range of data used in the development of this correlation is:

$$7.777 \leq \left(\frac{C}{H}\right) \leq 11.709$$

$$538°\text{C} \leq \text{T90} \leq 754°\text{C}$$

By implementing Eq. (22) into the pyrolysis process of waste tyres, thermogravimetric analysis does not need to be accomplished to determine the final temperature at which the waste tyre completes degrading. This equation can serve as a guide to determine a temperature which will prevent the thermal cracking of the pyrolytic oil products into the non-condensable gas. In minimizing the non-condensable gas fraction of waste tyre pyrolysis, more pyrolytic oil may be produced and used as an alternate fuel of other valuable chemical products.

Coupled with maximizing the pyrolytic oil yield of waste tyres, Eq. (22) will give a good indication of when to stop the ramp-up of temperature during pyrolysis. Vast amounts of time and energy savings can be achieved in knowing when the optimum pyrolysis temperatures are reached. To be able to produce marketable products from waste tyre pyrolysis it is vital to reduce costs and optimize process performance. This correlation provides a way to reduce the recurring costs of thermogravimetric analysis and redundant input of energy into the system.

4.2.3 Waste Tyre Kinetic Parameters

This section will focus on the effect temperature has on the pyrolysable fraction of waste tyres. All equations used for the calculation of these parameters were discussed in section 3.2.3. Figure 24 shows the conversion of the waste tyres over the pyrolysis timeframe. Given that all the tyres were studied under exactly the same processing conditions, the comparison between the different tyres degradations are simplified. No significant differences are observed in the initial stages of pyrolysis or in the evolution of the conversion of the pyrolysable content. As is quantitatively observed, the slopes of conversion in terms of the expulsion of the volatile content of tyres occurs at approximately the same rate.

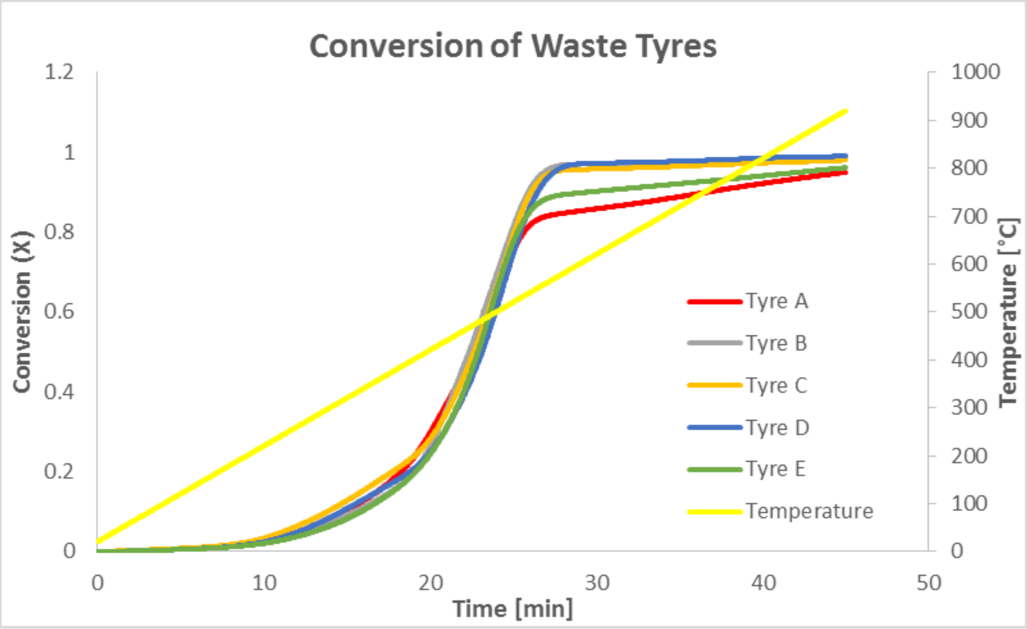

Figure 23: Plot of Mass Loss with Time and Temperature

Tyres A and E shows significantly lower conversions once the final pyrolysis temperatures are reached, as was previously determined. Conversion for tyres A and E are 84.6% and 89.6% respectively, while tyres B, C and D gave 96.9%, 95.6% and 97.2% respectively at their respective final temperatures. These lower conversions for tyres A and E at the final pyrolysis temperature are as a result of a combination of low total elemental carbon and high total elemental oxygen. The lower total elemental carbon content results in less carbon available to react with hydrogen and form the hydrocarbons in the pyrolytic gaseous and liquid products. The higher ash content and in turn total elemental oxygen favours the formation char/coke deposited in the ash surface as discussed in the previous section. From both sets of results, it can be understood that for tyres A and E pyrolysis would cease earlier than that of the remaining tyres, but continue in the partial removal of char/coke deposited on the ash surface.

Figure 24 shows the Arrhenius plots corresponding to the runs of the different tyres. A certain degree of scattering is noticeable for the experimental data fitting the Arrhenius equation at lower temperatures which corresponds to observations made by Lopez, Aguado, Olazar *et al.* (2009). As the temperature of pyrolysis is increased the experimental tyre data fitted to the Arrhenius equation tends to follow a straight line plot. Due to the high pyrolysis heating rate the thermal degradation of natural rubber, styrene butadiene and polybutadiene rubbers shifts to higher temperatures and overlap to give the impression of a single degradation step.

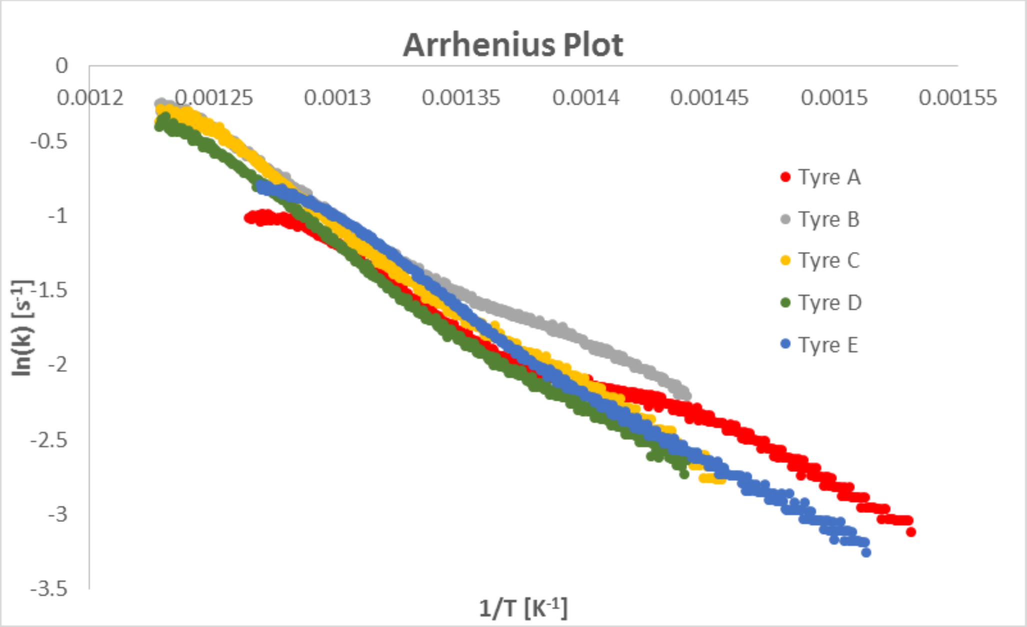

Figure 24: Comparison of Tyre kinetics

By ascertaining the tyres experimental data shows straight-lines at higher heating rates, a linear trend line is incorporated to the individual tyres graphs.

Table 13 shows the results of the trend line equations fitted to the straight-line Arrhenius plots of the respective tyres. The high regression (R^2) substantiates a good fit for the data to a straight line.

Table 13: Trend line data for the Arrhenius plots

Sample	Gradient	Intercept	R^2
Tyre A	7682.2	8.699	98.1
Tyre B	9295.4	11.117	98.6
Tyre C	10866.0	13.072	99.6
Tyre D	11379.0	13.615	99.3
Tyre E	11265.0	13.591	99.5

The activation energy's and pre-exponential factors for the tyres were calculated according to Eq. (15) and shown in **Table 14** all with very good data fits. The results are similar to those reported by other authors researching similar process conditions and heating rates.

Table 14: Tyres Activation Energy's and Pre-exponential factors

Sample	Activation Energy	Pre-exponential Factor
Tyre A	63.87	5996.91
Tyre B	77.28	67305.68
Tyre C	90.34	475441.91
Tyre D	94.60	818312.85
Tyre E	93.65	798907.14

Qu, Jiang and Gao (2012) investigated the relationship of activation energies with respect to the total volatile matter contents of coal samples. By using the principles set out by Qu, Jiang and Gao (2012) the rank of the experimental tyres results in terms of their respective activation energies is as follow: Tyre D > Tyre E > Tyre C > Tyre B > Tyre A according to **Table 14**. From these results Figure 25, Figure 26 and Figure 27 has been plotted to show this relationship between the reactive kinetic parameters and the total volatile matter contents of the waste tyres.

From **Figure 25** a clear tendency is observed by a decrease in activation energy when the total volatile matter content increased. This happens because volatile matter is directly proportional to easy at which tyres can be ignited with the combustion of its volatile matter. Meaning that the higher the activation energy present in waste tyres the less volatile matter is present. This relationship is quantified by adding a linear trend line to the data with a good fit of $R^2 = 94.88\%$:

$$E = -2.658 * (VM) + 253.78 \tag{23}$$

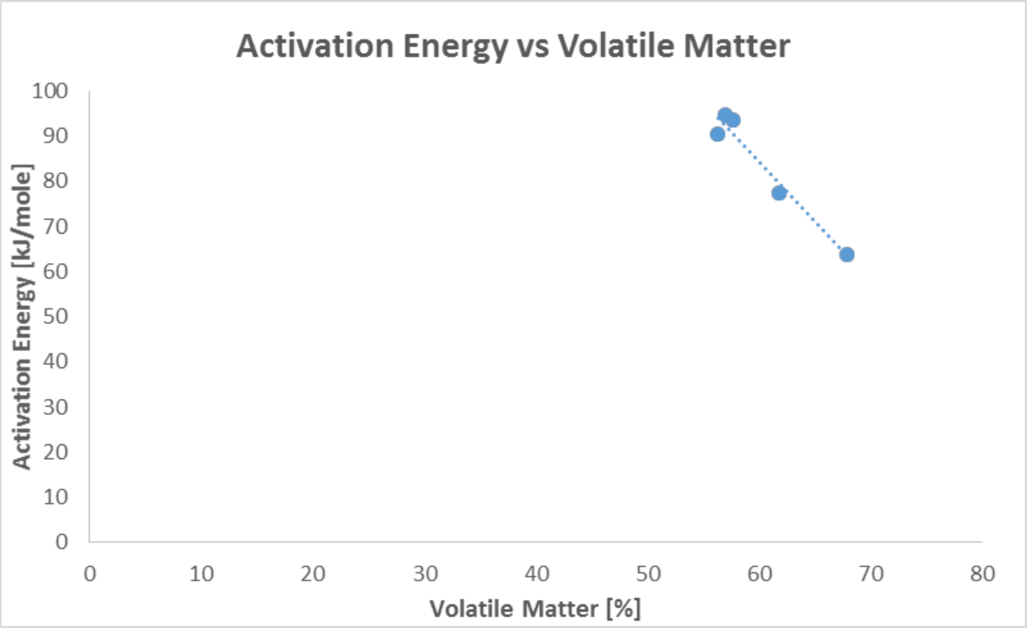

Figure 25: The relationship between tyres activation energy and total volatile matter content

It can further be deduced from Figure 26 that the pre-exponential factor of the waste tyres also decreases with an increase in the total volatile matter content. This is relatable to the activation energy of waste tyres as seen in Figure 27 where the pre-exponential factor increases with activation energy. These results are comparable to work published by Qu, Jiang and Gao (2012) who found similar relationships for the testing of coal to determine its spontaneous combustibility. By using Qu, Jiang and Gao (2012) these relationships for waste tyres may be deemed appropriate.

It can be concluded that using Eq. (23) will eliminate the prerequisite of performing the thermogravimetric analysis of waste tyres prior to calculating the activation energies using the Arrhenius equation as described in section 3.2.3. Thus a simple, but reliable correlation has been developed to increase the performance of waste tyre pyrolysis to the point of no preliminary waste tyre analysis costs and allocated time for testing.

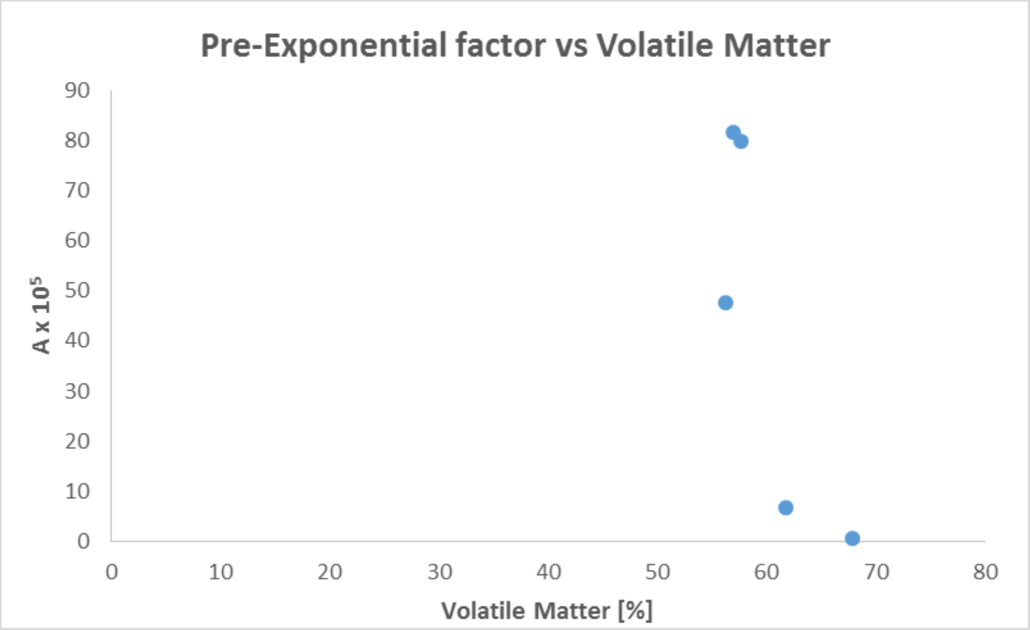

Figure 26: The relationship between tyres Pre-Exponential factor and total volatile matter content

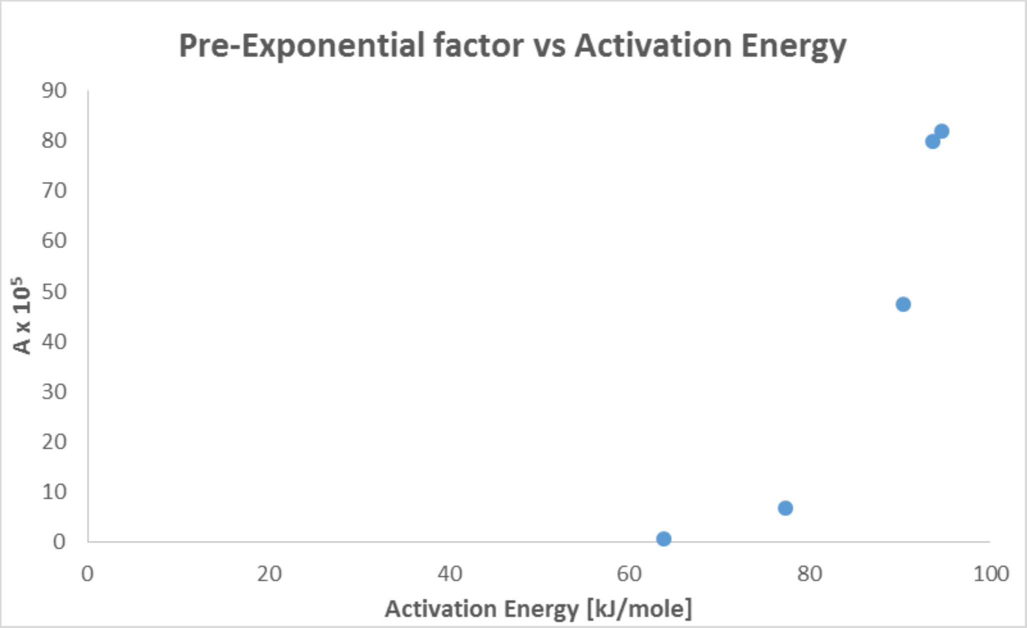

Figure 27: The relationship between tyres Pre-Exponential factor and activation energy

Following the prediction of activation energy from the total volatile matter contents of tyres, a diagram may be used to summarize the conversion of waste tyres, the temperatures at which those conversions takes place and their respective activation energies. **Figure 28** shows the plot of the temperature at which certain pyrolysis conversions takes place against the previously calculated activation energies while **Table 15** shows the fit of a trend lines to the data.

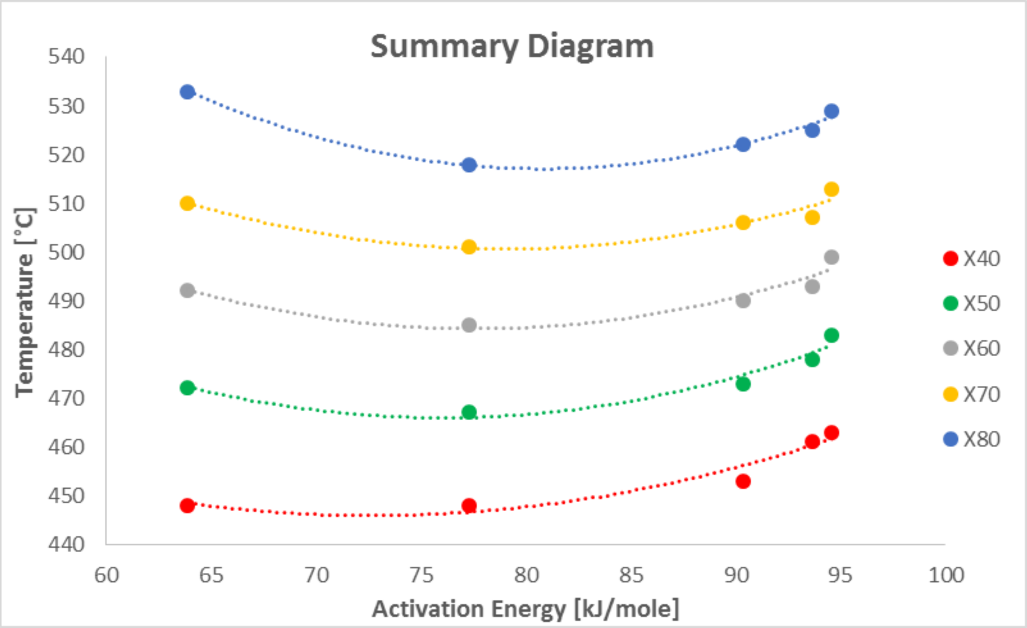

Figure 28: Summary diagram of waste tyre data

Table 15: Trend lines to data fit of **Figure 28**

Conversion [%]	Trend Line	R^2 [%]	Eq.
80	$T = 0.0558E^2 - 9.0165E + 881.35$	97.49	(24)
70	$T = 0.0415E^2 - 6.5576E + 759.59$	85.61	(25)
60	$T = 0.0422E^2 - 6.5574E + 738.74$	87.52	(26)
50	$T = 0.0429E^2 - 6.5157E + 713.64$	92.79	(27)
40	$T = 0.0327E^2 - 4.7472E + 618.31$	92.95	(28)

The fit is the trend lines to the experimental data are all deemed statistically acceptable due the high regression analysis values of above 85%. This summary graph may be used as a tool in the waste tyre pyrolysis process to quickly estimate the temperatures and energies required to reach certain waste tyre conversions. Due to the limitations set by the data published by other authors, the specific data needed to validate this graph could not be obtained. However data published by Haydary, Jelemenský, Gašparovič *et al.* (2012) can be used to estimate the data required to validate the summary waste tyre pyrolysis graph. Haydary, Jelemenský, Gašparovič *et al.* (2012) calculated the activation energy for the waste tyre used in their experiments to be 78 kJ/mole which is in the exact range of the current experimental data. By interpolating the conversions used in the present study to the graph of waste tyre conversion from Haydary, Jelemenský, Gašparovič *et al.* (2012) the specific temperatures can be estimated by reading off from the graph.

It was found that validation temperatures are: X40 – 410°C, X50 – 430°C, X60 – 450°C, X70 – 470°C, X80 – 485°C and X90 – 495°C. These temperatures are slightly lower than those of the summary graph, but still in the sample range of data temperatures. This proves that the graph may be used as a simple and easy guide to waste tyre pyrolysis activation energies and conversion temperatures, but should not be relied upon to provide exact measurements.

4.3 Scanning Electron Microscopy

In Figure 29 to Figure 33 scanning electron microscope images (SEM) at a magnification of 5000x of both the tyre powder and pyrolytic char are shown. These images show similar pyrolytic char structures to experiments by Helleur, Popovic, Ikura *et al.* (2001). Helleur, Popovic, Ikura *et al.* (2001) pyrolyzed tyre shreds in a commercialized process known as Continuous Ablative Regenerator (CAR) at 550°C, residence time of 0.6s and Nitrogen as the carrier gas. This char was shown to have similar properties to commercial carbon black, however the high ash content limits its use to tyre manufacturing. It was noticed by Helleur, Popovic, Ikura *et al.* (2001)that by further carbonising the pyrolytic char for 3 hours at 600°C unwanted odours and trace amounts of oil may be removed and enables the carbonized char to have superior absorption capabilities for heavy metals than activated carbons (Mui, Ko and McKay, 2004).

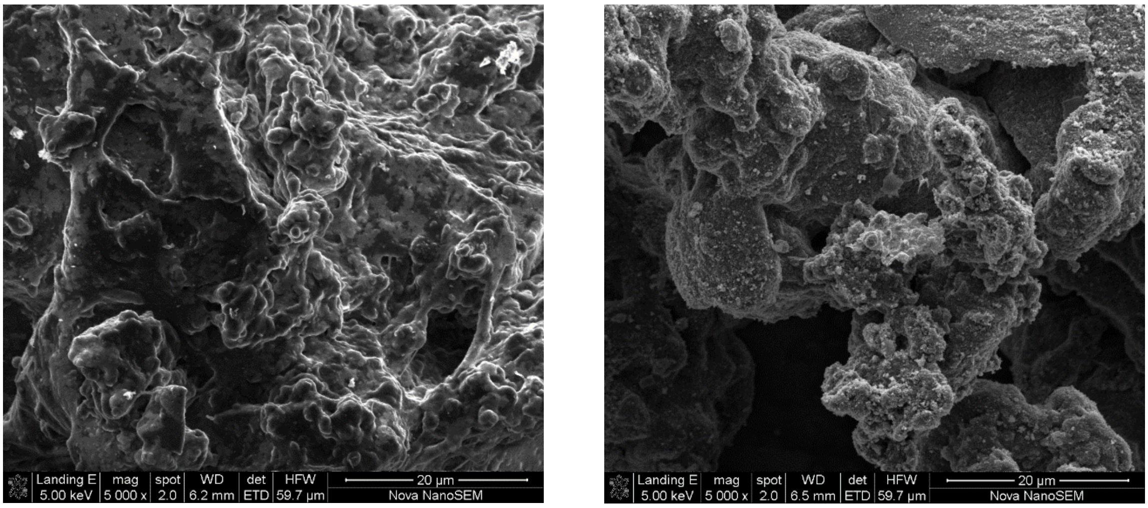

Figure 29: SEM image of Tyre A powder, magnification 5000x (a) Dry Powder; (b) Char after pyrolysis

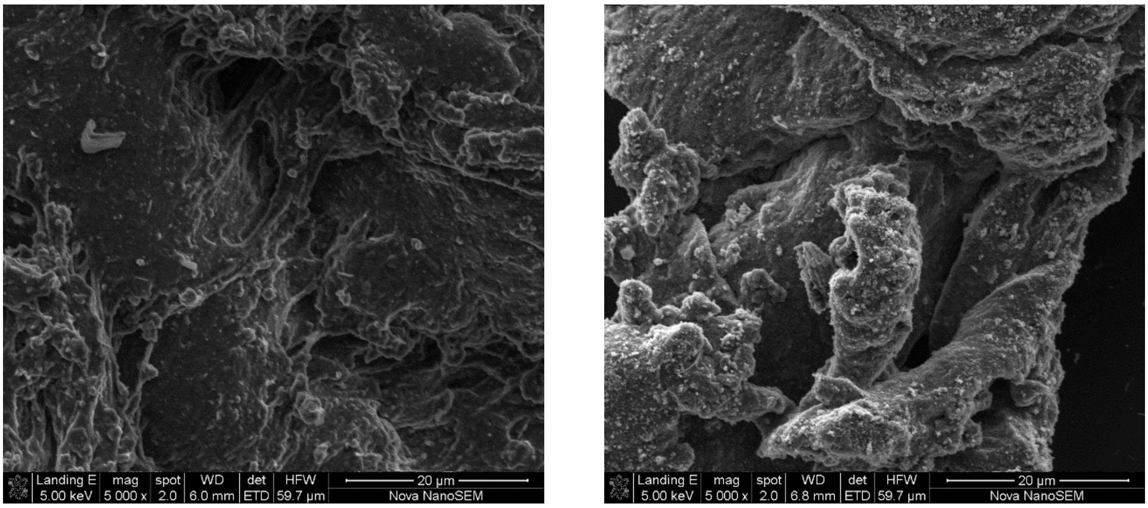

Figure 30: SEM image of Tyre B powder, magnification 5000x (a) Dry Powder; (b) Char after pyrolysis

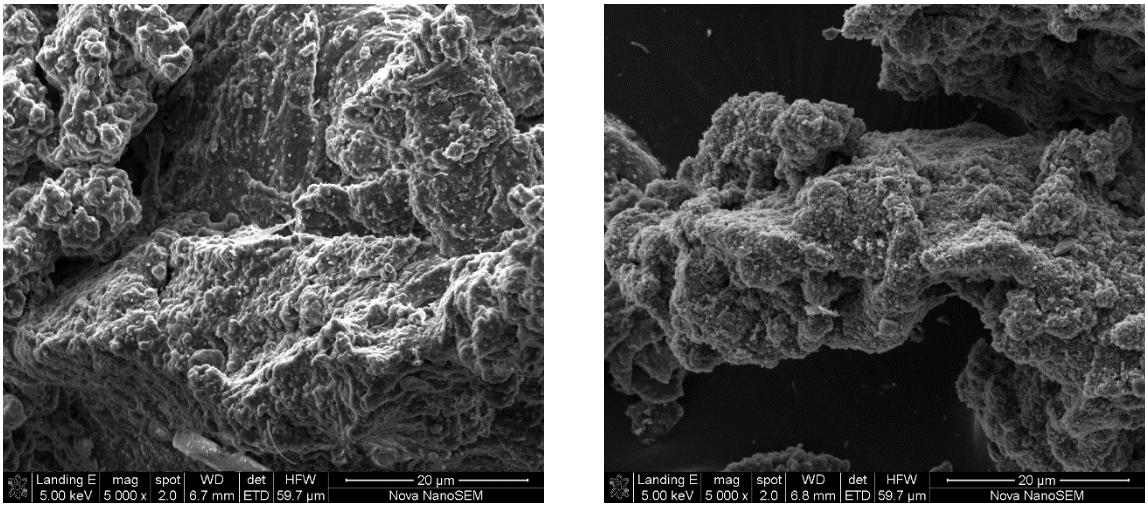

Figure 31: SEM image of Tyre C powder, magnification 5000x (a) Dry Powder; (b) Char after pyrolysis

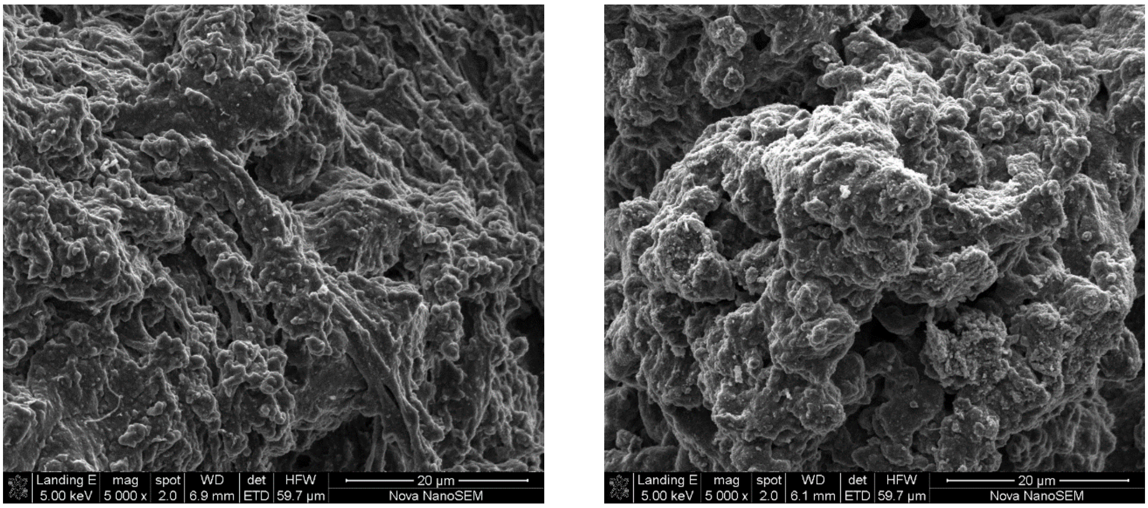

Figure 32: SEM image of Tyre D powder, magnification 5000x (a) Dry Powder; (b) Char after pyrolysis

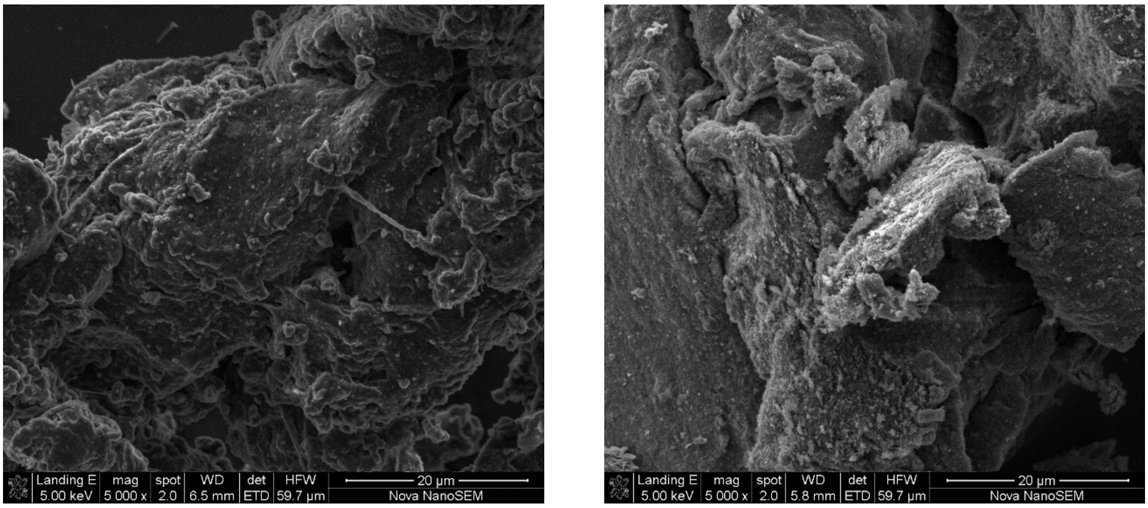

Figure 33: SEM image of Tyre E powder, magnification 5000x (a) Dry Powder; (b) Char after pyrolysis

Further analysis of Figure 29 Figure 30 shows some agglomeration of the pyrolytic char particles. This indicated pyrolysis has not been fully completed. Individual particles are not as clearly distinguishable in Figure 31Figure 32Figure 33 due to residual polymeric matrix and other organic substances as in Figure 29 Figure 30. Higher volatile matter in both tyres A and B may be the cause of these residual polymeric matrixes present in the SEM images evidently shows pyrolysis was incomplete at the time of experimentation. This is consistent with the work of Undri, Sacchi, Cantisani et al. (2013) that observed macroporous structures in the fully pyrolyzed char in the scanning electron microscope images while none in some deemed partially pyrolyzed. These partially pyrolyzed images are visually similar to those of the unpyrolyzed waste tyre powder (López, Centeno, Alguacil et al. 2011, Tang and Huang 2005, Undri, Sacchi, Cantisani *et al.* 2013). Lian, Huang, Chen *et al.* (2011) states that while the polymeric phase of pyrolytic char get converted into a gaseous phase the chars surface area, hydrophobicity and aromaticity increases dramatically with increases in pyrolysis temperature.

4.4 Pyrolysis products

The analyses only focus on the oil (this is together with the condensable gases) and the char that remains after the pyrolysis is stopped. This is due to the inability to measure te gas produced separate from the carrier gas used. A simple method to determine when the volatile matters pyrolysis is completed is when the gases from the reactor is still combustible. This is done by putting a flame to the gas.

Even though the mass losses of the tyres only start at approximately 200 °C, significant reduction is noticed from around 400 °C. Therefore, the reaction was conducted in a fixed-bed reactor with nitrogen as the inert gas varying the temperature from 400 - 700 °C at a constant heating rate of 10 °C. The most valuable product obtained from tyre pyrolysis is the oil fraction. Therefore, the influence of the principal process variables on this oil yield was studied.

The oil and char yield (as percentage of powdered tyre) is calculated thus:

$$Y = \frac{weight\ of\ oil\ (or\ char)}{weight\ of\ powered\ tyre\ in\ reactor}$$

The oil and char yield is plotted against the pyrolysis temperature and presented in Figure 35. It can be seen that the maximum oil yield of 60.0 wt.% oil was obtained at 550 °C. As the temperature is increased, the oil yield decreases while the char increases. It was noted that raising the temperature in a fixed bed reactor system beyond where the rubber has been thermally degraded only marginally increases the yield of oil and beyond 650 °C start falling. This indicated that at higher temperatures, there is cracking of the oil into gases. The oil fraction from the chromatogram was found to be a mixture of aliphatic and aromatic hydrocarbons.

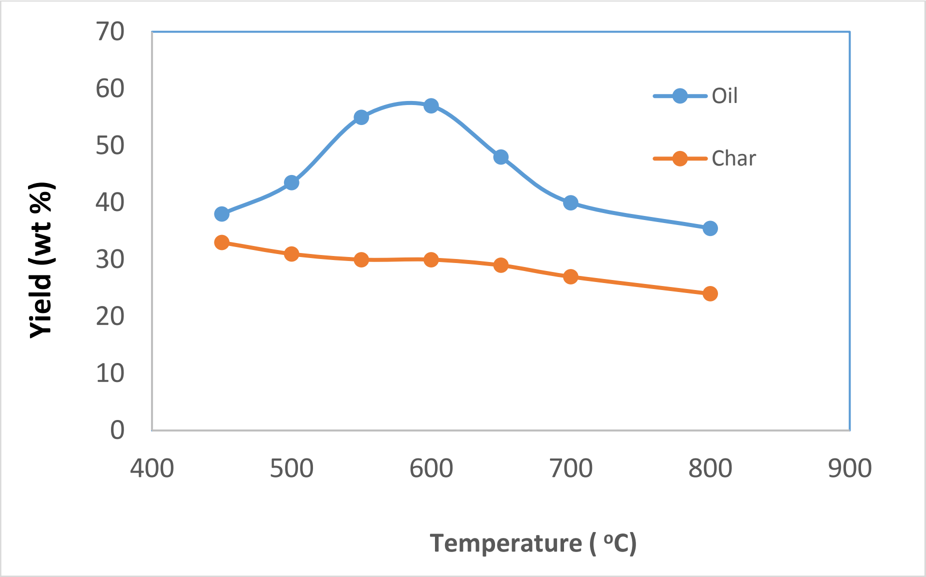

Figure 34: Oil and Char Yield versus pyrolysis temperature

5

Conclusions and Recommendations

5.1 Conclusions

In this study the effect of mechanism and kinetics of thermal degradation of different waste tyres were evaluated. The effect of temperature on the pyrolysis were also evaluated specifically focusing on maximizing the pyrolytic oil produced. The pyrolysis of waste tyres at the optimal temperature ensures that a maximum recovery of the materials (carbon black) and the energy content (of the rubber components) is possible.

It can be concluded that the correlations developed to predict the elemental composition of waste tyre from the cheap and straight forward proximate analysis gave a good estimation of the C and H content. These elements are important for the fact that the hydrocarbons formation during pyrolysis depends on the C/H ratio. The thermal degradation behaviour as well as the optimal pyrolysis temperature were found to depend on the C and H contents as expected.

It is seen from the results presented that thermogravimetric and derivative thermogravimetric analyses yielded good result on the degradation mechanism as well as the kinetics of the natural and synthetic rubbers contents and other volatile compounds in waste tyres. The data also give a good estimate of the final temperature at which the volatile matter in the waste tyre completes has been converted into hydrocarbons. Hence, the temperature chosen for pyrolysis should be chosen depending on the chemical C and H content of the tyre samples. This is the optimum temperature at which the pyrolysis reactor must be maintained to prevent thermal cracking of the pyrolytic oil products into the non-condensable gas.

In minimizing the non-condensable gas fraction of waste tyre pyrolysis more pyrolytic oil may be produced and used as an alternate fuel of other valuable chemical products. This will as well save cost by eliminating redundant input of (costly) energy into the system. The model developed can serve as a guide to determine a temperature which will prevent the thermal cracking of the pyrolytic oil.

The pyrolysis temperature was found to be slight different for the different tyre samples studied between 570 °C to 610 °C. This is also the case with the conversion ranging from a minimum of 85 per cent to a maximum of 97 per cent. By taken the average conversion at which waste tyre pyrolysis reaches completion to be approximately 90 per cent, the optimal temperature for pyrolysis was found to be 538 °C to 754 °C. At higher temperatures a decrease in oil yield was noted yielding more gaseous products and hence undesirable.

The pyrolytic oil falls within the diesel oil range and hence can be used as transportation fuel. The oil fraction from the chromatogram was found to be a mixture of aliphatic and aromatic hydrocarbons. However, the sulphur content is very high. The conventional refining method, hydrotreating is suggested to lower the Sulphur content to acceptable level. Otherwise the oil can be used to power farm machineries and equipment where the fuel specifications is not that stringent.

The char or black carbon can be formed into pellets and used as derived fuels at home in place of domestic kerosene. It can also be used as filler for asphalt to make rubberized asphalts.

5.2 Recommendations

The effects of heating rate on the product distributions of the pyrolysis oil and gas must be investigated to be able to correlate the hydrocarbons formed with the volatile matter contents of the various tyre samples.

Also the use of catalysts that will permit lower temperature of pyrolysis will result in significant savings in energy input and hence the overall economics of the process. Zeolite catalysts are another interesting groupof catalysts that have been suggested to improve the quality of the process. These will permit an instant removal of any heavy metals in the tyre unto the zeolite structure and hence produce metals-free oil.

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Appendices

A: Data

Published Data

Table 16: Summary Data from Martínez, Puy, Murillo *et al.* (2013)

Ultimate Analysis [wt%]					Proximate Analysis [wt%]				CV [MJ/kg]
C	H	N	S	O	VM	FC	A	M	
83.8	7.6	0.4	1.4	3.1	67.3	28.5	3.7	0.5	36.45
82.36	6.92	2.3	1.4	2.03	73.74	20.22	4.95	1.09	37.06
75.5	6.75	0.81	1.44	15.50	57.5	20.85	20.1	1.53	29.18
85.9	8	0.4	1	2.3	66.5	30.3	2.4	0.8	40
75.4	7.03	0.21	1.62	5.09	62.32	26.26	10.21	1.31	33.29
84.33	7.81	0.49	1.66	3.32	62.2	29.4	7.1	1.3	40
82.8	7.6	0.5	1.3	4.5	68.7	27.2	3.3	0.8	36.46
86.7	8.1	0.4	1.4	1.3	61.9	29.5	8	0.7	36.2
80.29	7.25	0.31	1.84	4.9	67.5	25.2	5.3	2.1	37.3
85.05	6.79	0.5	1.53	1.75	62.24	32.28	4.35	1.14	34.9
81.5	7.1	0.5	1.4	3.4	64.87	28.56	6.07	0.5	36.8
86.7	6.9	0.3	1.9	0.9	64	30.7	4.4	0.9	31.8
83.92	6.83	0.78	0.92	3.39	64.97	30.08	4.16	0.75	38.6
83	6.79	0.32	1.37	3.46	64.1	29.7	5	1.2	35
67.08	6.12	0.17	2.05	24.58	59.69	19.45	19.1	1.72	27.37
81.79	7.99	0.48	1.81	3.04	65.74	28.98	4.88	0.4	38.3
84	7.19	0.49	1.42	3.3	65.6	30	3.6	0.8	38.8
83.15	6.78	0.28	1.77	0.84d	61.9	29.9	7.1	1.1	37.35
74.3	7.2	0.9	1.71	15.89	58.2	21.3	18.9	1.6	30.5
83.2	7.7	1.5	1.44	6.16	66.1	27.5	5	1.4	33.4

Table 17: Summary Data from Lung (2009)

Ultimate Analysis [wt%]					Proximate Analysis [wt%]				CV [MJ/kg]
C	H	N	S	O	VM	FC	A	M	
83.2	7.7	1.5	1.44	6.16	66.1	27.5	5	1.4	33.4
74.3	7.2	0.9	1.71	15.89	58.2	21.3	18.9	1.6	30.5
89.5	7.3	0.3	1.9	1	61.9	29.9	7.1	1.1	37.35
86.4	8	0.5	1.7	3.4	62.2	29.4	7.1	1.3	40
86.7	8.1	0.4	1.4	3.4	61.9	29.5	8	0.7	36.2
82.8	7.6	0.5	1.3	7.8	68.7	27.2	3.3	0.8	36.46
80.3	7.18	0.5	1.19	10.83	62.7	32.31	4.17	0.82	33.3
75.5	6.75	0.81	1.44	15.5	59.5	20.85	18.12	1.53	29.18
74.5	6.5	0.95	1.63	16.42	55.2	22.3	21	1.5	28.75
86.7	6.9	0.3	1.9	4.2	64	30.7	4.4	0.9	31.8
74.41	6.94	0.21	1.6	15.33	62.32	26.26	10.21	1.31	33.28
85.9	8	0.4	1	4.7	66.5	30.3	2.4	0.8	40
84.08	6.71	0.49	1.51	6.08	62.24	32.28	4.35	1.14	34.92
81.5	7.1	5	1.4	9.5	65.2	28.7	6.1	5	36.8
74.2	5.8	0.3	1.5	18.2	58.8	27.7	13.5		31.8
83.8	7.6	4	1.4	6.8	67.3	28.5	3.7	0.5	36.45
78.6	7.1	3	1.8	10.1	67.5	25.2	5.3	2.1	37.3

Carbon Prediction

Waste tyre properties are important Waste tyre properties are important parameters that effect from the way a tyre degrades to

Table 18: Total elemental carbon prediction for Table 1.

Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
86.4	84.304	2.426	-2.426
74.3	69.461	6.513	-6.513
86	86.553	0.643	0.643
74.3	69.461	6.513	-6.513
88.64	90.311	1.885	1.885
84.05	84.482	0.514	0.514
88.64	90.311	1.885	1.885
86.7	84.218	2.862	-2.862
78.6	81.409	3.573	3.573
89.5	84.744	5.314	-5.314
77.6	89.197	14.944	14.944
82.8	85.410	3.153	3.153
85.16	88.622	4.066	4.066
89.4	86.638	3.090	-3.090
77.3	82.030	6.119	6.119
67.08	66.881	0.297	-0.297
83.92	87.209	3.919	3.919
82.52	78.331	5.076	-5.076
86.39	86.424	0.039	0.039
81.84	80.880	1.173	-1.173
75.5	69.382	8.103	-8.103
87.9	88.451	0.627	0.627

Table 19: Total elemental carbon prediction for WTP Review Carbon

Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
81.72	85.467	4.586	4.586
83.80	86.503	3.226	3.226
83.80	86.539	3.268	3.268
82.36	74.766	9.220	-9.220
75.50	68.289	9.551	-9.551
85.90	88.591	3.133	3.133
75.40	79.939	6.019	6.019
84.33	84.304	0.031	-0.031
82.80	85.410	3.153	3.153
86.70	84.218	2.862	-2.862
80.29	81.409	1.393	1.393
85.05	87.987	3.453	3.453
81.50	85.011	4.308	4.308
86.09	86.638	0.636	0.636
86.70	87.338	0.736	0.736
83.92	87.209	3.919	3.919
85.25	87.978	3.200	3.200
83.00	86.073	3.702	3.702
67.08	66.881	0.297	-0.297
81.79	86.205	5.397	5.397
84.00	87.545	4.220	4.220
83.15	84.744	1.916	1.916
74.30	69.461	6.513	-6.513
83.20	84.253	1.266	1.266

Table 20: Total elemental carbon prediction for Design of WTPP

Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
82.8	85.410	3.153	3.153
89.4	86.638	3.090	-3.090
83.92	87.209	3.919	3.919
86.39	86.424	0.039	0.039
86	86.553	0.643	0.643
83.2	84.321	1.347	1.347
85.16	88.622	4.066	4.066
78.6	81.409	3.573	3.573
81.84	80.880	1.173	-1.173
77.3	82.030	6.119	6.119
89.5	84.744	5.314	-5.314
86.7	84.218	2.862	-2.862
77.6	89.197	14.944	14.944
82.52	78.331	5.076	-5.076
75.5	69.382	8.103	-8.103
74.3	69.461	6.513	-6.513
67.08	66.881	0.297	-0.297

Hydrogen Prediction

Table 21: Total elemental hydrogen prediction for Table 1

Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
8	7.147	10.660	-10.660
7.2	6.486	9.919	-9.919
8.4	7.509	10.611	-10.611
7.2	6.486	9.919	-9.919
8.26	7.709	6.672	-6.672
7.99	7.520	5.883	-5.883
8.26	7.709	6.672	-6.672
8.1	7.121	12.080	-12.080
7.1	7.535	6.124	6.124
7.3	7.136	2.245	-2.245
7	8.033	14.762	14.762
7.6	7.713	1.488	1.488
7.27	7.208	0.858	-0.858
7	7.470	6.717	6.717
6.2	7.563	21.986	21.986
6.12	6.611	8.016	8.016
6.83	7.443	8.970	8.970
6.95	7.297	4.991	4.991
6.91	7.417	7.342	7.342
7.6	7.668	0.901	0.901
6.75	6.610	2.069	-2.069
7.4	7.372	0.385	-0.385

Table 22: Total elemental hydrogen prediction for WTP Review Carbon

Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
6.54	7.209	10.225	10.225
6.9	7.301	5.809	5.809
7.6	7.616	0.211	0.211
6.92	8.216	18.734	18.734
6.75	6.403	5.138	-5.138
8	7.600	4.996	-4.996
7.03	7.048	0.256	0.256
7.81	7.147	8.487	-8.487
7.6	7.713	1.488	1.488
8.1	7.121	12.080	-12.080
7.25	7.535	3.928	3.928
6.79	7.256	6.868	6.868
7.1	7.379	3.925	3.925
6.74	7.470	10.834	10.834
6.9	7.370	6.817	6.817
6.83	7.443	8.970	8.970
7.94	7.395	6.861	-6.861
6.79	7.344	8.156	8.156
6.12	6.611	8.016	8.016
7.99	7.479	6.397	-6.397
7.19	7.501	4.332	4.332
6.78	7.136	5.252	5.252
7.2	6.486	9.919	-9.919
7.7	7.209	3.069	-3.069

Table 23: Total elemental hydrogen prediction for Design of WTPP

Measured [wt%]	Predicted [wt%]	Average Absolute Error [%]	Average Bias Error [%]
7.6	7.713	1.488	1.488
7	7.470	6.717	6.717
6.83	7.443	8.970	8.970
6.91	7.417	7.342	7.342
8.4	7.509	10.611	-10.611
7.7	7.466	3.039	-3.039
7.27	7.208	0.858	-0.858
7.1	7.535	6.124	6.124
7.6	7.668	0.901	0.901
6.2	7.563	21.986	21.986
7.3	7.136	2.245	-2.245
8.1	7.121	12.080	-12.080
7	8.033	14.762	14.762
6.94	7.297	5.142	5.142
6.75	6.610	2.069	-2.069
7.2	6.486	9.919	-9.919
6.12	6.611	8.016	8.016

Published Correlations

Table 24: Carbon data using the Parikh, Channiwala and Ghosal (2007) biomass predictive correlation

Sample	Predicted [wt%]	Absolute Error [%]	Bias Error [%]
Tyre A	40.258	43.852	-43.852
Tyre B	49.395	40.703	-40.703
Tyre C	50.714	40.685	-40.685
Tyre D	49.759	42.342	-42.342
Tyre E	41.542	41.737	-41.737

Table 25: Hydrogen data using the Parikh, Channiwala and Ghosal (2007) biomass predictive correlation

Sample	Predicted [wt%]	Absolute Error [%]	Bias Error [%]
Tyre A	4.974	46.050	-46.050
Tyre B	5.568	30.655	-30.655
Tyre C	5.539	25.745	-25.745
Tyre D	5.479	25.661	-25.661
Tyre E	4.825	33.074	-33.074

Table 26: Carbon data using the Shen, Zhu, Liu *et al.* (2010) biomass predictive correlation.

Sample	Predicted [wt%]	Absolute Error [%]	Bias Error [%]
Tyre A	39.049	45.539	-45.539
Tyre B	49.286	40.834	-40.834
Tyre C	50.613	40.804	-40.804
Tyre D	49.532	42.605	-42.605
Tyre E	40.186	43.638	-43.638

Table 27: Hydrogen data using the Shen, Zhu, Liu *et al.* (2010) biomass predictive correlation.

Sample	Predicted [wt%]	Absolute Error [%]	Bias Error [%]
Tyre A	5.101	44.671	-44.671
Tyre B	5.716	28.822	-28.822
Tyre C	5.735	23.129	-23.129
Tyre D	5.673	23.031	-23.031
Tyre E	5.046	30.014	-30.014

Table 28: Predictive data using the Vista User Group et al. (2014) coal predictive correlation.

Sample	Predicted [wt%]	Absolute Error [%]	Bias Error [%]
Tyre A	65.402	8.783	-8.783
Tyre B	77.025	7.533	-7.533
Tyre C	78.012	8.758	-8.758
Tyre D	76.806	11.002	-11.002
Tyre E	65.636	7.944	-7.944

Table 29: Hydrogen data using the Vista User Group et al. (2014) coal predictive correlation.

Sample	Predicted [wt%]	Absolute Error [%]	Bias Error [%]
Tyre A	5.402	41.411	-41.411
Tyre B	6.051	24.648	-24.648
Tyre C	6.000	19.578	-19.578
Tyre D	5.940	19.400	-19.400
Tyre E	5.250	27.191	-27.191

13 Addendum A: Poster Presentation

Enhanced Waste Tyre Pyrolysis for Production of Diesel Range Hydrocarbons

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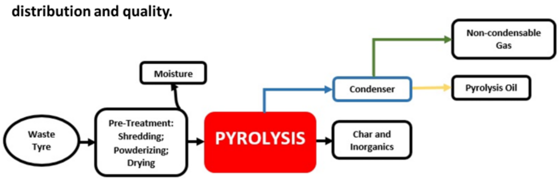
1. INTRODUCTION

Latest statistics show that 60 million waste tyres are stockpiled and scattered throughout the country while 11 million is added to that annually. Therefore the correct disposal of End of Life Tyres is becoming an increasing environmental problem and health risk. From an economic standpoint no feasible way to effectively recycle the waste tyres has been found. This study focussed on optimizing the waste tyre pyrolysis process to produce diesel range hydrocarbons and/or high value chemicals.

As the pyrolysis of waste tyres is a highly endothermic process the governing variable that is used to initiate and sustain the process is temperature. Temperature thus forms a vital part in the effect of conversion, product distribution and quality.



2. AIMS AND OBJECTIVES

- Investigate the mechanism of thermal degradation of waste tyres in terms of their individual ultimate and proximate analyses.
- Determine the rate kinetics and create a model that simulates the degradation.

3. OPERATING CONDITIONS

Ultimate and Proximate Analysis – Various ASTM test methods

Thermogravimetric analysis:

1. Heat in N_2 20 – 920°C at 20°C/min – Volatile Matter
2. Hold at 920°C for 15min in N_2 – Fixed Carbon
3. Hold at 920°C for 15min in O_2 – Ash

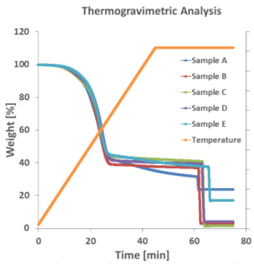
4. Ultimate and Proximate Analysis

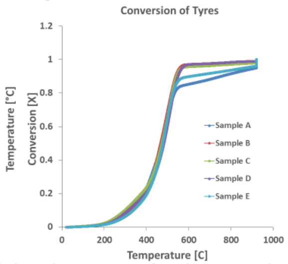
	Ultimate Analysis [%]				Proximate Analysis [%]				CV [MJ/kg]
	S	C	H	N	Moisture	Ash	Volatile	Fixed C	
Sample A	1.8	71.7	9.22	0.17	1.2	16	67.9	14.7	37.6
Sample B	1.74	83.3	8.03	0.01	1.1	3.7	61.8	33.4	39.9
Sample C	1.48	85.5	7.46	0.11	1.1	3.2	56.3	39.4	41.9
Sample D	1.23	86.3	7.37	0.12	1	4.6	57	37.4	42.5
Sample E	1.9	71.3	7.21	<0.01	1.5	16.8	57.7	24	34.6

From these analyses, it was found that samples with higher sulphur content added during vulcanization, required more energy to pulverise. High carbon level also resulted in the formation of smoke and soot during the powderizing step.

Theoretically the hydrocarbon gas product of tyre pyrolysis should correspond to the volatile matter found in the tyre whilst the remaining char coincides with the fixed carbon and non-volatile matter. These differences in proximate results affect the product yield and quality.

5. Effect of Temperature


Thermogravimetric Analysis

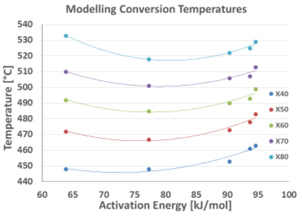

Conversion of Tyres

From the graphs the optimum thermal degradation point of each tyre can be determined, the differences observed are attributed to the varying chemical constituents of the samples. After this point, thermal cracking starts to occur whereby the non-condensable gas yield increases at the expense of the pyrolysis oil.

6. Rate of Reaction

*	Activation Energy [kJ/mol]	Pre-exponential factor [1/s]
Sample A	63.87	6 000
Sample B	77.28	67 300
Sample C	90.34	475 000
Sample D	94.61	818 300
Sample E	93.66	798 907

*Assuming 1st order kinetics


Modelling Conversion Temperatures

Reaction kinetics confirm that waste tyres with lower volatile matter content requires a higher activation energy to initiate the degradation reaction and vice versa.

A parabolic trend is observed when modelling the conversion temperature with activation energies. Subsequently when aiming for a specific conversion rate the Temperature and Activation Energy can determined by reading it off the graph.

7. CONCLUSIONS

- All tyre chemical characteristics and kinetics obtained agreed with literatures.
- Above 80% conversion the energy required for complete pyrolysis is impractical compared to the product yield gained from an economical perspective.
- Prediction of temperature and activation energy can be achieved by selecting a target conversion.

FUTURE WORKS

- Optimization of reactor temperatures in a pyrolysis pilot plant to measure product yield and distribution.

Reference

1. **Williams, P. T. & Besler, S. 1995.** Pyrolysis-thermogravimetric analysis of tyres and tyre components. Fuel, 74, 1277-1283.
2. **Lopez, G., Aguado, R., Olazar, M., Arabiourrutia, M. & Bilbao, J. 2009.** Kinetics of scrap tyre pyrolysis under vacuum conditions. Waste Management, 29, 2649-2655.

Acknowledgements

Financial support from *CPUT* is gratefully appreciated.

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Figure 35: CPUT Postgraduate Research Day Presentation 2013 (2nd Place)

Addendum B: ISTEC Article

PYROLYSIS PROCESS OPTIMISATION FOR THE PRODUCTION OF DIESEL-RANGE HYDROCARBONS AND CHEMICALS FROM SCRAP TYRES

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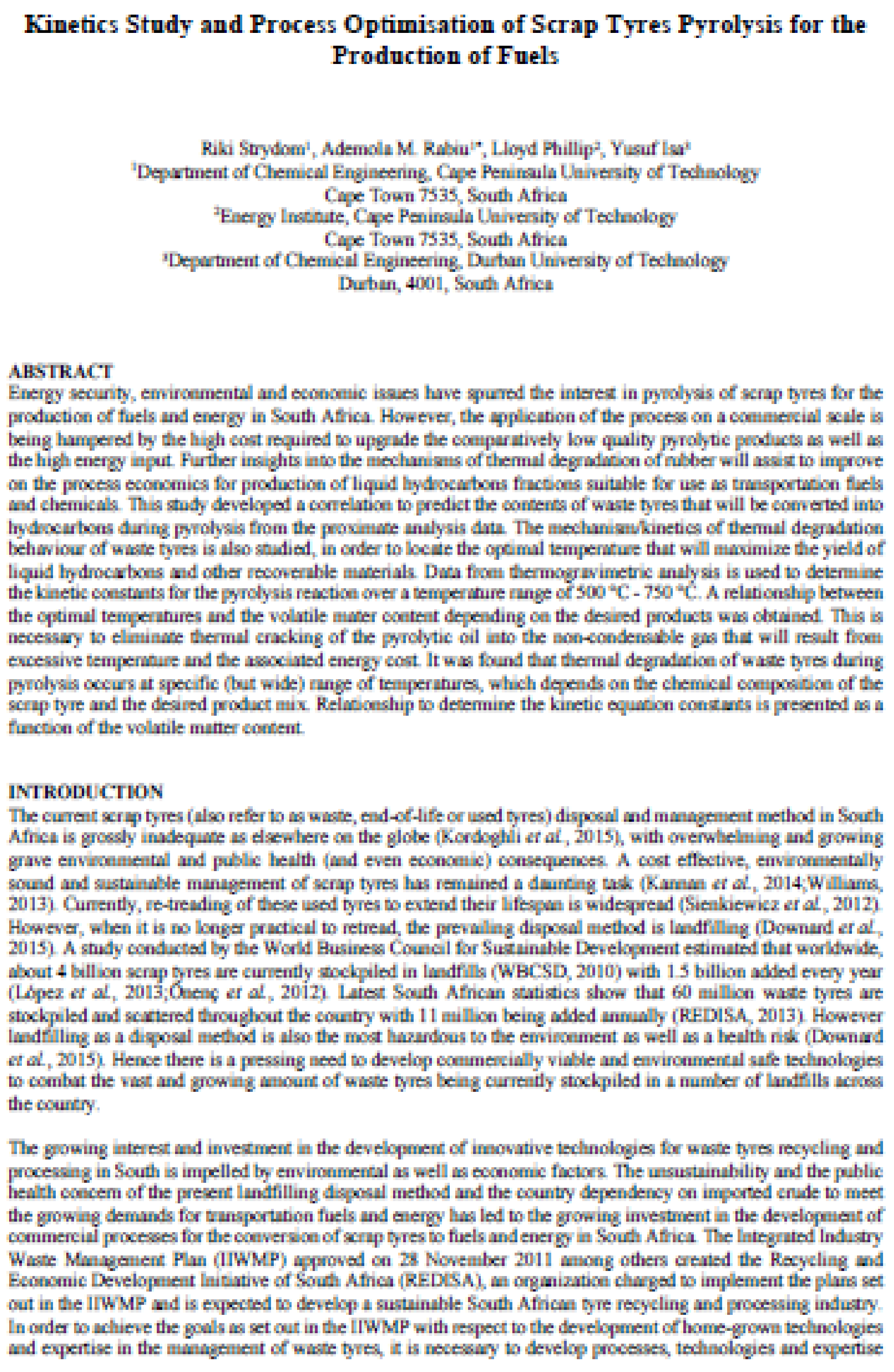
Abstract: Energy security, environmental and economic issues have spurred the interest in pyrolysis of scrap tyres for the production of fuels and energy in South Africa. However, the application of the process on a commercial scale is being hampered by the high cost required to upgrade the comparatively low quality pyrolytic products as well as the high energy input. Further insights into the mechanisms of thermal degradation of rubber will assist to improve on the process economics for production of liquid hydrocarbons fractions suitable for use as transportation fuels and chemicals. This study developed a correlation to predict the contents of waste tyres that will be converted into hydrocarbons during pyrolysis from the proximate analysis data. The mechanism/kinetics of thermal degradation behaviour of waste tyres is also studied, in order to locate the optimal temperature that will maximize the yield of liquid hydrocarbons and other recoverable materials. Data from thermogravimetric analysis is used to determine the kinetic constants for the pyrolysis reaction over a temperature range of 500 °C - 750 °C. A relationship between the optimal temperatures and the volatile mater content depending on the desired products was obtained. This is necessary to eliminate thermal cracking of the pyrolytic oil into the non-condensable gas that will result from excessive temperature and the associated energy cost. It was found that thermal degradation of waste tyres during pyrolysis occurs at specific (but wide) range of temperatures, which depends on the chemical composition of the scrap tyre and the desired product mix. Relationship to determine the kinetic equation constants is presented as a function of the volatile matter content.

INTRODUCTION

The current scrap tyres (also refer to as waste, end-of-life or used tyres) disposal and management method in South Africa is grossly inadequate as elsewhere on the globe (Kordoghli *et al.*, 2015), with overwhelming and growing grave environmental and public health (and even economic) consequences. A cost effective, environmentally sound and sustainable management of scrap tyres has remained a daunting task (Kannan *et al.*, 2014;Williams, 2013). Currently, re-treading of these used tyres to extend their lifespan is widespread (Sienkiewicz *et al.*, 2012). However, when it is no longer practical to retread, the prevailing disposal method is landfilling (Downard *et al.*, 2015). A study conducted by the World Business Council for Sustainable Development estimated that worldwide, about 4 billion scrap tyres are currently stockpiled in landfills (WBCSD, 2010) with 1.5 billion added every year (López *et al.*, 2013;Önenç *et al.*, 2012). Latest South African statistics show that 60 million waste tyres are stockpiled and scattered throughout the country with 11 million being added annually (REDISA, 2013). However landfilling as a disposal method is also the most hazardous to the environment as well as a health risk (Downard *et al.*, 2015). Hence there is a pressing need to develop commercially viable and environmental safe technologies to combat the vast and growing amount of waste tyres being currently stockpiled in a number of landfills across the country.

The growing interest and investment in the development of innovative technologies for waste tyres recycling and processing in South is impelled by environmental as well as economic factors. The unsustainability and the public health concern of the present landfilling disposal method and the country dependency on imported crude to meet the growing demands for transportation fuels and energy has led to the growing investment in the development of commercial processes for the conversion of scrap tyres to fuels and energy in South Africa. The Integrated Industry Waste Management Plan (IIWMP) approved on 28 November 2011 among others created the Recycling and Economic Development Initiative of South Africa (REDISA), an organization charged to implement the plans set out in the IIWMP and is expected to develop a sustainable South African tyre recycling and processing industry.

15 Addendum C: Article



Kinetics Study and Process Optimisation of Scrap Tyres Pyrolysis for the Production of Fuels

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