Process Simulation, Optimization and Economic Evaluation of Waste Tyre Pyrolysis for Fuel Production

Emmanuel N. Mchunu

BSc Chemical Engineering (UKZN)

This dissertation is submitted in partial fulfilment of the academic requirements of Master of Science in Chemical Engineering

School of Engineering
College of Agriculture, Engineering and Science
University of KwaZulu-Natal
Howard College Campus
Durban, South Africa

March 2023

Supervisor: Prof Amir H. Mohammadi

PREFACE

The research contained in this dissertation was completed by the candidate while based in the discipline of Engineering, School of Chemical Engineering of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College, Durban, South Africa. The research was financially funded by the University of Kwa-Zulu Natal: Strategic Funds and Fee Remission as well as supervisor's cost centre.

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

____

Signed: Prof Amir H. Mohammadi

Date: 6 July 2022

DECLARATION: PLAGIARISM

I, Emmanuel Nkosinathi Mchunu, declare that

1. The research reported in this dissertation, except where otherwise indicated, is my original research.
2. This dissertation has not been submitted for any degree or examination at any other university.
3. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
4. This dissertation does not contain other person's writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:
    a. Their words have been re-written but the general information attributed to them has been referenced
    b. Where their exact words have been used, then their writing has been placed in italics and inside quotation marks, and referenced.
5. This thesis does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

Signed

…………………….

Signed: Emmanuel Nkosinathi Mchunu

Date: 5 July 2022

ABSTRACT

Management of waste tyres is increasingly becoming a global challenge; the problem is only projected to get worse in future as worldwide tyre production is continually on the rise in response to the growing global population. Managing waste tyres through traditional landfilling approach has proven to be an unsustainable approach due to the associated environmental concerns. The said concerns include posing toxic gas emitting fire risks, contaminating ground water and housing disease carrying insets. Despite these challenges, a huge percentage of tyres are still managed through legally and illegally landfilling. Waste tyre recycling and retreating has proven to be a useful and sustainable management alternative, these technologies are however limited to only handle up to 13 % of global waste tyres.

The detrimental environmental problems associated with traditional waste tyre management has resulted in a significant rise in a number of studies focusing on investigating waste tyre management alternatives. Of the means investigated, waste tyre pyrolysis has emerged as the most manageable approach as it yields easy to handle products and has the ability to handle huge waste tyre volumes. In addition to the said benefits, tyre pyrolysis technology harnesses energy from tyres that would have been lost to the landfills. Tyre pyrolysis products are energy rich oil, char and gases. The process of tyre pyrolysis entails volatilization of tyres at temperatures above 400 ^{o}C in the absence of oxygen. There are a number of governing factors associated with tyre pyrolysis process, viz. type of pyrolysis rector used, operating temperature, heating rate, particle size, residence time, operating pressure, and a presence of the catalyst. The governing factors outlined are mainly focused on maximizing the oil yield and minimizing char and non-condensable gaseous products. Of the governing factors influencing tyre pyrolysis process, operating temperature has the biggest impact. According to the literature studies, the typical optimum oil yield is between 38 % and 60 % by weight of waste tyre, achievable between 425 ^{o}C and 720 ^{o}C.

On this study, a ASPEN Plus simulation computer software was used to develop a tyre pyrolysis process model. From the developed simulations a number of investigations were undertaken to understand the impact of the key process governing factors. Investigations conducted were on the operating temperature, reactor type, dimensions of the reactor, residence time, reactor operating pressure, heating rate, presence of the catalyst and tyre particle size

The reactor type investigations showed that the reactors with some level of mixing favoured higher oil yield. This premise was evident in the investigation between the CSTR and PFR. The CSTR presented oil yield increase from 50.93 % to 51.13 % while the PFR showed an increase from 44.02 to 44.13 % for the temperature range between 400 and 700 ^{o}C. To incorporate a kiln reactor comparison, the temperature was kept constant at 550 ^{o}C on all the reactors investigated. The CSTR and kiln reactor showed higher oil yields than PFR, with oil yields of 51.01 %, 50.93 % and 44.09 % respectively. The

results obtained from the kiln reactor and CSTR showed to be relatively similar since the kiln reactor was modelled using CSTRs in series.

In the reactor size investigation which is linked to the residence time. For the PFR, no further improvements on the yield were noticed at the reactor diameters above 1m. The CSTR showed the yield to remain constant above a 1 hour residence time. The investigation on the operating pressure showed that the higher oil yields are achieved at lower operating pressure. When the pressure was increased from 0.1 atm to 1 atm, the CSTR oil yield decreases from 50.98 % to 50.97 %.

Increasing the reactor heating rate showed positive impact on the oil yield, an improvement from 50.75 to 50.89 % was achieved when the heating rate was increased from 5 to 15 K/min. However, at 20 K/min the oil yield decreased to 50.87 %. The use of the catalyst showed positive impact on the oil yield, an increase from 49.92 % to 51.7 % was noted from no catalyst basecase. Two size classes were considered in the particle size investigation, viz. 0.1 mm – 0.8 mm and 0.8 mm – 4 mm. The investigation showed that the lower particle size results in higher oil yield. The CSTR showed an increase with the increase in the residence time, an increase of 0.04 % points was noted when the residence time was increased from 0.1 to 1 hr.

A different tool was used to check the validity of the simulation findings, for this investigation a numerical model from literature was employed. The model was based on a laboratory study incorporating the particle size, temperature and feed rate. The un-optimised conditions of the model showed oil yield of 26.3 % while the optimum conditions showed oil yield of 47.9 %. The optimum conditions were identified be at a temperature of 400 ^{o}C, particle size of 1.0 mm and a feed rate of 0.78 kg/hr.

Based on the results of this study encompassing both numerical and simulation findings, conclusion were drawn that the optimum oil yield is obtainable from the CSTR operated at a temperature range between 400 ^{o}C and 550 ^{o}C, tyre particle size less than 1 mm, operating pressure below 1 atm, heating rate between 10-15 K/min and residence of time of less than 1 hour. The economic evaluations showed that the tyre pyrolysis plant only starts yielding positive ROI at least after 3.7 years of operating. This is relatively an acceptable ROI period pertaining to the investment decision making.

ACKNOWLEDGEMENTS

The following individuals have contributed immensely in making this work a success,

- Professor Amir H. Mohammadi for contributing towards funding my studies through his research grant and giving me unfailing guidance and supervision throughout the project.
- Preyo Nayager (Chemical engineering, UKZN) for ASPEN installation and monthly licence renewals.
- Sihle Mngadi for assisting with technical laptop issues.
- Nosihle Jeza, my fiancée for understanding, giving me encouragement, motivation and support.
- Bonginkosi Ndwandwe for technical support and guidance.
- Lastly I would like to thank Jehovah God for giving me the strength, ability and perseverance to seeing this work through.

DEDICATIONS

I dedicate my dissertation work to my family and a special dedication to my fiancée who showed great support in encouraging me on getting this work to completion.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

Abbreviations

A	Pre exponential term
CPR	Chloroprene rubber
CV	Calorific value
d_p	Particle size
E	Activation energy
FBR	Fixed bed reactor
K	Rate constant
K_i	Rate constant of component i
n	Temperature coefficient
NTR	Nitril rubber
OTR	Off the-road
PAH	Polycyclic aromatic hydrocarbons
PBD	Polybutadiene
Pct	Passenger car tyres
R	Universal gas constant
ROI	Return on investment
SBR	Styrene-butadiene copolymer
T	Temperature
TDF	Tyre derived fuel
TDR	Tyre derived oil
t_m	Residence time
Tt	Truck tyres
VM	Volatile matter
W_f	Final weight
W_i	Initial weight
W_t	Weight at time t
X	Mass fraction of the limiting reactant

Units

atm	Atmospheres
g	grams
hr	Hour
J	Joules
K	Kelvin
kg	Kilograms
m^3	Cubic metres
min	Minutes
mR	Million Rands
^{o}C	Degrees Celsius
Pa	Pascals
ppm	Parts per million
s	seconds
$	US dollar
t	tons
ZAR	South African Rands

Unit prefixes

k	kilo
m	Milli
M	mega

Expressions

%	Percentage
wt. %	Weight percentage

CHAPTER 1: Introduction

1.1. Background

The management of tyres that have reached end of life is increasingly becoming a global environmental concern. Galvagno et al. (2002) reported that the global waste tyres generation is estimated to be 5 × 10^6 tons/year and accounts for 2 % of the total solid waste. In 2015, Danon et al. (2015) delineated that approximately 1.5× 10^6 billion unit tyres are generated globally. In 2012, South Africa's contribution to the tyre generation was estimated to account for 11 million units per annum which is equivalent to 275 000 tons (REDISA, 2012). These figures are continually on a rise year on year relative to the growing global automobile demand. According to the projects into the near future, the tyre production is estimated to grow by 3.4 % year on year to 2024 (SMITHERS, n.d.). A growth in the global tyre production directly increases the amount of waste tyres generated and as such this implies a growing problem in the management of tyres that have reached end of life. Approximately 65-70 % of tyres that have reached end of life are landfilled, this practice has over the years proven to be an unsustainable approach (Galvagno, et al., 2002).

Tyre landfilled results in a loss of high value constituents that may be recovered (Galvagno, et al., 2002). Also, due to tyre make up there are several environmental concerns associated with disposing waste tyres in landfills (Alsaleh & Sattler, 2014). The tyre's primary function requires them to be manufactured to high durability standards, this in turn makes dealing with scrap tyres very problematic. About 75 % of tyre volume is empty and this results in them occupying a lot of valuable landfill space when disposed (Alsaleh & Sattler, 2014). The chemical make-up of tyres generally makes them possess non-destructible and non-biodegradable properties, hence occupying landfill space for long periods of time (Aslan, et al., 2017). Alsaleh and Sattler (2014) reported that scrap tyres lifetime in landfills is estimated to range between 80-100 years. The run-off from waste tyres in landfills pollutes ground and underground water (Aslan, et al., 2017). Tyres discarded in landfills also creates breeding habitats for the disease carrying insects such as mosquitos which in effect endangers human health (Aslan, et al., 2017). Tyres in landfills are exposed to open air and this pose a risk of the occurrence of potential accidental fires difficult to manage (Ismail, et al., 2016). Kordoghli et al. (2014) reported one incident of such accidental fire which burnt for 9 months in Huntington (United States). When tyres burn, they released gases and particulate matter harmful to the environment and nearby population (Aslan, et al., 2017). Gases emitted from tyre fires are known to be both carcinogenic and mutagenic, hence similar to landfilling, waste tyre incineration is proving to be not a feasible approach in dealing with waste tyres due to the associated harmful emissions (Kordoghli, et al., 2014).

Given the environmental problems posed by waste tyres, over the past two decades research space has seen a growing number of studies in the field of investigating alternative waste tyre management technologies. The shortcomings from landfilling and incineration directed research studies towards alternative solutions that are both feasible and economically viable to handle huge tyre volumes as the problem is only projected to grow going into the future. The studies investigated range from simulations to lab and pilot scale, in some countries research has reached a commercial phase where working plants have been developed to alleviate waste tyre problem. Some countries have gone to the extents of putting measures in place through regulations to contribute in mitigating waste tyre problems. Kordoghli et al. (2014) reported that the European Union and European commission's landfill Directive (1999) banned discarding waste tyres in landfills since 2006 while European End Life Vehicle Directive 2000 conditions that 80 % of waste tyres must be recycled. Applying the reduce, reuse and recycle approach also referend to as the 3R principle is always the first price in dealing with waste management. In various applications the 3R principle has proven to yield several benefits (Kordoghli, et al., 2014). However, there are limitation in applying the 3R principle when dealing with waste tyres. Hence to date, particularly in the developing countries a huge percentage of waste tyres are still managed through unsustainable stockpiling approach and through legally or illegally discarding them in landfill sites (Kordoghli, et al., 2014). Reducing volumes is not feasible as the tyre production is on a continuous increase relative the growing population driving automobile global demand. Only 13 % of scrap tyres undergoes the recycle and reuse route (Kordoghli, et al., 2014). Areas where scrap tyres are reused include but not limited to applications such as in agriculture as weights for silage cover sheets, landscaping as erosion protections, seashores as breakwaters, in fishing as artificial reefs for fish breeding, shoemaking for making soles, heels and straps and in road construction where they are mixed with asphalt cements (Kordoghli, et al., 2014)

Recycling is considered the most preferred method for waste tyre management, Kordoghli et al. (2014) reported that this method may yield savings of up to 45 % in tyre production cost. However, caution should be taken in retreating as the number of times a tyre may be retreated depends strongly on its primary source (Kordoghli, et al., 2014). Recycling may be done once for passenger cars, twice for Lorries and up to seven times for airplane (Kordoghli, et al., 2014). Other limitations associated with retreating waste tyres are that the customers turn to be less accepting of the retreated tyres. In some low-income countries, tyres are used well beyond end-of-life point making them not suitable to undergo retreatment process (Kordoghli, et al., 2014). These limitations have made the reuse and retreatment of waste tyres to only be useful in dealing with only a said small percentage of the total global waste tyre production (Kordoghli, et al., 2014). In light of the challenges associated with traditional waste tyre management methods, energy conversion has emerged as an attractive alternative measure in dealing with high scrap tyre volumes (Kordoghli, et al., 2014). Not only does tyre energy conversion deals with a growing waste tyre problem, but it is also a lucrative development towards the direction of solving the global energy crisis (Dogan, et al., 2012). According to Dogan et al. (2012) the demand for energy is growing rapidly due to the growing population and rapid industrialization. Hence harnessing waste tyre energy may be considered a positive contribution towards solving the growing global energy problem.

Kordoghli et al. (2014) reported that tyres are very volatile, contains high fixed carbon content, have moderate sulphur, low ash content, have high calorific value and all the components making up a tyre are 100 % recyclable. Relative to coal and biomass, tyres possess better energy content and lower ash content (Leung & Wang, 2003). The outlined tyre properties make them very attractive for energy conversion applications (Kordoghli, et al., 2014). Research studies show that pyrolysis process is the most manageable technology for tyre energy conversion and can handle huge waste tyre volumes. Given the tyre pyrolysis process attributes, tyre pyrolysis has emerged as the most attractive approach in dealing with the surplus that may not be handled through retreatment and reuse means (Kordoghli, et al., 2014). Pyrolysis process is mainly a volatilization process where feedstock (scrap tyres) is heated to temperatures above 400 ^{o}C in the absence of oxygen (Alsaleh & Sattler, 2014). Two main products are obtainable from this process, viz. gases rich in hydrocarbons and solid char consisting of carbon black (Alsaleh & Sattler, 2014). The hydrocarbon gases are passed through a condenser where condensable hydrocarbons also referred to as tyre derived oil are recovered from the non-condensable gases (Martinez, et al., 2013). From the energy point of view, tyre pyrolysis process is a self-reliant process as the resulting char and non-condensable gases may be brunt to recover energy for tyre drying and heating requirements (Martinez, et al., 2013). The key governing factor of a successful tyre pyrolysis process is chiefly based on the percentage of tyre derived oil production (Martinez, et al., 2013).

As the tyre derived oil yield is the key governing factor, the tyre pyrolysis process is generally optimised for a maximum oil yield at a feasible running and investment cost (Alsaleh & Sattler, 2014). There are several pyrolysis factors that contributes towards optimizing a tyre pyrolysis process. Apart from the type of pyrolysis rector used, oil yield is influenced by operating temperature, heating rate, particle size, feedstock composition, residence time, carrier gas flow, operating pressure, presence of steam in the carrier gas and a catalyst (Alsaleh & Sattler, 2014). According to Alsaleh & Sattler (2014), together with other driving factors the optimal temperatures for maximum oil production ranges between 425 ^{o}C to 720 ^{o}C giving oil yields between 38 % to 60 %.

This study was undertaken to investigate the optimum tyre pyrolysis process conditions for achieving a maximum oil yield. As part of the investigation, an econmic feasibility study was conducted to understand if the tyre pyrolysis process is a profitable operation. This study was conducted using an ASPEN Plus computer simulation software, the economic feasibility studies were done based on the prices attained from literature studies. The findings from this study may be useful in the decision-making process of setting up a tyre pyrolysis plant as the study gives both the operational and economic understanding of the process.

1.2. Aims

The main aims of the research study conducted were to:

- Simulate and investigate optimum operating conditions for the tyre pyrolysis process using ASPEN Plus V11 computer simulation software.
- Undertake economic evaluation analysis of the tyre pyrolysis process.

1.3. Objectives

To accomplish the aims of the research, the following objectives were set for this study:

- Objective 1: Investigate waste tyre pyrolysis processes and the relevant kinetics.
- Objective 2: Develop an ASPEN Plus simulation model applying objective 1 learnings.
- Objective 3: Investigate various process conditions and scenarios.
- Objective 4: Identify optimum operating conditions through objective 3 learnings.
- Objective 5: Undertake economic evaluation of the pyrolysis plant.

1.4. Dissertation structure

This dissertation consists of 6 main chapters which were collectively developed such that they cover the objectives of this study as set out in subsection 1.3 above. Some chapters of this dissertation address more than one objective while others are mainly focused on discussions and summary. Below is a breakdown of the respective chapter's contents:

Chapter 1:

Gives the background on the issues associated with waste tyre management thereby establishing the justification of the study. To substantiate the seriousness of the waste tyre problem, Chapter 1 provides a brief literature review on the environmental problems associated with waste tyres, traditional waste tyre management methods and their related limitations. The limitations associated with the traditional tyre management methods are delineated towards probing a need for an alternative solution. As part of mitigating the waste tyres problem, chapter 1 gives a brief review on the changes enforced by the developed countries legislature. Chapter 1 closes with a brief description of the manageable alternative method of dealing with waste tyres, an alternative method that is a focus of this study. Finally, the chapter closes with outlining the aims and objectives of this research work in relation to tyre management method to be studied.

Chapter 2:

Addresses objective 1 as it provides a detailed review on the literature work specific to the tyre chemical make-up, problems associated with waste tyres and a comprehensive review on different management strategies. The focus then moves to outlining the pyrolysis process overview, the associated governing operating parameters, the pyrolysis possible products that may be achieved and their respective areas of applications. The chapter closes with an economical evaluation approach from literature investigations. Finally, a brief review on ASPEN plus simulation flowsheet of the tyre pyrolysis process from the literature is provided with the respective reaction kinetics.

Chapter 3:

Chapter 3 briefly covers the methodologies followed in literature studied from which the best approach for this study is established. Where applicable, alterations to the selected methodology from literature are provided in this section to best accommodate the requirements of this study. This chapter then moves the focus to achieving objectives 2 and 3 by addressing how each subsection of the chosen pyrolysis process technology is built into the ASPEN simulation software. Chapter 3 also provides details on the kinetics used in developing the ASPEN simulation models. The level and details of the kinetics provided are strongly dependent on the specific parameters investigated, hence different respective scenario kinetics with their associated basecase kinetics are provided.

Chapter 4:

Chapter 4 is mainly centred around providing simulation results and sensitivity assessment from chapter 3 developed models. The focus covers the outcomes from both the process and economic point of view. As such, chapter 4 thereby address objective 4 and 5 in a broader sense as it details out the best probable conditions that are suitable for maximizing tyre derived oil yield.

Chapter 5:

Chapter 5 provides detailed discussions and observations from the findings outlined in Chapter 4.

Chapter 6:

Summarises the key findings of this study and provides recommendations for the future work.

Below is a schematic representation summarising the main sections contained in this dissertation and a brief review on their respective contents.

Dissertation structure

Chapter 1	Chapter 2	Chapter 3	Chapter 4	Chapter 5	Chapter 6
Background	Objective 1	Objectives 2 & 3	Objectives 4 & 5	Discussions	Summary
Background of the study Outlines the study aims and objectives	Literature review on: Tire make up and problems associated with waste tire disposal Waste tire management technologies Waste tire pyrolysis description, PFD and associated parameters	Outlines the methodology followed in conducting the research	Provides results attained from the research work undertaken	Discusses results presented in Chapiter 4	Highlights key findings of the study Recommendations for the future work

Figure 1.1: Schematic breakdown of the dissertation structure

CHAPTER 2 : Literature review

2.1. Chapter overview

This chapter addresses objective 1, where various traditional waste tyre management technologies are discoursed. From the traditional technologies discussed, pyrolysis is outlined in more details as a possible sustainable method for waste tyre management. To fully address objective 1 requirements, in addition to this subsection, this chapter contains eight subsections. Subsection 2.2 and 2.3 evaluates the tyre make-up and the problems associated with dealing with tyres that have reached end of life. To a large extent the background given in subsections 2.2 and 2.3 points to the motivation driving the need to investigate a suitable waste tyre management method. Subsection 2.4 detail out methods of dealing with waste tyres. The subsection 2.4 also provides the outlined tyre management associated limitations. In subsection 2.5 more emphasis is placed on waste tyre pyrolysis method and its governing operating parameters. Subsections 2.6 delineates tyre pyrolysis typical process flow diagrams (PFD). Subsection 2.7 gives the economic aspects of waste tyre pyrolysis process where a principle of return of investment is employed. The last subsection (2.8) highlights and sums up the entire chapter.

2.2. Tyre make-up

According to Kordoghli et al. (2014), a tyre is made up of vulcanized rubber that is composed of long chain polymer, namely, polyisoprene, polybutadiene and styrene-butadiene copolymer cross linked with sulphur bonds. Tyres are protected by antioxidants and antiozonants to make them resistant against degradation (Kordoghli, et al., 2014). Tyres are fitted with steel and carbon black for reinforcement and aromatic extender for softening purposes (Kordoghli, et al., 2014). The rubber used in tyres is a blend from two sources, Heave tree (natural rubber) and petroleum products (Alsaleh & Sattler, 2014). Styrene-butadiene copolymer (SBR) is the most commonly used synthetic rubber in tyre manufacturing (Mulaudzi, 2017). Apart from SBR, Mulaudzi (2017) reported polyisoprene natural rubber, polybutadiene (PBD), nitril rubber (NTR) and chloroprene rubber (CPR) as other types of rubber that are used in tyre manufacturing. The type of rubber used, and the respective weightings are the major determining factor of chemicals that may be recovered from waste tyres (Mulaudzi, 2017). Lorry and off the road tyres (OTR) contain higher natural rubber in comparison to the passenger car tyres (Evans & Evans, 2006). Williams (2013) reported that tyres consist of up to 30 types of synthetic rubbers and 8 types from natural sources. In some cases, silica is used to replace some of the carbon black used in tyres (Evans & Evans, 2006). According to Evans & Evans (2006), in addition to the tyre outlined constituents, tyres also consist of up to 40 other chemicals such as waxes, oil, pigments, silica and clay. Table 2.*1* below gives an outline of the typical tyre constituents breakdown and their respective weightings, the breakdown provided is for the passenger and truck tyres for United States of America (USA) and European Union (EU) regions.

Table 2.1: Tyre composition breakdown (Mulaudzi, 2017)

Component (wt. %)	**USA**	**EU**	**USA**	**EU**
Vehicle type	Passenger car tyres		Truck tyres	
Natural rubber	14	22	27	30
Synthetic rubber	27	23	14	15
Carbon black	28	28	28	20
Steel	14.15	13	14-15	25
Nylon, fillers, accelerators and sulphur	16-17	14	16-17	10

A functioning tyre is made up of 6 major sections, each section serves a different purpose and as such the chemical make-up differ to suite the specific desired section needs. Combined, the different sections function as a single unit to achieve the desired purpose of the tyre. Below is a breakdown of the 6 tyre sections and their associated details around the respective constituents and functions. The tyre sections breakdown numbering of the tyre sections provided in Table 2.*2* corresponds with the numbering on Figure 2.*1*.

Table 2.2: Major tyre components, compositions and function (American tyre distributors, 2019; Mulaudzi, 2017)

Component	**Composition**	**Function**
1. Rubber liner	synthetic rubber	holds air inside the tyre
2. Carcass ply	textile fibre cables and rubber	serves as a shock absorber
3. Bead	steel wires hard rubber	fasten the tyre to the rim
4. Sidewall	rubber, carbon black and additives	protects the carcass
5. Crown piles	rubber, nylon and metal	centrifugal and lateral support
6. Tread	natural and synthetic rubber	component in contact with the road

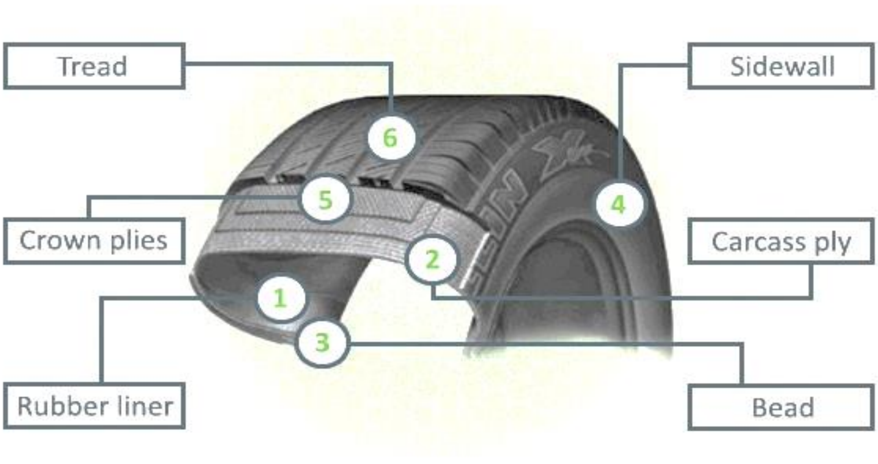


Figure 2.1: Structural outline of tyre make-up (ATD, 2019)

Depending on the nature of the tyre properties, the governing constituents may be broken down in two main subcategories, viz. proximate and ultimate analysis. The two categories play a crucial role in the understanding and determination of the possible products, by-products and possible associated weightings attainable from subjecting tyres through various chemical treatment processes. Table 2.*3* and Table 2.*4* below gives a breakdown of the weightings on each of the respective tyre components from the associated grouping as reported by various literature sources. Mainly the figures presented in Table 2.*3* and Table 2.*4* below show that the compositions of tyres do not differ much, rather they maintain an almost consistent footprint across the various studies. By extension this implies that tyres generally exhibit consistent properties. Majority of the data presented in Table 2.*3* and Table 2.*4* spans over a period of a decade, hence based on the presented data, consistency also holds true when viewing the composition figures over the years reported (Table 2.*3* and Table 2.*4*). By extrapolation from the tyre constituents, compositions and their respective weightings, tyres may be understood as a product not expected to change its properties in the near future. As such, findings from studies and investigations around tyre management may be qualified solutions that will be applicable in dealing with the growing waste tyre problem well into foreseeable future.

Table 2.3: Tyre proximate analysis as reported by different sources over two decades, majority of the data covering the past decade.

Parameter (wt. %)	(Williams, et al., 1990)	(Dai, et al., 2001)	(Galvagno, et al., 2002)	(Li, et al., 2004)	(Kar, 2011)	(Banar, et al., 2012)
N	0.400	0.500	0.380	0.490	0.170	0.470
C	85.9	82.8	85.2	84.1	67.1	82.5
H	8.00	7.60	7.27	6.71	6.12	6.94
S	1.00	1.30	2.30	1.51	2.05	1.70
O	2.30	4.50	0.540	1.73	24.6	8.37

Table 2.4: Tyre ultimate analysis as reported by different sources over two decades

Parameter (wt. %)	(Williams, et al., 1990)	(Dai, et al., 2001)	(Galvagno, et al., 2002)	(Li, et al., 2004)	(Kar, 2011)	(Banar, et al., 2012)
Moisture	0.80	0.80	-	1.14	1.72	0.840
Ash	2.4	3.3	5.22	4.35	19.1	9.63
Volatiles	66.5	68.7	61.3	62.2	59.7	65.5
CV*	40.0	36.5	38.5	34.9	27.4	37.5
Fixed carbon	30.3	27.2	33.5	32.3	19.5	24.1

* Units for CV are MJ/kg, VM = volatile matter, CV = calorific value

It may be noted that the majority of parameters presented in Table 2.4 are weight percentages, however the calorific value (CV) denoted with an asterisk (*) superscript has different units which is the MJ/kJ.

2.3. Waste tyres environmental issues

Tyre structure and chemical make-up makes their management extremely difficult after they have reached end of life. As reported in subsection 2.2 above, tyre function only points to having it manufactured in a manner that will enable it to be both durable and resistant to various environments elements that it is subjected to during its lifetime. As such, waste tyres pose a number of environmental concerns that makes them difficult to dispose using traditional means. Mulaudzi (2017) and Alsaleh & Settler (2014) delineates one of the tyre fundamental requirements as the ability to possess properties that enable them to endure conditions harmful to rubber material, these conditions include ozone, light and bacteria. This tyre property in effect makes it difficult for it to degrade when dumped in landfills, as a result the lifetime of tyre is relatively a long period, estimated to be between 80 and 100 years (Alsaleh & Sattler, 2014). Due to the high resistance of tyres against decomposition, Mulaudzi (2017) describe tyres as a non-biodegradable material. The structure of a tyre enables them to possess low bulk density as 75 % of its volume is empty, this entails that tyres occupy considerably large space in a landfill (Alsaleh & Sattler, 2014). Hence landfilling of waste tyre consumes valuable space which could be used to house other forms of waste. Tyres are generally a thermoset polymer in nature, this makes them impossible to be melted back to their basic chemical components (Alsaleh & Sattler, 2014). Given the outlined tyre fundamental properties, tyres require to be handled differently from the traditional easily biodegradable waste materials in order to minimise their environmental impact. It may also be deduced that every tyre produced, upon reaching end of life it can potentially present a problem that lasts more than a human lifetime.

2.4. Waste tyre management methods

This subsection outlines the traditional waste tyre management technologies and their associated limitations. Three major management approaches are discussed, viz. landfilling, reuse, retreating and thermal treatment technologies. Figure 2.*2* below gives a schematic breakdown of the said main tyre management technologies. This subsection closes with a summary of the discussed management technologies. Based on the discussed management methods, the summary section of subsection 2.4 also identifies the sustainable and feasible method of dealing with waste tyres. To a large extent, the identified suitable management technology highlighted in the summary of this subsection serves as a guide in the direction pointing towards the focus of the research work undertaken. Hence the remainder of chapter 2 dives deeper into establishing a more detailed understanding of the suitable method identified in subsection 2.4 summary.

Figure 2.2: Tyre management technologies (Akbas & Tyhana, 2021)

2.4.1. Landfilling and stockpiling

The said structural properties and chemical make-up of tyres enables them to pose a serious environmental and health concerns. When tyres are disposed in landfills they act as breeding site for disease carrying pests and insects such as mosquitos (Aslan, et al. 2017 and Islam, et al. 2011). Tyres poses a huge fire risk difficult to extinguish as in landfill they are generally exposed to open air. Tyre fires releases harmful particulate matter and toxic gases to the atmosphere harmful to the environment (Ismail , 2016 and Mulaudzi, 2017). Gases resulting from waste tyre fires are both carcinogenic and mutagenic (Kordoghli, et al., 2014). The run-off from waste tyres in landfills pollutes ground and underground water which in effect poses a health concern on the surrounding population (Aslan, et al., 2017). The outlined environmental impacts in this subsection deems management of waste tyres through stockpiling and disposing them in landfill sites an unsustainable and an environmentally unfriendly practice. Despite these environmental implications, landfilling and stockpiling remains the easiest method of dealing with waste tyres. Galvagno, et al. (2002) reported that approximately 65-70 % of waste tyres are landfilled. A 2014 study by Kordoghli, et al. reported that a huge percentage of waste tyre are still managed through unsustainable stockpiling approach and through legally or illegally discarding them in landfill sites. As such, the current huge landfilling and stockpiling percentages of waste tyres implies that there is a need for investigations into sustainable management technologies. In accordance with the outlined challenges, the context of a sustainable management technology implies a solution that is environmentally friendly and the one that is able to match the growing global waste tyre problem. As some dumping of waste tyres occurs illegally, finding a sustainable waste tyre management method will require to be coupled with some level of enforcement that will discourage unbecoming practices.

2.4.2. Recycling and reuse

In waste management techniques, the concept of recycling is generally coupled with reuse applications. Concerning waste tyre management, there are a number areas where scrap tyres may be reused. According to Kordoghli, et al. (2014) below is compilation of areas where scrap tyres may be resued (Table 2.*5*). It should be noted that Table 2.*5* may by no means be considered an exhaustive list, according to Kordoghli, et al. (2014) resuse applications collectively may only handle up to 13 % of the global scrap tyres generated.

Table 2.5: Areas where waste tyres may be reused (Kordoghli, et al., 2014)

Application area	Application
Agriculture	Weights for silage cover sheets
Landscaping	Erosion protection
Shore protection	Breakwaters
Harbours and docks	Dock bumpers and ship fenders
Fishing industry	Artificial reefs for fish breeding
Household	Garage bumpers and playground equipment
Shoemaking	Heels and straps for sandals
Road construction	Mixed with asphalt cement

2.4.3. Waste tyre retreatment

Retreatment is generally the most preferred form of waste tyre management. Retreatment also applies the reuse principle. The difference from subsection 2.4.2 outlined reuse applications being that retreatment reverts scrap tyres back to their original primary use. Thus, retreatment reduces the load and thereby reducing impact to the environment through depressing generation volumes. Retreatment benefits extends to the reduction in the number of raw materials required to manufacture new tyres. The retreated tyres are made from 15 % lower crude oil relative to new tyres (Kordoghli, et al., 2014). As a result, the retreated tyres costs 45 % lower while providing consumers with the similar desired quality as that presented by new tyres (Kordoghli, et al., 2014). Tyre retreatment however comes with limitations pertaining to the number of times retreatment may be done. Kordoghli, et al. (2014) reported that car tyres may only be retreated once, lorry tyres may only retreated twice while airplanes tyres has a retreatment abiliy of up to seven times.

Hence tyre retreatment is not able to deal with the entire volume of waste tyres generated globally due to the said limitaions around the number of times they may be retreated. Other factors limiting retreatment is the consumer's lack of confidence on the retreated tyre products. In some cases, dominantly on the low income communities, the condition of waste tyres from such communityres may render them not feasable to be retreated. The limiting factor on the low income communities waste tyre reusability stems from the fact that tyres from the said regions are often used well beyound their life time, often used until they start exposing the threads (Kordoghli, et al., 2014). As such, this practice renders the resulting scrap tyres from such communities not reusable.

2.4.4. Waste tyre thermal treatment technologies

Subsections 2.4.1, 2.4.2 and 2.4.3 above exposed that scrap tyre management through landfilling, recycling, reuse and retreatment present with them a number of challenges. The outlined challenges stem from a number of aspects, viz. degradation resistance, environmental pollution, possibility of accidental fire risks and lack of customer acceptance of retreated tyres, amongst others. According to Kordoghli, et al. (2014), the said challenges only sustainably permits a small percentage of waste tyres to be managed through traditional means without causing detremental harm to the environment. In light of this, thermal treatment means are emerging as an alternative approach that may handle the surplus large tyre volumes. Kordoghli, et al. (2014) deliberated on this, repoting that thermal technologies are able to deal with much higher tyre volumes in relation to the amount managed through legal landfilling, reuse and retreatment means.

Based on the tyre chemical make-up and compositions, tyre thermal treatment technologies are an attractive alternative due the linked potential energy recovery opportunities enveloped within them. Evidently, the high carbon and hydrogen content in tyres is a clear indication of high energy content

(Kordoghli, et al., 2014). Typically, tyres possess calorific values around 33.03 MJ/kg, some studies have reported tyre calorific values as high as 40.0 MJ/kg (Table 2.*4*). The calorific values of tyres are relatively higher than some of the traditionally used energy sources such as wood, municipal solid waste, lignite and subbituminous coal. Wood, municipal solid waste, lignite and subbituminous coal calorific values are 10.2 MJ/kg, 12.4 MJ/kg, 16.9 MJ/kg and 24.4 MJ/kg respectively, of which all are relatively lower that those reported for tyres (Conesa, et al., 2004). Hence disposing of waste tyres in landfill does not only qualify this practice an environmental unfriendly approach, but it also implies a disposal and loss of potential energy that can be harnessed (Dai, et al., 2001). Acording to Kaminsky, et al. (2009), valorisation of waste tyres into fuels is essential in easing the pressure posed by the high oil prices on the consumers. Given the growing global energy crisis fuelled by the growing population, particularly more problematic in the underdeveloped and developing countries. The disposing of energy rich materials may be considered an unethical and vice practise. A vice practice that penalises humanity through inflicting a number of unbecoming harmful complications.

The main thermal technologies investigated in literature pertaining scrap tyre management are pyrolysis, gasification and combustion. Kordoghli, et al. (2014) difines pyrolysis as a tyre degradation process occurring in the absence of oxygen while describing gasification as tyre degradation that is carried out in the presence of water vapor and defines combustion as the degradation in the presence of oxygen. Table 2.*6* below highlights major differences of the said thermal tyre treatment technologies on the grounds of the governing degradation setting standpoint:

Table 2.6: Main waste tyre thermal treatment technologies

Thermal technology	**Degradation setting**
Pyrolysis	Absence of oxygen
Gasification	Presence of water vapor and air
Combustion	Presence of oxygen

Some considerations should however be taken into account when dealing with thermal treatment technologies in a broader sense as not all waste tyre thermal technologies are feasible. Combustion thermal treatment presents with it a number of toxic gases and particulate matter emissions that are harmful to the environment and human health (Kordoghli, et al., 2014). As reported in subsection 2.4.1 gases resulting from waste tyre fires are both carcinogenic and mutagenic (Kordoghli, et al., 2014). Hence, in principle to a large extent combustion permit environmental problems similar to those constituted by tyre accidental fires. The said challenges attached to combustion of scrap tyres reduces the thermal treatment technologies scope to only two main feasible possibilities. Evidently so, Kordoghli, et al. (2014) reported that the feasible considerable thermal waste tyre treatmnent options are pyrolysis and gasificatoin. Of the said feasible thermal treatment technologies, pyrolysis is considered the most manageable in dealing with waste tyres (Kordoghli, et al., 2014). Subsections 2.4.4.1 and 2.4.4.2. dives deeper into outlining gasification and pyrolysis thermal treatment technologies. More emphasis is however placed on the pyrolysis process as it is considered a more manageable thermal treatment approach with easy to handle products (Kordoghli, et al., 2014). Hence the focus of the remainder of chapter 2 is centred around how pyrolysis technolgy is carried out, its associated key driving factors, products obtainable, product application areas and the associated limitions.

2.4.4.1. Gasification

In a gasification process, waste tyres are exposed to temperatures in the range between 700 ^{o}C and 800 ^{o}C in the presence of air and steam or oxygen as reactive catalysts (Mulaudzi, 2017). Although waste tyre gasification produces carbon black, the main product from this process is the syngas which is used as the energy source when exposed through combustion processes. Other applications of syngas are in gas turbines, as raw materials in fuel and in chemical production (Mulaudzi, 2017). An observation can be made that gasification is a relatively energy intensive process as it requires high operating temperatures. As such, majority of the syngas generated from tyre gasification is used back in the process to achieve the required gasification degradation temperatures.

2.4.4.2. Pyrolysis of waste tyres

Kordoghli, et al. (2014) outlines pysolysis as a process whereby organic matter is subjected to hight temperatures in the absence of oxygen. During pyrolysis, tyres are endothermically decomposed at temperatures between 300 ^{o}C and 700 ^{o}C (Altayeb, 2015). Waste tyre pyrolysis generates lower nitrogen oxide and sulphur oxide emission relative to those from the incineration process (Altayeb, 2015). Apart from manageable emission, pyrolysis is considered environmentally attractive as its products are relatively easy to handle, store and transport (Aydin & Lilkilic, 2012). Due to the said energy recovery benefits and minimum environmental impacts, pyrolysis technology has over the past few decades found applications in arears such as varolising of oily sludge, fuel residue, lubrication oil residue, oily wastes, municipality waste, soap, waste, plastic and textile (Kordoghli, et al., 2014). Figure 2.*3* and Figure 2.*4* below gives a schematic depicting of tyre pyrolysis process, the associated products and their respective applications (Martinez, et al., 2013).

Figure 2.*5* and Figure 2.*6* provides detailed process flow diagrams depicting tyre pyrolysis process. The main difference between Figure 2.*5* and Figure 2.*6* is the associated process energy recovery for heating up tyres to the required temperatures for the degradation to take place. In Figure 2.*5*, carbon black is used as the soruce of energy while in Figure 2.*6* non-condensable gases referred to as pyro gases are used to heat up tyres. From an easy to handle standpint, using pyro gases as source of energy is considered a more feasible and practical approach for providing heat for the process.

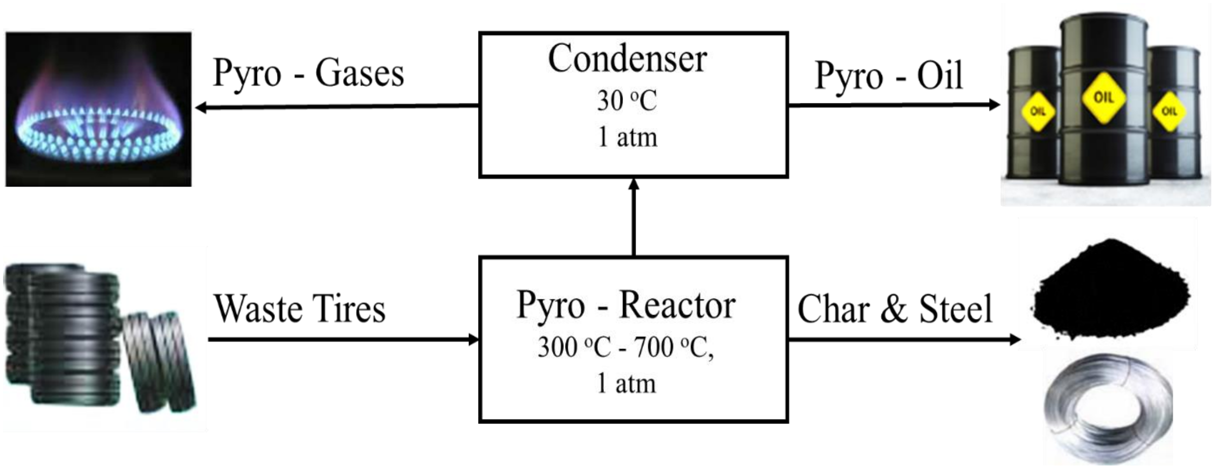


Figure 2.3: Schematic overview of a waste tyre pyrolysis process (Ismail, et al., 2016)

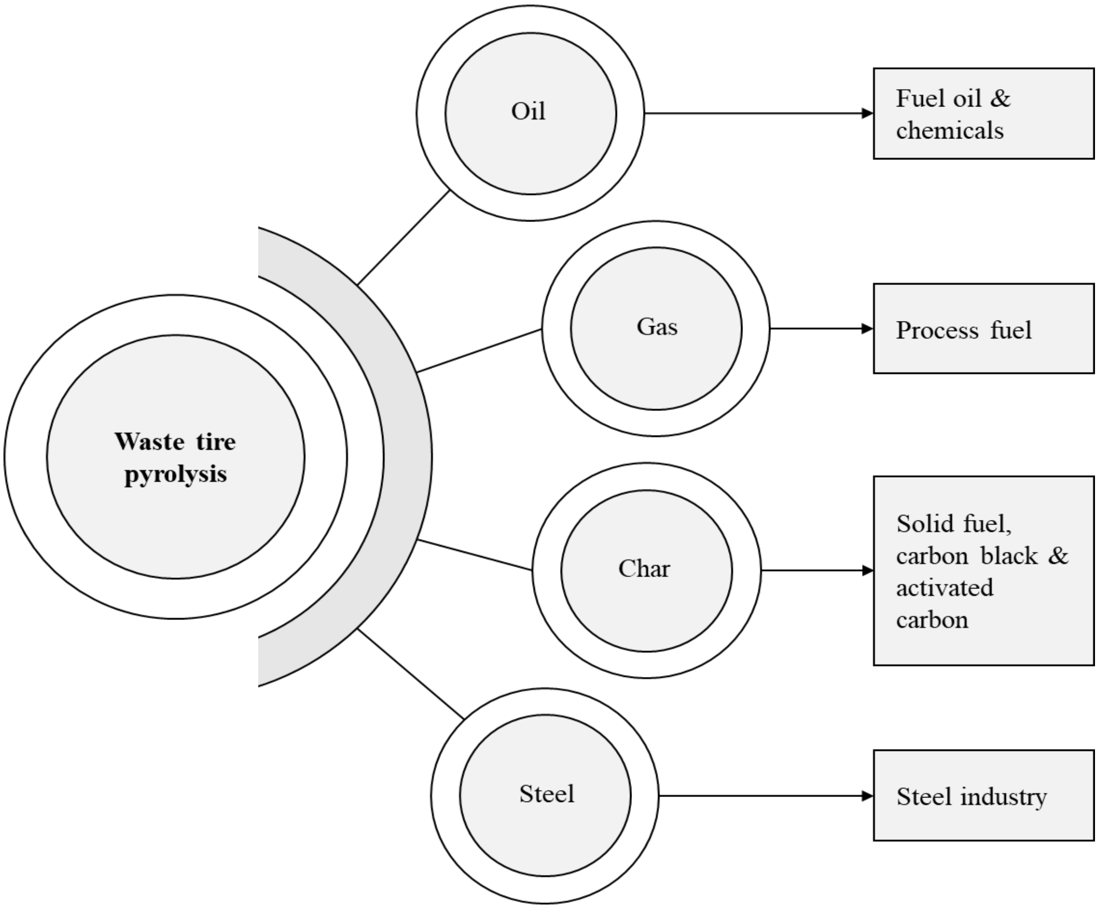


Figure 2.4: Waste tyre pyrolysis products (Altayeb, 2015)

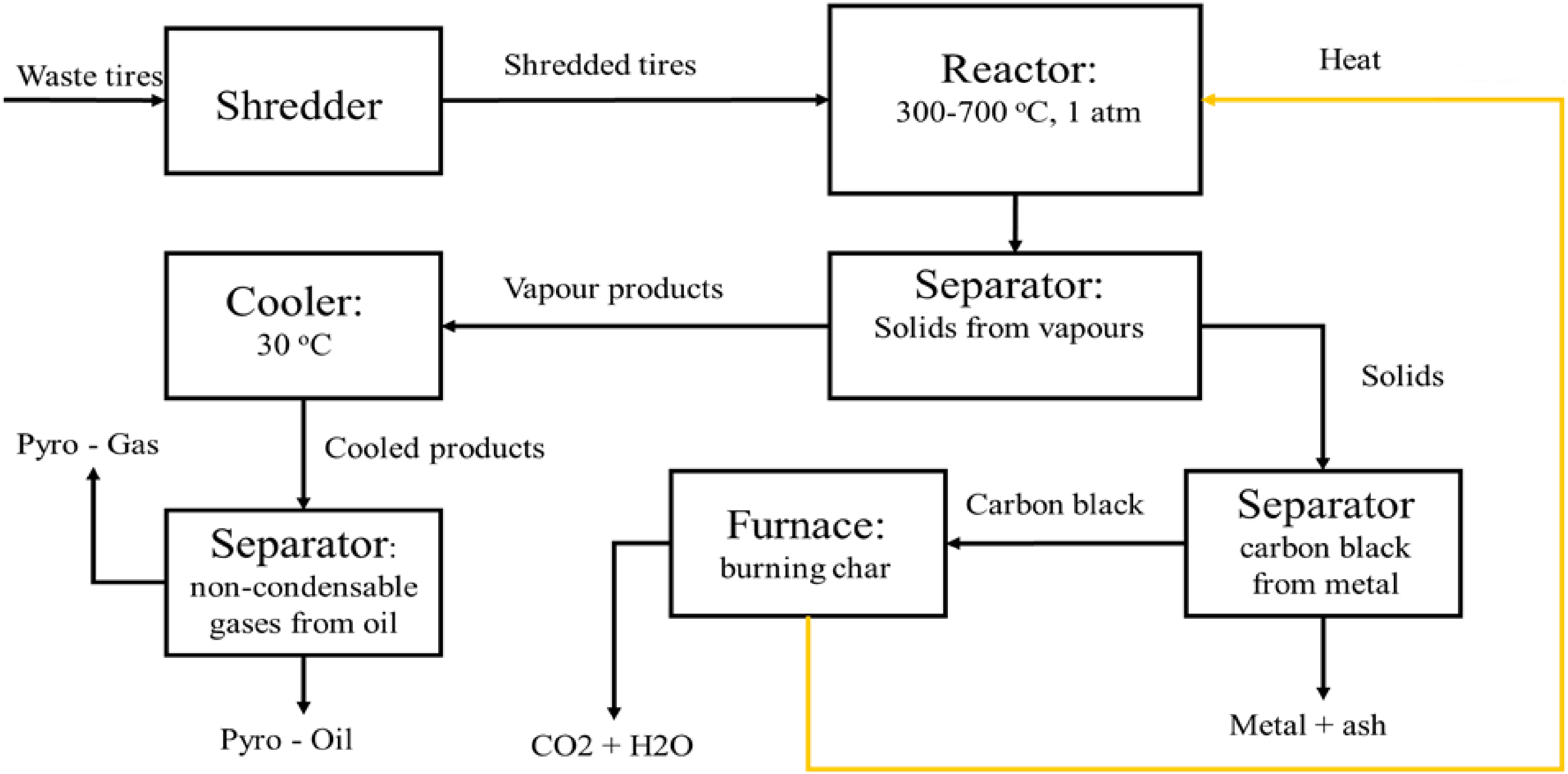


Figure 2.5: Waste tyre pyrolysis PFD - Carbon black as source of energy (Ismail, et al., 2016)

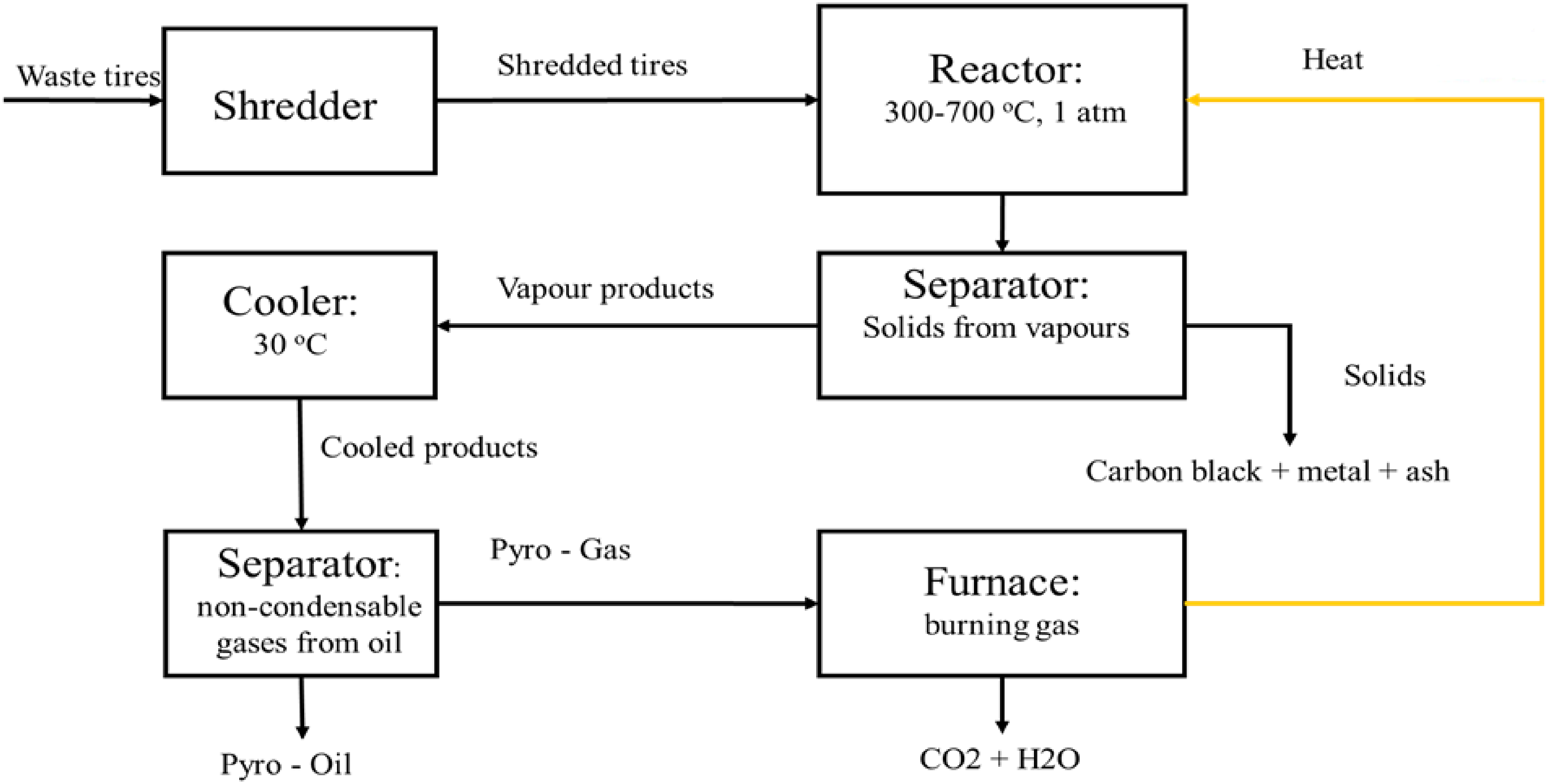


Figure 2.6: Waste tyre pyrolysis PFD - Pyro Gas as source of energy (Martinez, et al., 2013)

2.5. Factors affecting tyre pyrolysis

This subsection outlines the main factors impacting a tyre pyrolysis process, the different associated influencing factors and the relevant outcomes. The chapter closes with giving a summary of the discussed factors, placing the focus on the conditions that will be investigated for this study. According to Alsaleh and Sattler (2014), tyre pyrolysis process is strongly driven by the reactor type used, reactor temperature, heating rate, particle size, feedstock composition, residence time, reactor operating pressure and the application of a catalyst. Independent of the type of reactor used, pyrolysis operating temperature is considered the key driving factor in influencing the resulting products from the composition and yield perspective.

2.5.1. Reactor type

In any manufacturing process plant the size of the reactor is generally determined by the volumes of feedstock to be process, according to Akbas & Tyhana (2021) typically waste tyre pyrolysis plants use reactors sizes ranging between 3 m^3 to 20 m^3. The commonly used types of reactors are the kiln, fixed bed, rotatory kiln and fluidized bed. Depending on the operating conditions and reactor type used and process condition, a slow or fast pyrolysis process may be achieved.

Slow pyrolysis, also referred to as carbonization is undertaken at low temperatures which in effect results is slow waste tyre decomposition (Akbas & Tyhana, 2021). Slow pyrolysis is achieved through slow heating rates to the operating temperatures between 400 ^{o}C and 450 ^{o}C, long solids and vapour residence times which are typically in the region of minutes to hours. Slow pyrolysis results in higher coke, tar, and char. Usually fixed bed reactors are used for this type of pyrolysis (Akbas & Tyhana, 2021). In cases where a catalyst is used for a slow pyrolysis, the accessibility onto the catalyst surface area is restricted due to the associated limitations presented by the use of a fixed bed and its geometry (Alsaleh & Sattler, 2014).

On the other hand, a fast pyrolysis is achieved at a higher pyrolysis temperature, between 500 – 600 ^{o}C. This is obtained through running higher heating rates thereby aiding shorter resident times in the region of milliseconds to seconds (Alsaleh & Sattler, 2014). Fast pyrolysis requires relatively small particle size and is usually carried out using fluidised beds (Akbas & Tyhana, 2021). Given the high volumes of waste tyres ending up in the landfill sites (65-70 %), fast pyrolysis may be considered a feasible approach in dealing with this surplus. Apart from the benefits of processing higher volumes, fast pyrolysis fits well within the current industrial economic landscape. This time and age processes are preferably operated at relatively higher processing rates as this directly translates to higher returns and better turn-around time.

2.5.2. Pyrolysis reactor temperature

Temperature is the main governing parameter responsible for the degradation of tyres and volatilization of the solid material into gas. In effect the resulting pyrolytic product properties are strongly dependent on the reactor operating temperature (Alsaleh & Sattler, 2014). Alsaleh and Sattler (2014) reported that the optimum oil yield achievable through pyrolysis can be between the region of 38 % and 60 %, attainable at temperature ranges between 425 °C and 720 °C. Of the tyre pyrolysis products, derived oil is considered the most valuable product, as such tyre pyrolysis are set up for maximizing oil production (Alsaleh & Sattler, 2014). Together with temperature optimization, achieving the optimum oil yield is to some extent influenced by other parameters such as heating rate, reactor residence time, particle size and reactor type. Hence as much as temperature is the chief parameter for maximizing oil yield, temperature consideration should be coupled with other parameters. A pyrolysis process that is not optimized presents a risk of the occurrence of secondary undesired reactions. The secondary reactions occurs when the formed gaseous products convert to solid. This in effect increases the value of the solid char product formed thereby reducing the desired quality and yield of the oil products (Alsaleh & Sattler, 2014). Hence the phenomenon of secondary reactions occurrence hinders oil yield and may in effect constitute tyre pyrolysis process an ineffective tyre treatment technology.

2.5.3. Reactor pressure

Alsaleh and Sattler (2014) reported that higher operating pressure increases the oil viscosity. However vacuum operation has shown to result in lower temperature requirements and assists in hindering the occurrence of gas phase secondary reactions (Alsaleh & Sattler, 2014). Thus, operating the tyre pyrolysis process at lower pressure may results in lower operating temperature requirements for the same oil yield. The lower operating temperature in effect results in lower energy requirements for the process (Alsaleh & Sattler, 2014). Reducing the operating pressure of the pyrolysis reactor can make the process more economic through reducing the running costs. Lopez, et al. (2009) reported that the pyrolysis reaction starting temperature under vacuum may be typically in the region of 485 K while under atmospheric pressure conditions the reaction temperature of 495 K may be required. In the similar study by Lopez, et al. (2009), it was delineated that the vacuum conditions activation energy was lower than those at atmospheric conditions. In the three steps decomposition stages, activation energies of 43.5, 104.7 and 243.0 kJ/mol were reported for operating pressure of 0.25 atm while 50.6, 130.8 and 245.9 kJ/mol activation energy at 1 atm operating pressure were reported (Lopez, et al., 2009). Furthermore, Lopez, et al. (2009) reported that higher reaction rates are achievable under vacuum conditions when compared with atmospheric operating pressure. An increase of 1.7 times higher for the kinetic constant of devolatilization was reported for 0.25 atm compared to that obtained from atmospheric operating pressure (Lopez, et al., 2009).

2.5.4. Resident time

Higher carrier gas flow enables a faster removal of the generated pyrolysis gases, this phenomenon in effect reduces the reactor residence time (Alsaleh & Sattler, 2014). Short resident times for the gases is desirable as longer residence time permits for secondary reactions to take place (Alsaleh & Sattler, 2014). Secondary reactions that generally presents a negative impact on oil quality and yield (Alsaleh & Sattler, 2014).

2.5.5. Catalyst

Some studies have reported that a use of catalysts such as HMOR zeolite, perlite, activated alumina, Y zeolite and zeolite ZSM improves the yield and quality of oil generated (Alsaleh & Sattler, 2014). The addition of steam in the catalytic hydrolysis also helps in slowing down the catalyst deactivation rate (Alsaleh & Sattler, 2014).

2.5.6. Waste tyre particle size

Studies have shown that the smaller tyre particle size favours higher tyre conversion rate thereby enabling conditions favourable for higher oil yields (Alsaleh & Sattler, 2014). The larger particle size may require longer residence times thereby requiring higher temperatures and heating rates. The challenges presented by larger tyre particle size also implies requirements of a larger reactor, all of which in effect negatively drives up the capital, operational and maintenance costs (Alsaleh & Sattler, 2014). The large particles also negatively impact packing in the reactor. This results in the reactor processing capacity not being utilized efficiently thereby causing the reactor to process smaller total mass of tyres. This is not a desired outcome as one of the requirements to be met by the thermal treatment technology is to handle large surplus tyre volumes not absorbed by the traditional management means.

2.5.7. Feedstock composition

Scrap tyres rich in petroleum synthetic based rubber have higher oil yield and produce better quality as opposed to those from natural rubbers. This is attributed to higher aromatic content found in the synthetic rubber (Alsaleh & Sattler, 2014). Based on the learnings from Table 2.*3* and Table 2.*4* in section 2.2, it was deduced that tyre compositions do not differ much as reported by various sources. The compositions presented in section 2.2 also showed to present no significance difference when compared across the period presented. As such, it holds true that the properties of tyres remain relatively consistent across different regions and over the years.

2.5.8. Heating rate

Heating rate plays a huge role in pyrolysis economic considerations as it is one of the key energy requirements drivers (Alsaleh & Sattler, 2014). However, when heating rates are increased considerably, secondary reactions start forming and this negatively effects oil quality and yield (Alsaleh & Sattler, 2014).

2.5.9. Steam incorporation

Incorporating some steam in the pyrolysis gas products has shown to result in the H_2 content increase through hydrocarbon steam reforming reactions (Alsaleh & Sattler, 2014). Higher H_2 content is desirable as it improves the energy value of the gas (Alsaleh & Sattler, 2014). As with the use of the catalyst, steam incorporation also constitutes an additional cost to the operation of the tyre pyrolysis plant. Hence careful considerations need to be taken into account from the benefits versus the operational cost point of view.

2.5.10. Impact of operating parameters overview

There are a number of parameters impacting the operation of the tyre pyrolysis process, viz. reactor type used, reactor temperature, heating rate, particle size, feedstock composition, residence time, reactor operating pressure and the application of a catalyst. Optimization of the said operating conditions is chiefly depended on the tyre derived oil yield. As such, it may be deduced that reaching optimum operating conditions of a tyre pyrolysis process may prove be to a complicated task as all the said parameters have to be collectively considered. Most of the studies undertaken in literature do not cover simulations or experimentation work where all the parameters discussed in subsection 2.5 are optimized in one study. As such, in most literature studies the contributions of each parameter reported is chiefly investigated and understood independently.

Based on subsection 2.5 learnings, a summary Table 2.*7* below was developed where the recommended conditions are qualitatively depicted for each of the operating parameter. For purposes of maintaining consistency, the numbering on the parameters in Table 2.*7* was kept similar to that used in subsection 2.5. Apart from maximizing oil yield, some of the conditions outlined in subsection 2.5 have other limitations, viz. the possibility of the occurrence of secondary reactions. Secondary reactions are not desired in the tyre pyrolysis process as they reverse formed gases back to char and thereby increasing char yield and effectively reducing the oil quality and yield. Secondary reactions are potentially possible in cases where the residence time is too high and in cases where the heating rate is increased considerably.

Table 2.7: Summary of parameters impacting tyre pyrolysis process

Parameter	**Summary**
2.5.1. Reactor type	Fixed bed reactor – slow pyrolysis, poses difficulty in catalyst surface area accessibility. Fluidised bed reactor – fast pyrolysis, able to process higher tyre volumes, higher turn-around time (Nitrogen gas as fluidisation medium).
2.5.2. Pyrolysis reactor temperature	Temperature is the main governing parameter responsible for the degradation of tyres and volatilization of the solid material into gas. The typical pyrolysis temperatures range between 425 ^{o}C and 720 ^{o}C.
2.5.3. Reactor pressure	Lower pressure results in lower operating temperature requirements for the same oil yield, the lower operating temperature in effect results in lower energy requirements.
2.5.4. Resident time	Short residence times for the gases is desirable as longer residence time permits for secondary reactions to take place.
2.5.6. Catalyst	Improves the yield and quality of tyre derived oil generated, a consideration to be assessed based on the benefits versus the additional cost of incorporating a catalyst.
2.5.7. Waste tyre particle size	The smaller tyre particle size favours higher tyre conversion rate thereby enabling conditions favourable for higher oil yields.
2.5.8. Feedstock composition	Tyres rich in petroleum synthetic based rubber have higher oil yield and produce better quality as opposed to those from natural rubbers.
2.5.9. Steam incorporation	Incorporating some steam in the pyrolysis gas products result in the H_2 content increase through hydrocarbon steam reforming reactions. As the case with the catalyst, incorporating steam comes at an additional cost that require to be assessed from a benefit versus cost point of view.

Ismail, et al (2016) developed a summary presented in Table 2.*8* depicting comparative studies on some of the factors outlined in subsection 2.5, viz. reactor type, reactor temperature, reactor pressure, use of a catalyst and the influence of the residence time. The results are arranged with respect to the type of operating reactor in the following order below:

1. Fluidised bed reactor
2. Fixed bed reactor
3. Rotary kiln (hearth furnace) and lastly
4. Batch reactor

Each of the respective reactor type outlined in Table 2.*8* is presented with the respective different operation conditions in terms of the operating temperature, pressure residence time and presence of the catalyst. On the said reported parameters in Table 2.*8*, the main observations from literature studies reported by Ismail, et al (2016) showed to be relatively in line with the discussion on the parameter impacts as outlined in subsections 2.5. Overall, the reactors that promote mixing (fluidized bed and kiln) show to be depicting higher oil yields when compare with fixed bed reactors (Table 2.*8*). The operating temperatures reported in Table 2.*8* are mostly within the range reported in subsection 2.5.2.

In another study by Alsaleh & Sattler (2014) a comparative study was developed focusing on the temperature as this is the parameter with the highest influence on the pyrolysis process (Table 2.*9*). The findings in Table 2.*9* also showed to be in line with the discussed operating ranges reported in subsection 2.5.2. Table 2.*9* also presents the temperatures for maximum oil yield, on average, generally most of the optimum temperatures occurs around 500 ^{o}C. Table 2.*8* and Table 2.*9* in effect provides a basis for substantiating the criteria for the reactor selection and operating temperature range for the study to be undertaken in this research work.

Table 2.8: Impact reactor type and operating parameters (Ismail, et al., 2016)

Reference	**Reactor type**	**T (°C)**	**P (Pa)**	**t_m (min)**	**Oil yield (%)**
Araki et al. (1979)	Fluidized bed	350–500	101,325	12–20	38–45
Lee et al. (1998)	Fluidized bed	700–900	101,325	n.a	30–48
Kaminsky & Mennerich (2001)	Fluidized bed	>700	100,000	n.a	25–32
De Marco Rodriguez et al. (2001)	Fluidized bed	300–700	101,325	30	4.8–38
Williams and Brindle (2003)	Fixed bed + fluidized catalyst bed	300–720	101,325	60	3.6–54.8
Roy et al. (1999)	Fluidized bed	480–520	<10,000	n.a	10–60.7
Uçar et al. (2005)	Fixed bed	550–800	101,325	60	67.4–72.2
Zhang et al. (2008)	Fixed bed	400–560	3500–4000	n.a	36.5–48.5
Rombaldo et al. (2008)	Fixed bed	600–900	0.6–1 atm	n.a	44–52
Du˜ng et al. (2009)	Fixed catalytic bed	500	n.a	60	38–42
Mastral et al. (2000)	Swept fixed bed	400–600	10×10^6	30	36–45
Napoli et al. (1997)	Tubular furnace	380–550	101,325	Na	19
Mirmiran et al. (1992)	Multiple Hearth Furnace	200–500	<10,300	n.a	61
Shah et al. (2007)	Catalytic batch reactor	300–400	n.a	n.a	26–32

Table 2.9: Impact of temperature and heating rate (Alsaleh & Sattler, 2014)

Authors (Year)	Reactor type	Tyre mass	Temp. range (°C)	Heating rate (°C/min)	Oil yield optimal temp. (°C)	Max. oil yield (wt. %)
Williams, et al. (1990)	Fixed bed batch	50 g	300–720	5 to 80	600–720	54–58.8
Kar (2011)	Fixed bed batch	10 g	375–500	10	425	60.0
Aydın and Ilkılıc (2012)	Fixed bed batch	N/A	400–700	N/A	500	40.0
Aylon, et al. (2010)	Rotary kiln	3.5 to 8.0 kg/h	600–800	N/A	600	48.4
Galvagno, et al. (2002)	Pilot rotary kiln	4.8 kg/h	450–700	N/A	550	38.1
Li, et al. (2004)	Rotary kiln	N/A	450–650	N/A	500	45.1
Gonzalez, et al. (2001)	Vacuum	N/A	375–500	10	425	60.0
Williams and Brindle (2003)	fluidized bed	220 g/h	450–600	N/A	450	55.0
Dai, et al. (2001)	fluidized bed	N/A	360–810	N/A	450	52.0

2.6. Process modelling and simulation flowsheet

According to Morgan (2005), even outside the scientific community, the experimentation approach is a widely accepted tactic for testing theories. Experiments are known to be an economical technique of proving or disproving concepts if properly designed, executed and showing to display acceptable level of repeatability. Experimentation gets most of the acceptance on the grounds that it provides the artificial version of the real world, usually carried out in laboratory environment. Accordingly, an experimental approach affords outcomes from which patterns may be explored and to some degree provides confidence on the possibility that similar outcomes may be attained on large scale (Morgan, 2005). Hence prior to large scale investments, experiments have proven to be instrumental in closing the surprise gap on the possible expectations. Contrary to the experimentation approach, simulation models are not well understood outside the scientific community and often do not offer as much confidence as that given by experiments. This is generally due to the lack of understanding as to what simulation models are and what value do they add in the field of science (Morgan, 2005).

According to Morgan (2005), models act as autonomous investigation instruments and may be understood as supplementary experimentation representation that can also characterize large scale expectations. Models are strongly dependent on the basis from which they are constructed (Morgan, 2005). In summary, Morgan (2005) developed the summary below to demonstrate the major difference between experimentation and modelling approach (Table 2.*10*).

Table 2.10: Experiment versus modelling approach (Morgan, 2005)

Subsection	Mathematical model experiment	Ideal laboratory experiment
Construction and design	Create an artificial world in the model	Re-create part of the real world in an artificial environment
Relationship to subject matters	Represent theory or world	Replicate theory or world
Experimental control	By assumptions of model design and ceteris paribus conditions	By experimental design and physical controls
Demonstration method	Deductive/mathematical in model	Experimental in laboratory
Inference to world	Different materials problem of ‘realism’	Same materials problems of ‘validity’
Inference to theory	Same materials	Different materials
Design danger	Built-in justification	Over-tamed behaviour
Results potential	Surprise	Surprise and confoundment

Jebeile (2019) describes simulations and process modelling as the approach that falls between theoretical physical science and experimentation methods and concludes that the two are analogues. Hence simulation may be understood as an extension of experiments (Jebeile, 2019). Based on the established premise that links experiments and simulations, modelling is a relatively more economical approach of proving or disproving theories especially where experiments may be too costly (Jebeile, 2019). As much as experimentation is a well-accepted approach, experiments may be time-consuming, politically and ethically unwelcomed (Humphreys, 2004). If required, simulations are useful in enabling further investigations without having to re-conduct the experiments (Foo, et al., 2005). Guala (2002) reported that simulations provide as much a reliable knowledge as experiments. In some cases, simulations have been instrumental in undertaking investigations that may be difficult or impossible to run using traditional means (Barberousse, et al., 2009). Jebeile (2019) reported that simulations bridges the gap as they enable a move directly from theory to data thereby generating new knowledge more cost effectively.

Accoriding to Guala (2002) inferiority of simulations stems from the lack of developing a physical process that generate the desired phenomena but rather bases the outcomes solely on caluculations. Despite the limitations, similar to experimentation, simulations provide exploration, intervention, visulization and can function as black boxes. These articulates enabled simulations to provide new knowledge as experiments do (Jebeile, 2019). Using data obtained from experiments, mathametical models have been developed to accuratey predict a number of processes. Waste tyre pyrolysis process is no exception to this, among other authors, studies conducted by Olazar, et al,. (2008), Isamil et al (2016), Sharma, et al., (1998) have provided kinetics that well represents the experimental data. Such models when used in simulation softwares results in rather reliable findings with confidence backed by experimental data.

Given simulation accorlades and developments made on the field of tyre pyrolysis simulation kinetics, this research study was carried out using a simulaiton approach. Advanced System for Process Engineering, in short referred to as ASPEN is one of the useful simulation tools for developing process models for various process operations. ASPEN relies chiefly on chemical equilibrium, mass and energy balance principles to run the calculations. ASPEN is a simulation tool that was first developed in the 1970's through collaborative efforts between Massachusetts Institute of Technology and the USA department of energy (Aspentech, 2022). ASPEN plus has been used in a number of studies relating to the tyre pyrolysis process, below (Figure 2.*7*) is a depiction of a tyre pyrolysis ASPEN flowsheet as developed by Ismail, et al (2016). Figure 2.*7* mainly encompasses the main unit operations of waste tyre pyrolysis process as presented in a PFD for a similar study (subsection 2.4.4.2, Figure 2.*5*).

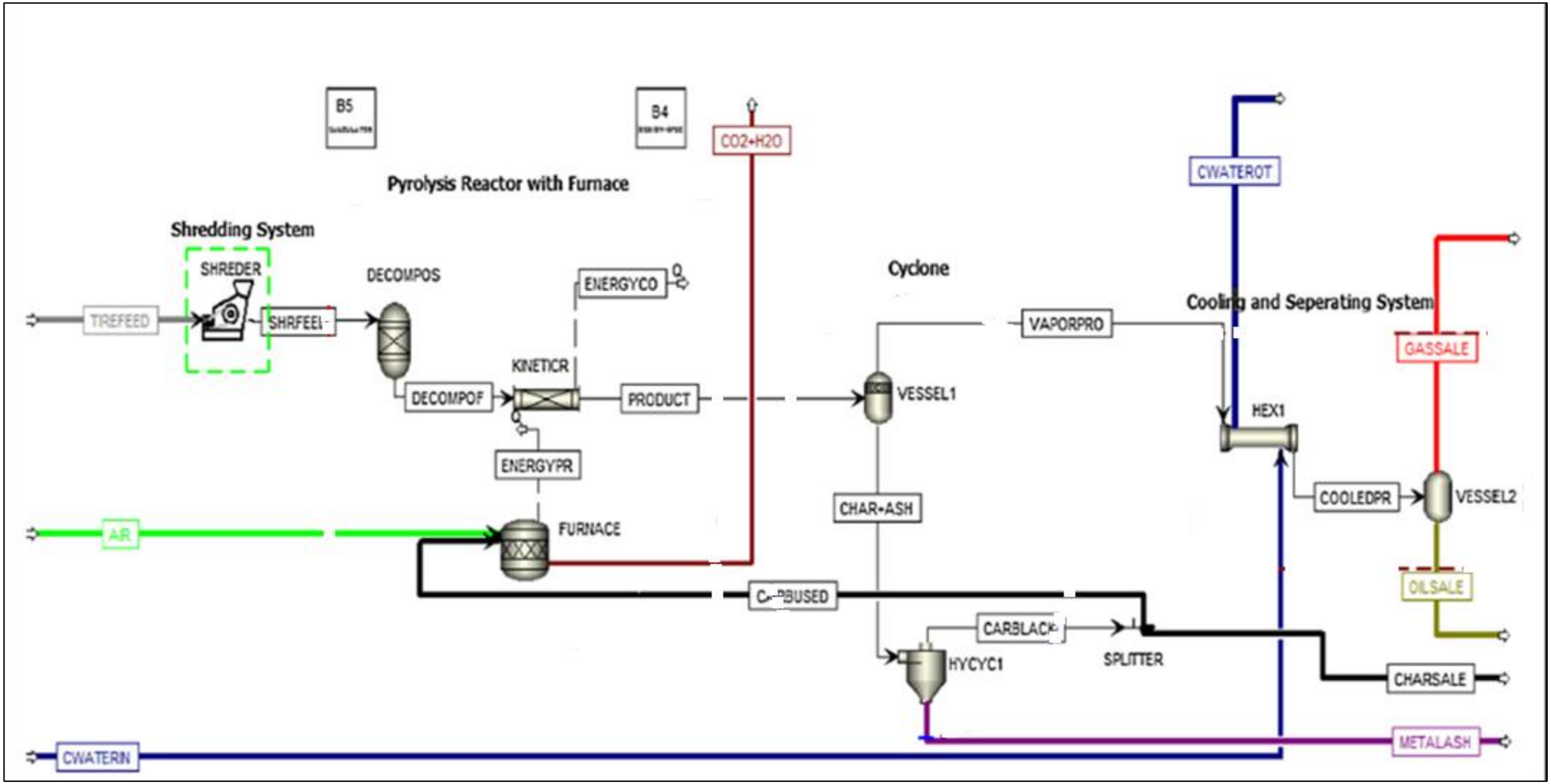


Figure 2.7: Waste tyre pyrolyses ASPEN flowsheet (Ismail, et al., 2016)

2.6.2. Reactions and reaction kinetics

Research studies have made huge strides in the simulation model developments of tyre pyrolysis processes depicting typical tyre derived oil yields. Different sources have developed and reported reaction kinetics specific to the operating parameters of the process. Generally, waste tyre pyrolysis is governed by the following main decomposition equation (Ismail, et al., 2016):

$$\mathrm{Tyres} = \mathrm{Solid} + \mathrm{Oil} + \mathrm{Gas} \qquad \text{Equation 1}$$

Equation 1 above is a simplified version of the tyre pyrolysis process, in principle there are a number of reactions taking place coupled with a number of components which are generated as a result of pyrolysis process. Appendix A gives a comprehensive list of the possible reactions attainable from a typical tyre pyrolysis process. Based on the simplified equation 1 above, a number of research studies have developed kinetics that encompasses the products as lumped components instead of individual components making up char, gas and oil products. Different studies have developed different kinetics with respect to the kind of pyrolysis parameters used in the process, according to Ismail, et al (2016), the tyre pyrolysis kinetics used in the ASPEN plus environment are generally based on the Arrhenius equations as showed below (Equation 2).

Equation 2: Arrhenius equations

$$\mathrm{K_i} = \mathrm{A} \times \mathrm{T^n} \times \exp\left(\frac{-\mathrm{E}}{\mathrm{RT}}\right)\mathrm{X_{H2}}$$

$$\mathrm{X_{H2}} = \frac{\mathrm{W_i} - \mathrm{W_t}}{\mathrm{W_t} - \mathrm{W_f}}$$

Where:

Variable	**Description**
A	Pre exponential term
T	Temperature
n	Temperature coefficient
E	Activation energy
X_{H2}	Limiting reactant (being H_2 for tyre pyrolysis)
R	Universal gas constant
k_i	Rate constant
W_i	Initial mass
W_t	Mass at time t
W_f	Final mass

2.7. Economics of waste tyre pyrolysis

Over the years a number of advances and developments have been made to optimize tyre pyrolysis plants. Coupled with the technological research on the area, there were also studies that considered economic feasibility of setting up and running a tyre pyrolysis plant. In a study conducted by Fels & Pegg (2018) for a China plant with a 10 000 t/year processing capacity, actual capital costing based on the actual quotaions were reported. After incoporating the running expenses and revenue in the costing, Fels & Pegg, (2018) reported a 15 % return on investment (ROI), this was achieved by fluctuating the selling price of the pyrolysis products. In a Ireland study, a payback period of 2.5 years was estimated from a case study of a 40 000 t/year waste tyre pyrolysis plant (Riedewald & Sousa-Gallagher, 2016). An investigation for a 9000 t/year Gauteng, South African case, between 29.79 % and 34.59 % potential return on investment was reported (Pilusa, et al., 2014).

2.8. Summary

The current traditional waste tyre management methods viz. landfilling, recycling, reuse and retreatment present with them a number of challenges stemming from the associated negative environmental impacts and the low customer acceptance when retreated. As such, only a small percentage of waste tyres may be managed through the outlined traditional means without causing a detremental harm to the environment. In light of the limitations associated with traditional management means, thermal treatment technologies are emerging as a viable alternative approach able to handle large tyre volumes. Apart from the ability of the thermal treatment technologies to handle large volumes, the basic tyre chemical make-up and composition makes it an attractive material that may present potential energy recovery when exposed to thermal treatment means. Evidently, among other tyre qualities, tyres have high calorific value, high carbon and hydrogen content, a clear indication of high energy content.

Of the possible tyre thermal treatment technologies, pyrolysis is considered a preferred method as it generates lower nitrogen oxide and sulphur oxide emission compared with the incineration process. Tyre pyrolysis is also considered an environmentally attractive method as its yields products that are relatively easy to handle, store and transport. Tyre pyrolysis generates three main products, char, oil and non-condensable gases, with oil being the main desired product. Tyre pyrolysis energy rich by-products may be combusted to sustain the entire process, a process quality that in effect constitutes tyre pyrolysis process an energy self-reliant process. With regards to the factors influencing tyre pyrolysis process for maximizing oil yield, the operating temperature is regarded a crucial process governing parameter. To attain added benefit in maximizing the oil yield other factors come into effect. These include running the pyrolysis plant using a mixed reactor (fluidised bed and kiln reactors) coupled with smaller particle size and lower operating pressure. Depending on the financial feasibility studies, a catalyst may be added to improve the oil production yield and quality. In terms of the optimum operating temperature, based on the reported findings in Table 2.*8* and Table 2.*9*, it may be observed that the optimum oil yield is generally attainable at temperatures averaging around 500 ^{o}C. The benefit of using reactors with some level of mixing aid faster reaction time and thereby improving the turn-around time. Higher residence time and heating rates may lead to improvements in the oil yield. Considerably increasing these parameters can result in the occurrence of the undesired secondary reactions. The secondary reactions negatively impact oil quality and yield as they favour the reversion of formed gases back to char products. The literature studies show that huge strides have been made on the simulation studies and a number of kinetics have been developed from experimentations to mimic an actual pyrolysis process. As such, pyrolysis simulations may be deemed reliable and acceptable. From the economic point of view, literature studies show that waste tyre pyrolysis process may be considered a feasible process, generally with payback periods less than of 4 years.

CHAPTER 3: Methodology

3.1. Overview of the chapter

This chapter details out the methodology followed in achieving the set objectives of this study. The chapter is divided into 5 subsections. Subsection 3.1 gives an overview of the entire chapter. Based on the learnings attained in chapter 2.6, the Section 3.2 presents the approach followed in this study and the relevant alterations thereof. Subsection 3.3 details out waste pyrolysis process description and how the said process was built into the ASPEN Plus simulation software. Subsection 3.4 gives an economic evaluation procedure followed in this study. The last section, subsection 3.6 summarises key points of the entire chapter.

3.2. Methodology followed in this study

This study was carried out using simulation approach as per the literature learnings detailed out in section 2.6. Literature studies delineated that simulations gives as much reliable knowledge as experiments (section 2.6). The simulation studies for this research were carried out using ASPEN plus computer simulation software. Following the development of the simulation and validation, an economical study was carried out using published costing models as outlined in section 2.7. To validate this study, the first point of reference was attained from the literature reported percentage error of the kinetics used as reported by various authors. Another point of reference used to validate this study was based on the typical pyrolysis product yields as depicted in Table 2.8 and Table 2.9 (section 2.5.10).

3.3. Process description

To develop a waste tyre pyrolysis simulation, various units from ASPEN Plus pallets were used to mimic a working model. The lay out followed in developing the model was taken from the simulation flowsheet reported by Ismail, et al (2016), some modifications were made to best accommodate the research objectives of the current study. The developed simulation specific to the current study consisted of the heat exchanger (HX-4) used to heat up tyres fed into the process. The heated-up tyres were fed into the DRYER where moisture is removed prior pyrolysis reactions. After drying and removal of the moisture from the tyres, the tyres are fed into the decomposition block, modelled using RYIED pallet named DECOMP in the simulation. In the DECOMP the tyres are decomposed into their basic ultanal components, viz. C, S, H_2, N_2, Cl_2, O_2 and ASH. The decomposed tyres are then fed into the EQUILIBRIUM block named H2S-EQUL in the simulation. The purpose of the H2S-EQUL block is by principle of equilibrium to form H_2S gas from reacting S with the required H_2 gas. The H2S-EQUL gives two stream products, one rich in H_2S and the other rich in other unreacted tyre ultanal components. The two products from the H2S-EQUL are combined and fed into the reactor block named CSTR. In the CSTR Arrhenius reaction kinetic are used to generate gases from which oil and non-condensable gases are derived using a COOLER heat exchanger. The non-condensable gases are combusted to generate heat which is used to heat up the tyres to the reaction temperature. The unreacted carbon from the reaction is recovered as char together with ash thorough a SEPARATOR block. Figure 3.*1* below gives a schematic outline of the model developed.

Two more different simulation set up were developed to achieve tyre pyrolysis, these were developed to mimic a PFR and a kiln reactor, the flowsheet for these are shown below in Figure 3.*2* and Figure 3.*3* respectively. ASPEN Plus simulation does not have a single model pallet for the kiln reactor, hence this reactor type was modelled using three CSTR reactors operated and different operating temperatures. Modelling of different reactors was crucial in enabling an understanding of the impact that the various reactor types have on the products yields. The simulation of each reactor had to be modelled independently as each reactor type carries with it a different set of governing factors. These differences in effect impacts the product yields and quality. The last simulation flowsheet done was based on the RGibbs reactor type where rigorous reactions were completed through equilibrium principles to generate products components outlined in Appendix B (Figure 3.4).

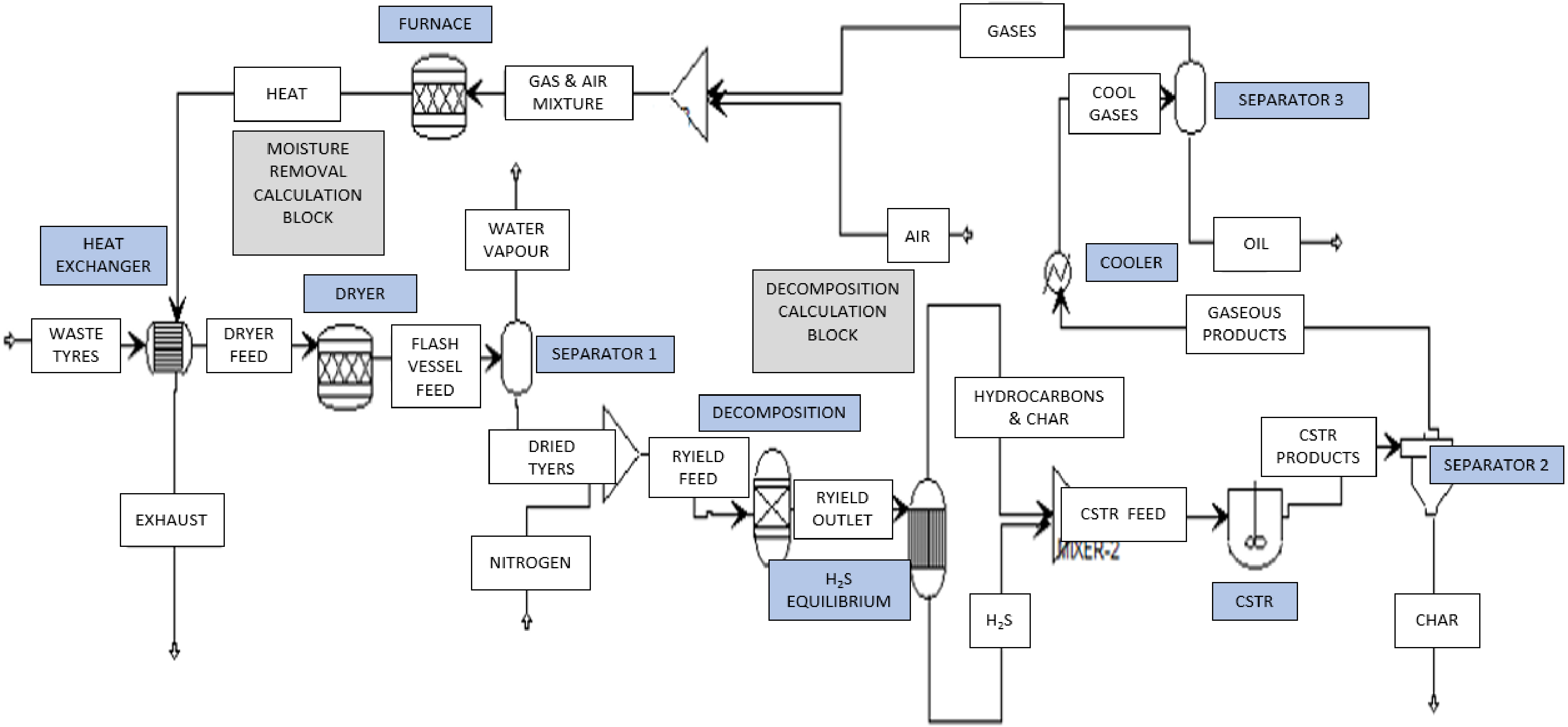


Figure 3.1: CSTR tyre pyrolysis ASPEN plus simulation flowsheet

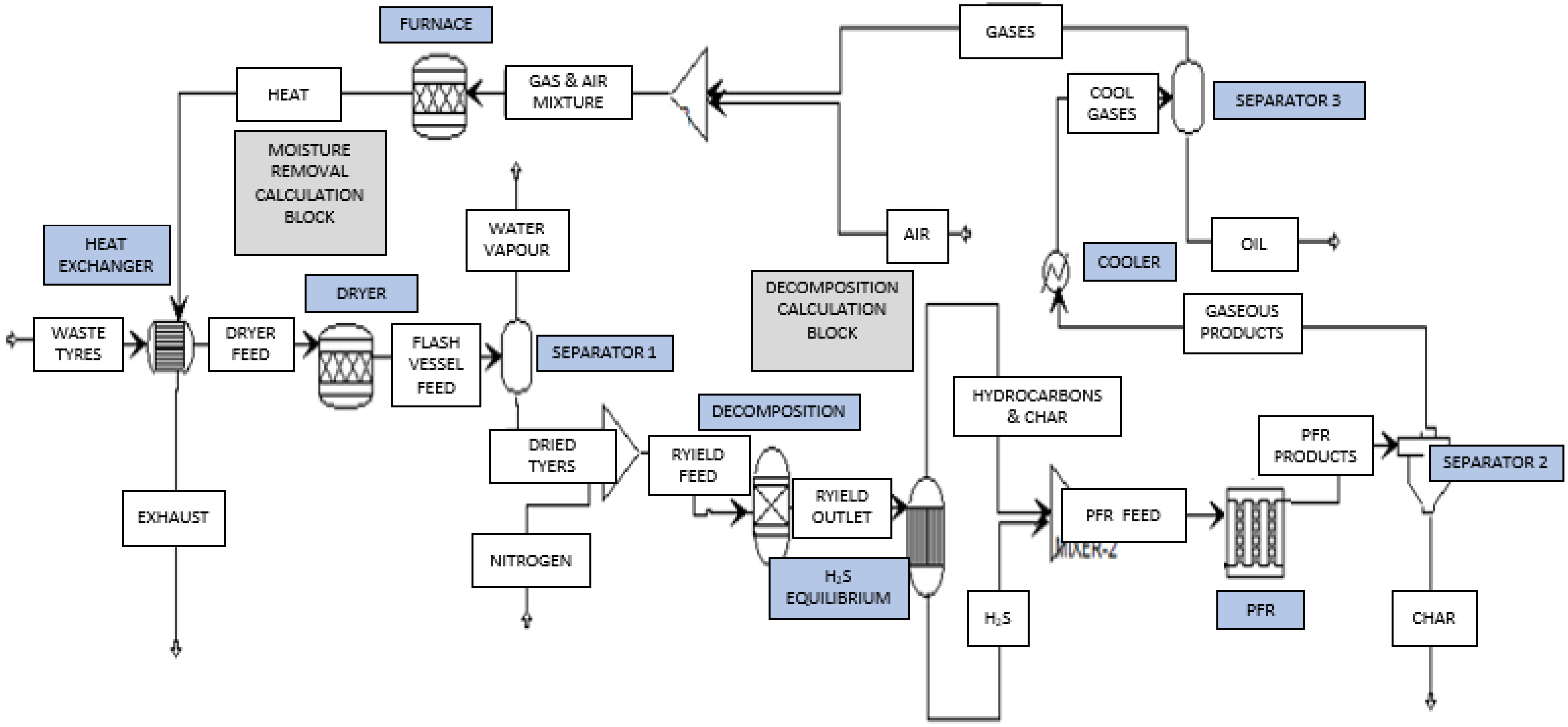


Figure 3.2: PFR tyre pyrolysis ASPEN plus simulation flowsheet

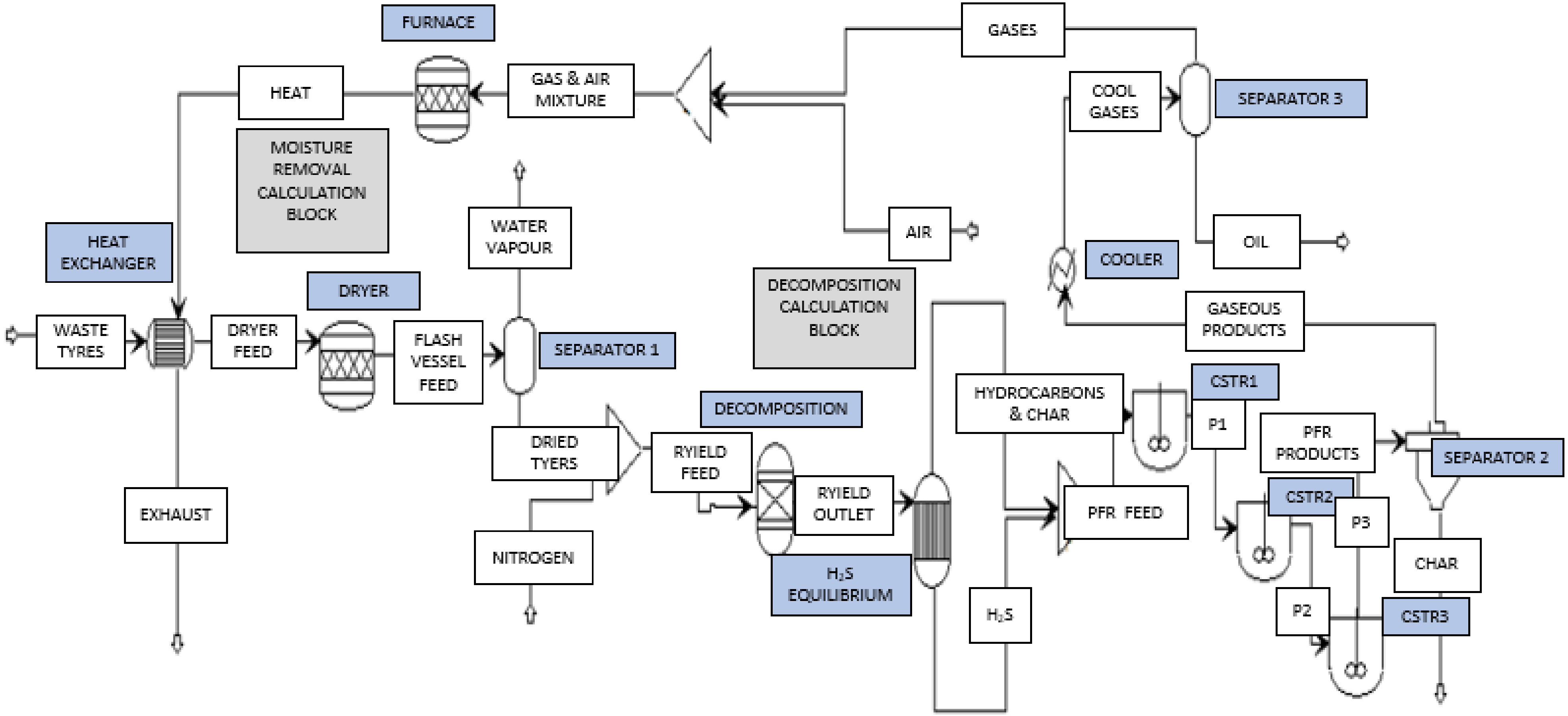


Figure 3.3: Kiln reactor tyre pyrolysis ASPEN plus simulation flowsheet

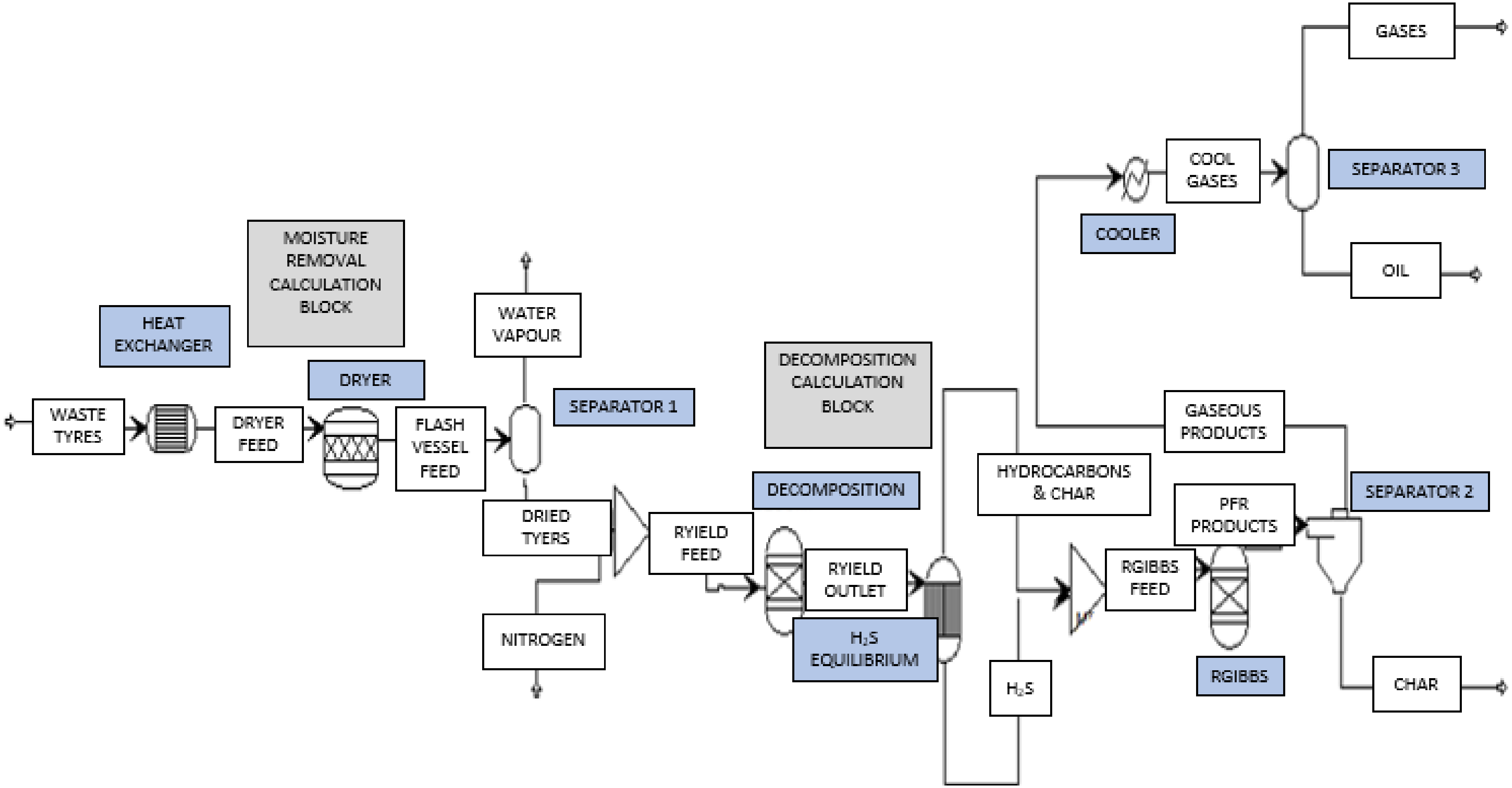


Figure 3.4: RGibbs reactor tyre pyrolysis ASPEN plus simulation flowsheet

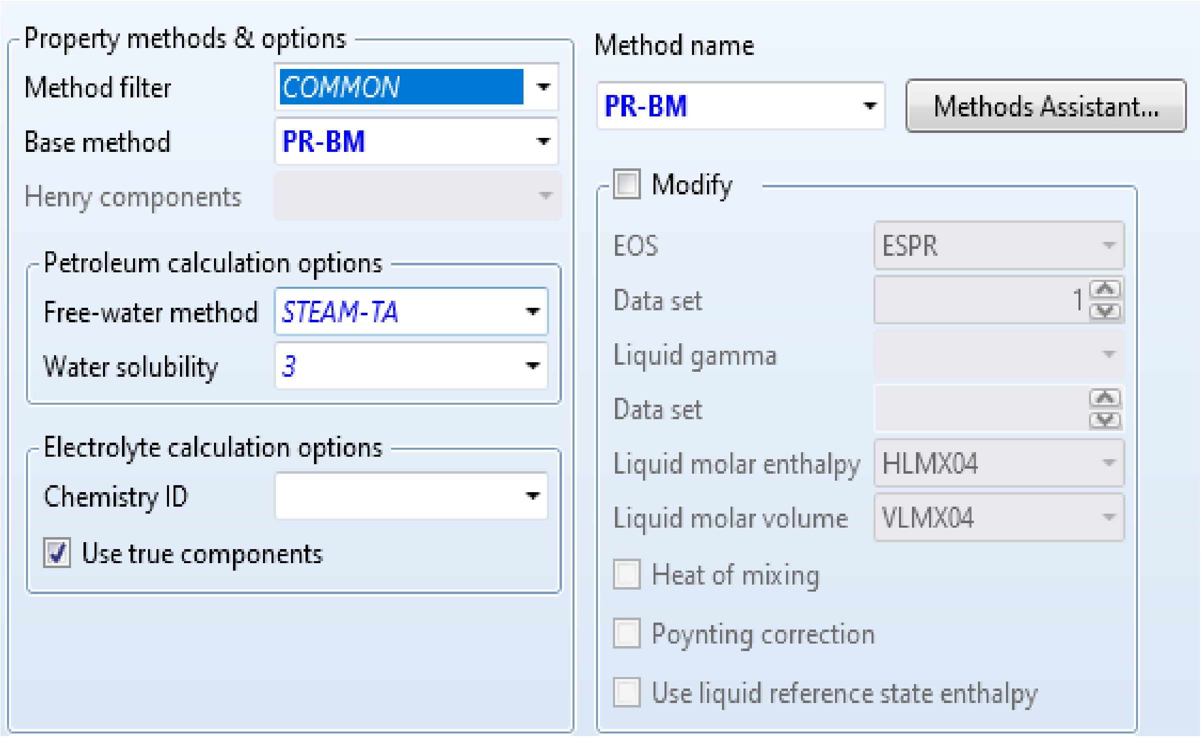
3.3.1. Assumptions

The following assumptions were made in undertaking this study:

- The system is in steady state
- The system is isothermal
- Ash does not take part in the reactions
- Carrier gas (N_2) does not take part in the reactions
- Carrier gas is sufficient to removal all the gases formed in the reactor
- The system is zero dimensional
- Pressure drop is negligible
- Complete combustion of the non-condensable gases in the furnace
- Tyres are fed into the process crushed

3.3.2. Property method and stream class

Different property methods were investigated in this study, of the methods investigated, two property methods showed to yield results relatively close to the typical product yield as reported in literature (*Table 2.8* and *Table 2.9*). These methods were Peng Robinson equation of state with Boston-Mathias (PR-BM) alpha and PR-BM78 modification. The findings were in line with the expectations as the PR-BM equation of state is recommended for use in the gaseous systems, refinery and petrochemical applications (Aspentech, 2022). As outlined in section 2.2, tyres contain petroleum products, when exposed to the pyrolysis process they yield products rich in hydrocarbons, evidently these attributes make PR-BM a suitable equation of state. One of the products from tyre pyrolysis process is the tyre derived oil with has properties close to those of diesel. Hence using PR-BM in this investigation further validates its use in the waste tyre pyrolysis applications. In conducting the current research study scenarios and comparative studies, only the standard PR-BM was considered as the two physical methods showed to yield similar outcomes. Figure 3.5 gives Aspen plus depiction of the method selection, in Figure 3.5 it may be observed that the PR-BM method is selected as the base method.


Property methods & options

Method filter: COMMON

Base method: PR-BM

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Method name: PR-BM

☐ Modify

EOS: ESPR

Data set: 1

Liquid gamma:

Data set:

Liquid molar enthalpy: HLMX04

Liquid molar volume: VLMX04

☐ Heat of mixing

☐ Poynting correction

☐ Use liquid reference state enthalpy

Figure 3.5: ASPEN Plus property method selection

Regarding the enthalpy and density model selection, HCOALGEN and DCOALIGT methods were selected respectively. The correct method selection for estimating various simulation aspects plays a crucial role in the reliability of the findings. Table 3.*11* below gives a summary of all the associated methods used for undertaking the tyre pyrolysis simulation studies:

Table 3.11: Property method

Property method	**Model**
Base method	PR-BM
Enthalpy model	HCOALGEN
Density	DCOALIGT

3.3.3. Feedstock

Table 3.12 and Table 3.13 below outlines feed stream breakdown with respect to the constituents, compositions and process specifications. Table 3.12 provides details on the feed stream specifications while Table 3.13 specifically gives the ultanal and proximal analysis for the waste tyre feed stream used for the current study.

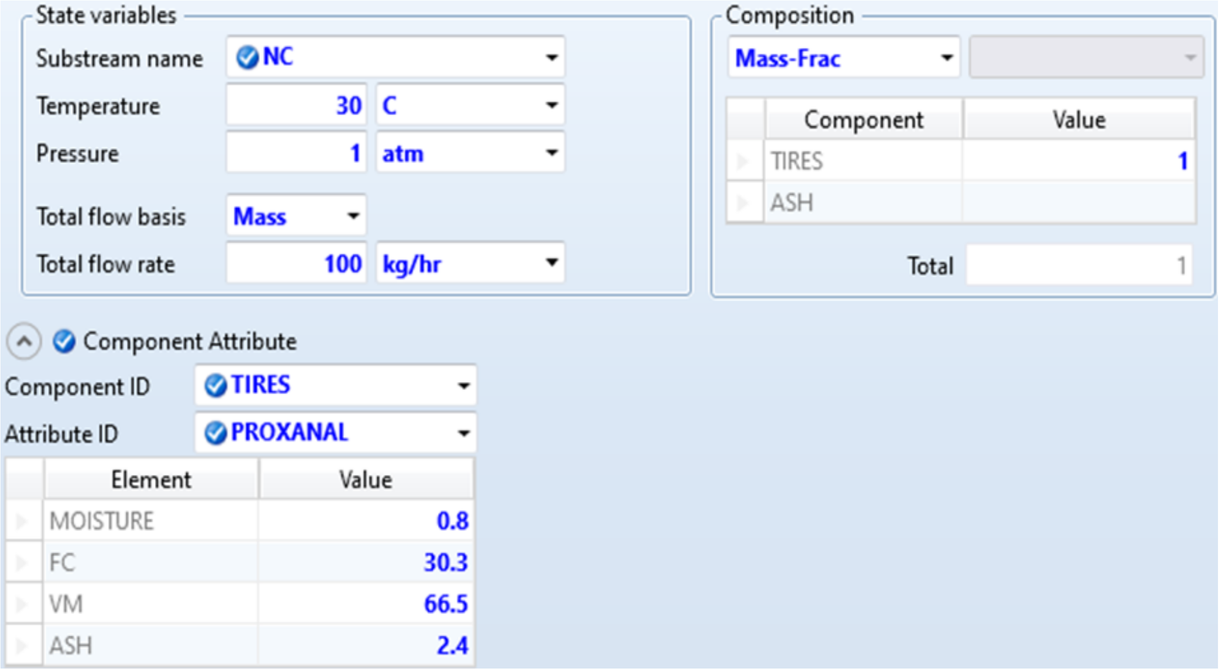
Table 3.12: Feed streams specifications (Williams, et al., 1990)

Stream	**Components**	**Pressure (atm)**	**Temperature (ºC)**	**Flow (kg/hr)**
Tyres	As reported in Table 3.13	1	30	100
N2	100 % Nitrogen (N_2)	1	150	1.6
Air	79 % N_2 and 21 % O_2	1	30	1088

Table 3.13: wet basis ultanal and proxanal elemental analysis used for this study (Williams, et al., 1990)

Ultanal analysis	**wt (%)**	**Proxanal analysis**	**wt (%)**
C	85.9	Ash	2.4
H	8	Moisture	0.8
N	0.4	Fixed carbon	30.3
Cl	0	Volatile material	66.5
S	1.0		
O	2.3		

Figures 3.6, 3.7 and 3.8 show the input of the tyre proxanal, ultanal and sulfanal in the ASPEN simulation environment. It may be observed that the tyre stream is categorized as nonconventional stream as tyres are not standard ASPEN Plus component, this category was also adopted for the ash component.



State variables

Substream name: NC
Temperature: 30 C
Pressure: 1 atm
Total flow basis: Mass
Total flow rate: 100 kg/hr

Composition: Mass-Frac

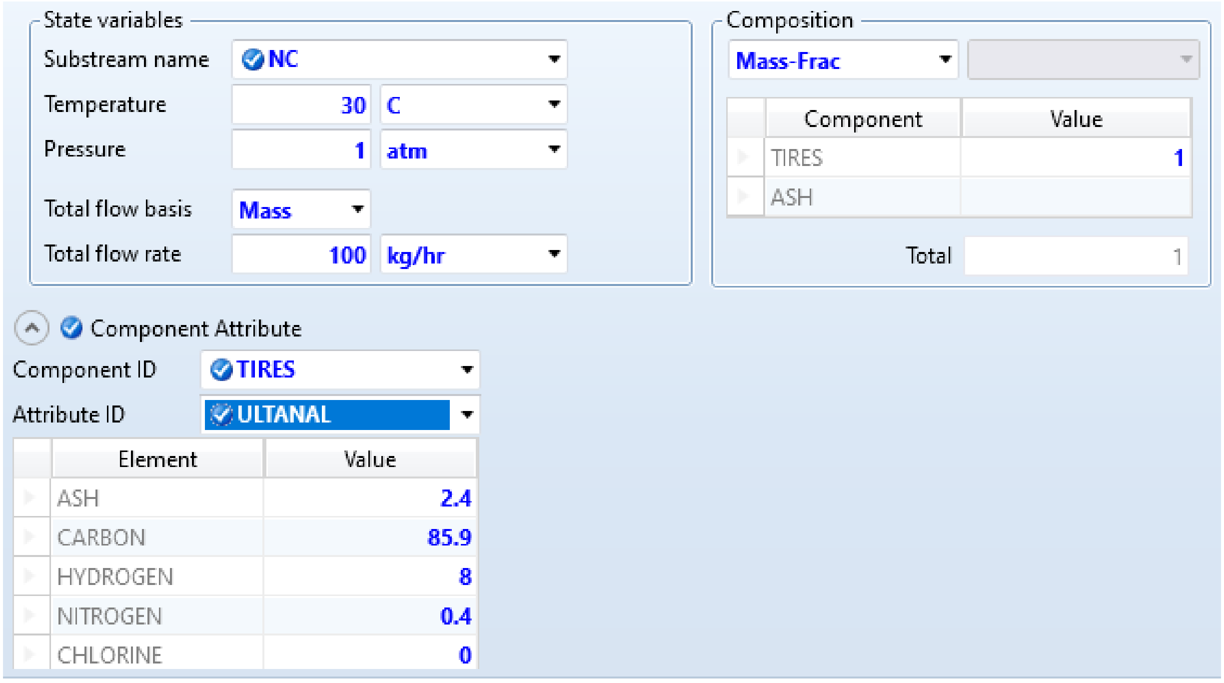
Component	Value
TIRES	1
ASH	
Total	1

Component Attribute

Component ID: TIRES
Attribute ID: PROXANAL

Element	Value
MOISTURE	0.8
FC	30.3
VM	66.5
ASH	2.4

Figure 3.6: ASPEN Plus tyre proxanal inputs



State variables

Substream name: NC
Temperature: 30 C
Pressure: 1 atm
Total flow basis: Mass
Total flow rate: 100 kg/hr

Composition: Mass-Frac

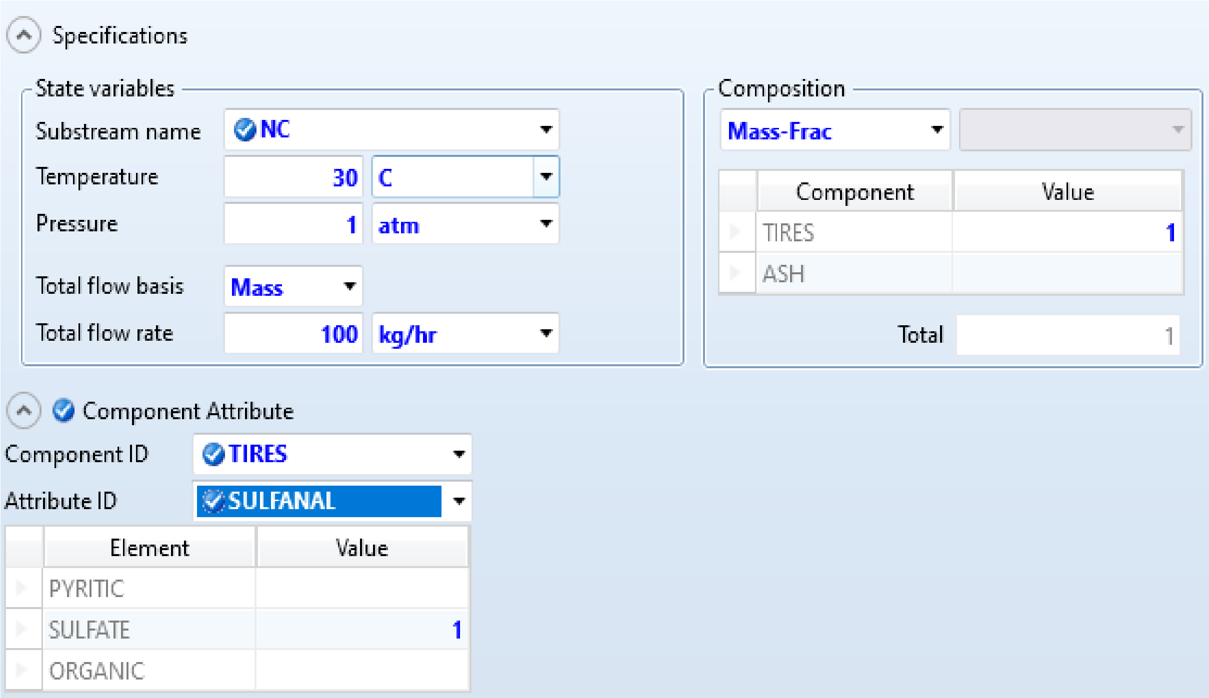
Component	Value
TIRES	1
ASH	
Total	1

Component Attribute

Component ID: TIRES
Attribute ID: ULTANAL

Element	Value
ASH	2.4
CARBON	85.9
HYDROGEN	8
NITROGEN	0.4
CHLORINE	0

Figure 3.7: ASPEN Plus tyre ultanal inputs



Specifications

State variables

Substream name: NC

Temperature: 30 C

Pressure: 1 atm

Total flow basis: Mass

Total flow rate: 100 kg/hr

Composition

Mass-Frac

Component	Value
TIRES	1
ASH	

Total: 1

Component Attribute

Component ID: TIRES

Attribute ID: SULFANAL

Element	Value
PYRITIC	
SULFATE	1
ORGANIC	

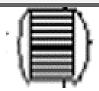
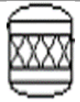
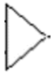
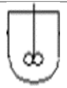
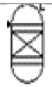
Figure 3.8: ASPEN Plus tyre sulfanal inputs

The other basic components used in the simulation such as basic tyre pyrolysis gaseous constituents were all simulated as standard conventional streams and were selected from the ASPEN Plus chemical data base. To simplify the study, a basic 100 kg/hr was used throughout the study, but the outcomes are not limited to the selected feed flow. Since the attained outcomes were presented and validated against literature in terms of percentages the outcomes may be scaled to the required feed rates.

3.3.4. Simulation blocks and specifications

Table 3.*14* below gives a comprehensive breakdown of the simulation blocks used in the development of the ASPEN plus waste tyre pyrolysis process. The breakdown given below are as depicted in Figures 3.1, 3.2, 3.3 and 3.4. The block naming on Table 3.14 was kept consistent with the naming used in the simulation environment. The blocks used collectively combine to form a working waste tyre pyrolysis process as the ASPEN Plus does not have a ready built in pyrolysis process. As such the blocks selected were based on the literature learnings with alterations specific to the current study to mimic the desired operating conditions. ASPEN Plus block selection was also done such that the model accommodates various investigations carried out through sensitively analysis.

Table 3.14: Block specifications used to model tyre pyrolysis

Block ID	**ASPEN ID**	**ASPEN Icon**	**Function**
Heater	HX4		Heats up tyres to the reactor temperature.
DRYER	Dryer		Liberates water from tyres.
MIXER (S)	Mixer-1		Used in the simulation to mix multiple streams into one stream.
RYIELD	Decomp		Decomposes tyres into the basic ultanal elemental components as provided in Table 3.*13*.
RYIELD	H2S-EQUL		Equilibrium conversion of S into H_2S.
REACTOR	CSTR		Through means of employing specific kinetics, converts the elements into gas and char products.
	PFR		
	RGIBBS		
SEPARATOR	Sep-1		Separates solid char from gases, dominantly solids are made up of unreacted solid carbon and ash while gases are rich in hydrocarbons.

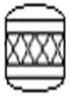
COOLER	Cooler		Cools the gases back to room temperature thereby condensing pyrotic oil and liberating the non-condensable gases
SEPARATOR	Sep-2		Separates the pyroltic oil from the non-condensable gases
FURNACE	Combust		Combustion of the non-condensable gases into CO$_2$ and Water. The resulting heat is used to heat up the incoming tyres to the desired rection temperature.

Table 3.15 below gives the operating conditions of the outlined simulation blocks outlined in Table 3.14.

Table 3.15: Block specifications

Block	Temperature (ºC)	Pressure (atm)
HX4	550	1
Dryer	125	1
Moist	125	1
Decomp	550	1
H2S-EQUL	550	1
Mixer-2	550	1
CSTR / PFR / RGibbs	550	1
Sep-1	550	1
Cooler	30	1
Sep-2	30	1
Mixer-3	30	1
Combust	900	1

3.3.5. Calculator blocks

In the development of the simulation, calculation blocks were used to conduct calculations that could not be modelled using the basic ASPEN simulation Palette blocks. The calculation blocks used in the simulation were named WATER and DECO. The Fortran statements were employed in the execution of the calculation blocks used in the simulation environment.

3.3.5.1. Water calculation block

The WATER calculation block was used to achieve 100 % removal of water from the waste tyre feed stream. In the calculation statement outlined, H2OIN refers to the water content pre drying, while H2ODRY refers to the H2O content post drying and the CONV is the calculation employed. WATER calculation block is therefore used as a dryer representation in the ASPEN simulation environment.

Fortran declarations:

$$\mathrm{H2ODRY} = 0$$

$$\mathrm{CONVE} = \frac{(\mathrm{H2OIN} - \mathrm{H2ODRY})}{(100 - \mathrm{H2ODRY})}$$

Tables 3.16, 3.17 and 3.18 below gives a summary of the WATER calculation block set up.

Table 3.16: Variable description

Variable name	Description
H2OIN	Dryer feed stream water content
CONVE	Conversion
H2ODRY	Dryer outlet stream water content

Table 3.17: Stream components

Variable	Type	Stream	sub stream	Component	attribute	Element
H2OIN	Compattr-Var	TYRES	NC	TYRES	PROXANAL	1

Table 3.18: Block components

Variable	Type	Block	Variable	Sentence	ID1	ID2	ID3	Element
CONVE	Block-Var	DRYER	CONV	CONV	1	-	-	-
H2ODRY	Block-Var	DRYER	COMPATT	COMP-ATTR	NC	TYRES	PROXANAL	1

3.3.5.2. DECO calculation block

The DECO block is used to liberate the ultanal components from the waste tyres into the individual elements. The DECO block outcomes are based on the ultanal components specified in Table 3.*13*. The associated calculations are as per the Fortran declaration outlined below. The Ult refers to ultanal parameter within which CARB (carbon), H_2, N_2, S and O_2 are contained. Since the simulation has a nitrogen stream which is used to drive off generated gases in the pyrolysis reactor, the N_2 calculation was set up such that the ultanal N_2 is considered independently from the N_2 fed as a 100 % stream. However, on the product stream the two N_2 components were combined in the calculation block for the mass balance to hold.

Fortran declarations:

$$\mathrm{ASH} = \frac{\left(\frac{\mathrm{ULT}(1)}{100} \times \mathrm{TYRES}\right)}{(\mathrm{TYRES} + \mathrm{NITROGEN})}$$

$$\mathrm{CARB} = \frac{\left(\frac{\mathrm{ULT}(2)}{100} \times \mathrm{TYRES}\right)}{(\mathrm{TYRES} + \mathrm{NITROGEN})}$$

$$\mathrm{H_2} = \frac{\left(\frac{\mathrm{ULT}(3)}{100} \times \mathrm{TYRES}\right)}{(\mathrm{TYRES} + \mathrm{NITROGEN})}$$

$$\mathrm{N_2} = \frac{\left(\mathrm{NITROGEN} + \frac{\mathrm{ULT}(4)}{100} \times \mathrm{TYRES}\right)}{(\mathrm{TYRES} + \mathrm{NITROGEN})}$$

$$\mathrm{S} = \frac{\left(\frac{\mathrm{ULT}(6)}{100} \times \mathrm{TYRES}\right)}{(\mathrm{TYRES} + \mathrm{NITROGEN})}$$

$$\mathrm{O_2} = \frac{\left(\frac{\mathrm{ULT}(7)}{100} \times \mathrm{TYRES}\right)}{(\mathrm{TYRES} + \mathrm{NITROGEN})}$$

Table 3.19: Variable description

Variable name	**Description**	**Variable name**	**Description**
ASH	Ash	S	Sulphur
CARB	Carbon	O_2	Oxygen
H_2	Hydrogen	ULT	Ultanal
N_2	Nitrogen		

Tables 3.20 and 3.21 below gives a summary of the DECO calculation block set up.

Table 3.20: Stream components

Variable	Type	Stream	sub stream	Component	attribute	Element	Units
WATER	Compattr-Var	RFEED	NC	TYRES	PROXANAL	1	-
NITROGEN	Mass-Flow	RFEED	MIXED	N2	-	-	kg/hr
TYRES	Mass-Flow	RFEED	NC	TYRES	-	-	kg/hr
ULT	Compattr-Vec	RFEED	NC	TYRES	ULTANAL	-	-

Table 3.21: Block components

Variable	Type	Block	Variable	Sentence	ID1	ID2
ASH	Block-Var	DECOMP	MASS-YIELD	MASS-YIELD	ASH	NC
CARB	Block-Var	DECOMP	MASS-YIELD	MASS-YIELD	CARBON	CISOLID
H2	Block-Var	DECOMP	MASS-YIELD	MASS-YIELD	H2	MIXED
N2	Block-Var	DECOMP	MASS-YIELD	MASS-YIELD	N2	MIXED
S	Block-Var	DECOMP	MASS-YIELD	MASS-YIELD	S	MIXED
O2	Block-Var	DECOMP	MASS-YIELD	MASS-YIELD	OXYGE-01	MIXED

3.3.6. Reaction kinetics

This subsection gives a detailed breakdown of the reaction kinetic used in this study. The kinetics used were sourced from various waste tyre pyrolysis research studies. The kinetics reported are grouped according to the parameters investigated. As such, each reaction grouping has its own basecase kinetics from which the scenarios kinetics were established. When the kinetics were developed in literature studies, the validations were done against experimental results. Based on the experimental results, some of the kinetics reported in this subsection have relative error presented against the experimental data from which they were developed. The kinetics used for this study were lumped, this entail that each product viz. char, tyre derived oil and non-condensable gases had its own governing kinetics. The lumping approach was adopted for this study as most of the literature studies also used this method. Ismail, et al (2016) reported the kinetics for the individual components of tyre pyrolysis products (Appendix A). Up to 96 components may be attained from a tyre pyrolysis process (Appendix A), as such this may prove to be complicated to simulate. Furthermore, there are limited studies done to the level of individual components. This limitation in effect limits the experiments against which the kinetics may be validated. Hence the lumped kinetics approach is a more acceptable method of dealing with waste tyre pyrolysis simulations.

3.3.6.1. Impact of temperature kinetics

Table 3.*22* below reports the operation temperature lumped kinetics developed by Ismail, et al (2016) against the experimental data. Ismail, et al. (2016) reported that the developed kinetics were within reasonable accuracy as they presented relative error of ±24.61 % at 400 ºC, ±17.95 at 500 ºC, ±9.93 at 600 ºC and ±9.09 at 700 ºC. Discrepancies reported were attributed to the difference in the heating rates between the experiment and the model. The heating rate gap identified by Ismail, et al. (2016) may not be considered in the simulation environment as the studies conducted in the ASPEN Plus environment are generally steady state while the heating rate is an unsteady state parameter. The kinetics developed by Ismail, et al. (2016) were all based on the Arrenhius model.

Table 3.22: Temperature studies kinetics (Ismail, et al., 2016)

Parameter	Gas	Non-aromatics oil	Aromatics oil
A (s^{-1})	0.40428	0.2	8.4214
n	0	0	0
E (J/mol)	2301	1590	32890

3.3.6.2. Heating rate kinetics

As outlined above, the heating rate is an unsteady state parameter and may prove difficult to simulate in the ASPEN plus environment. The gap identified in the heating rate parameter was addressed in various studies through running experiments at different fixed heating rates to a constant temperature. From the fixed heating rates experiments the models were developed. The literature developed investigations involving the heating rate were mainly focused on defining the kinetics specific to the impact of running pyrolysis at different heating rates. In a study by Uzun & Yamen (2014) a number of reaction models were used to develop kinetics for the different heating rates and different feed stocks. For the current study applications only the findings for the Arrenhius model were used from Uzun & Yamen (2014) investigations (Table 3.*22*). The new basecase was considered to be at 5 K/min.

Table 3.23: Kinetics for different heating rates (Uzun & Yamen, 2014)

Heating rate (K.min^{-1})	**E_a (kJ.mol^{-1})**	**Log A (min^{-1})**
5	69.11	5.27
10	79.73	6.41
15	60.99	4.69
20	67.03	5.34

3.3.6.3. Catalyst incorporation kinetics

For the catalytic kinetics, parameters developed by Mazloom, et al (2009) were used in this study. Mazloom, et al (2009) defined the lumped paramters for the lighter cuts as C and D while E was used to represent the heavier component. The reactions were described as follows (Equation 3):

$$\mathrm{A} \overset{k1}{\rightarrow} \mathrm{B}, \mathrm{B} \overset{k2}{\rightarrow} \mathrm{C}, \mathrm{B} \overset{k2}{\rightarrow} \mathrm{C}, \mathrm{B} \overset{k3}{\rightarrow} \mathrm{D} \text{ and } \mathrm{B} \overset{k4}{\rightarrow} \mathrm{E} \qquad \textbf{Equation 3}$$

In effect, the definition of lighter components in Mazloom, et al (2009) studies imply the tyre derived oil and non-condensable gases (C and D) while the heviour components entails the char products (E). In the catalytic investigations, the new basecase was considered to be the kinetics provided for the thermal pyrolysis column in Table 3.24 below while scenario was denoted the catalytic pyrolysis.

Table 3.24: Non catalytic and catalytic parameters (Mazloom, et al., 2009)

k_i	**Thermal pyrolysis**		**Catalytic pyrolysis**	
	A_i (h^{-1})	**E_i (J/mol)**	**A_i (h^{-1})**	**E_i (J/mol)**
k_1	1.21	5.90×10^3	30.6	5.59×10^5
k_2	8.57×10^{-1}	2.00×10^3	63.6	6.48×10^3
k_3	7.16×10^{-1}	0.00×10^0	116.40	3.48×10^3
k_4	3.08×10^{-1}	2.91×10^3	307.80	1.24×10^4
k_5	-	-	76.80	4.64×10^3

3.3.6.4. Particle size kinetics

From the studies by Olazar, et al. (2005) particle size reaction kientics reported in Table 3.*25* were developed. Olazar, et al. (2005) reported a ±5 % from the studies. Olazar, et al. (2005) kinetics were developed based on the experimental work that focused on the particle size of the tyres. In the studies, two particle size classes were investigated. There was no specification as to which class constituted a basecase. A comparison between the two classes was thus purely aimed at understanding the particle size influence.

Table 3.25: Particle size kinetics parameters (Olazar, et al., 2005)

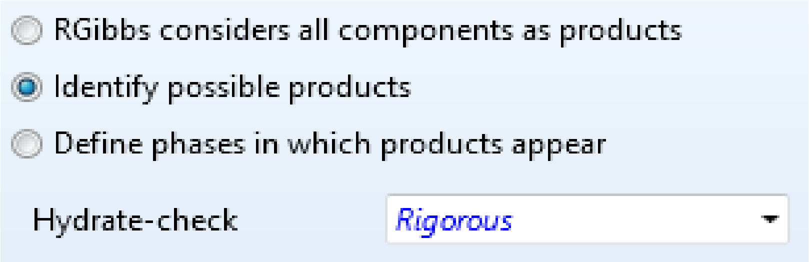
d_p (mm)	**T (°C)**	**k (s^{-1})**	**E (kJ/mol)**	**k_0 (s^{-1})**
0.8-4	450	0.00221	41.30	2.315
	500	0.00344		
	550	0.00509		
	600	0.00719		
0.1-0.8	450	0.00171	121.30	1×10^6
	500	0.00631		
	550	0.01987		
	600	0.05487		

3.3.6.5. Simulation used for the respective kinetics

The kinetics outlined in Table 3.*22* were used for reactor and temperature comparative studies using the developed models in Figure 3.*1*, Figure 3.*2* and Figure 3.*3* for the CSTR, PFR and Kiln reactor respectively. For the comparative studies employing kinetics reported in Table 3.*23* through to Table 3.*25* only simulation depicted in Figure 3.*1* was used. Limiting the studies from kinetics in Table 3.*23* through to Table 3.*25* to only Figure 3.*1* was done to limit the variability, as such only one parameter was varied for each investigation.

3.3.6.6. RGibbs modelling

The RGibbs simulations were done using a rigorous approach, a complete breakdown of the possible products identified from the feed components are reported in Appendix B. The set-up layout of the RGibbs reactor is presented in Figure 3.9 below.



○ RGibbs considers all components as products

● Identify possible products

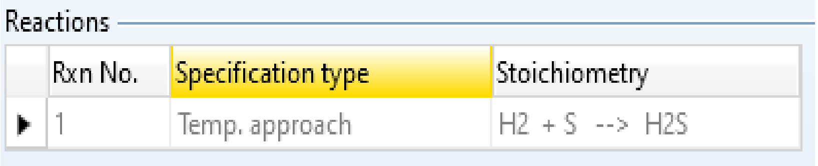
○ Define phases in which products appear

Hydrate-check: Rigorous

Figure 3.9: RGibbs set up

3.3.6.7. H_2S equilibrium modelling

The H2S generation was developed through an equilibrium reactor as depicted in *Figure 3.10* below.



Reactions

Rxn No.	Specification type	Stoichiometry
1	Temp. approach	H2 + S --> H2S

Figure 3.10: Generation of H2S

3.3.7. Optimum numerical model

In addition to the kinetic studies reported, Raj, et al (2013) developed a numerical model which encompasses different parameter into one equation with the aim of determining the optimum condition for maximum oil yield (Eq 4, Eq 5 and Eq 6).

Equation 4

$$\text{Oil (wt.\%)} = -28.03 + 0.42 \times A + 72.02 \times B - 4.71 \times C - 0.079 \times A \times B + 0.007 \times A \times C + 0.820 \times B \times C - 0.00057 \times A^2 - 28.94 \times B^2 + 0.01168 \times C^2$$

Equation 5

$$(\text{Gas})^3 \text{ (wt.\%)} = -267.716 + 891.23 \times A - 159 \times B + 11644.426 \times C + 2.199 \times A \times B - 40.42 \times A \times C + 9642.50 \times B \times C$$

Equation 6

$$\begin{aligned}\text{Char (wt.\%)} &= +221.339 - 0.698 \times \text{A} - 11.57 \times \text{B} - 1.287 \times \text{C} + 0.01 \times \text{A} \times \text{B} + 0.00897 \times \text{A} \times \text{C} \\ &\quad - 3.63 \times \text{B} \times \text{C} - 0.000535 \times \text{A}^2 + 37.19 \times \text{B}^2 - 0.000508 \times \text{C}^2\end{aligned}$$

Where:

Table 3.26: Numerical model variable description

Variable	Description	Units
A	Temperature	°C
B	Particle size	mm
C	Feed rate	g/min

As outlined above, a lot of research work around tyre pyrolysis modelling was carried out using lumped parameter kinetics. The complete reactions depicted in Appendix A and B are however only crucial to investigate in cases where final characteristics of the final products are considered. As such, complete reactions are more important in the case of characterising tyre derived pyrolysis oil against crude oil derived diesel. A number of aspects may be considered, these may be but not limited to the viscosity, CV and sulphur content. As such the layout of the study through lumped parameter kinetics was deemed sufficient for the aims and objectives set out for this study.

3.4. Economic evaluation of waste tyre pyrolysis

To understand the feasibility from the investment and running the pyrolysis plant perspective, a few case studies were reviewed. From the economic literature studies undertaken learnings were obtained with regards to the aspects of capital investment, running costs and the revenue point of view. Based on the number of years after start up, the analysis was conducted to understand the point at which tyre pyrolysis plant may start yielding a positive return on investment (ROI). Table 3.*27* below provides costing figures as reported in the literature studies, the reported prices were from three different regions, viz. China, Europe and South Africa from the studies by Fels & Pegg (2018), Riedewald & Sousa-Gallagher (2016) and Pilusa, et al, (2014) respectively. It may be observed that waste tyre pyrolysis products selling prices do not differ significantly from across the three regions investigated (Table 3.*27*). The figures from the literature were reported in $, for this investigation all figures were converted to ZAR, for the conversion an averaged 15 ZAR/USD exchange rate was used. In the South African study, the tipping fee was not reported, for the purpose of maintaining consistency in the investigations, an average between China and Ireland tipping values was used as South African tipping fee.

Table 3.27: Tyre pyrolysis plant costing

Source	(Fels & Pegg, 2018)	(Riedewald & Sousa-Gallagher, 2016)	(Pilusa, et al., 2014)
Region	China	Europe	South Africa
Waste tyres processed (t/year)	10000	40000	9000
Capital costs (mR)	75.6	425.7	64.05
Operating cost (R/ton)	3795	3855	4020
Tyre derived oil (R/ton)	6000	6315	8055
Carbon (R/ton)	4500	1575	4110
Steel (R/ton)	2250	1260	990
Tipping fee (R/ton)	1200	1530	1365*

*The tipping cost was not provided, an average of the two sources was used.

3.5. Summary

Based on the published work in line with this study, two methods applicable in achieving the objectives set out this study are delineated, namely, the experimentation and simulation approach. Based on literature learnings, it was concluded that simulations offer as much reliable data as that attained from experiments as they satisfy exploration, intervention, visulization requiremtns and can function as black boxe. Simualtions provide these aspects in a cost effective manner and allow further investigations that may prove impossible or difficults to be undertaken with experiments. The basis established substantiated confidence which allowed a decision for this study to also be carried out using the simulaion approach. ASPEN plus computer software was selected as a took to be used in undertaking the current study as it has the capabilities to mimic the complex mass and energy balance and equilibrium calculations. The models were independently developed for the four different types of reactors, vz. CSTR, PFR, Kiln reactor and RGibbs. The four developed reactor models were used to understand the impact of temperature and the reactor type on the tyre pyrolysis oil yield. Upon investigating other paramters through reactor kinetics and sensitivity analysis, only the CSTR model was used to understand their impact on the oil yield. Following the sensitivity analysis, an optimized numerical equation which considered temperature, perticle size and feed rate to determine the optimum conditions for the maximum oil yield was used. To some extent, the numerical approach was used as means of veriying the findings from the simulation studies. Other form of verificaiton was provided by reactor kinetics literature sources through reported relative error against the respective experimental data used. The section closes with an economic analysis section where costing figures from literature are provided.

CHAPTER 4: Results

4.1. Model validation

The developed model was based on various published literature work reaction kinetics developed from experimental data. From the validated literature kinetics, four simulations depicted in subsection 3.3 above were developed. The developed simulations were used extensively to investigate different scenarios for maximum tyre derived oil yield. Subsection 3.3.6 above provides both the kinetics used and the relative error obtained by the researchers. In particular the relative error for the catalyst and heating rate kinetics was not provided, however kinetics for the temperature impact by Ismail, et al (2016) and those by Olazar, et al., (2005) for the particle size were provied. The model outcomes were also checked against the typical oil yields as reported in Table 2.*8* and Table 2.*9*.

4.2. Physical property selection

In the investigations, the Peng Robinson equation of state with Boston-Mathias (PR-BM) modifications was used as the global physical property. Two forms of PR-BM were used, viz. the standard PR-BM and PR-BM78, the said equations of state were attained built in on the ASPEN plus simulation software. The simulation results from both PR-BM and PR-BM78 showed to be relatively in line with the expected oil yield as reported in Table 2.*8* and Table 2.*9*. The results in Figure 4.1 below show that the two physical property methods show relatively similar findings in terms of the oil yields.

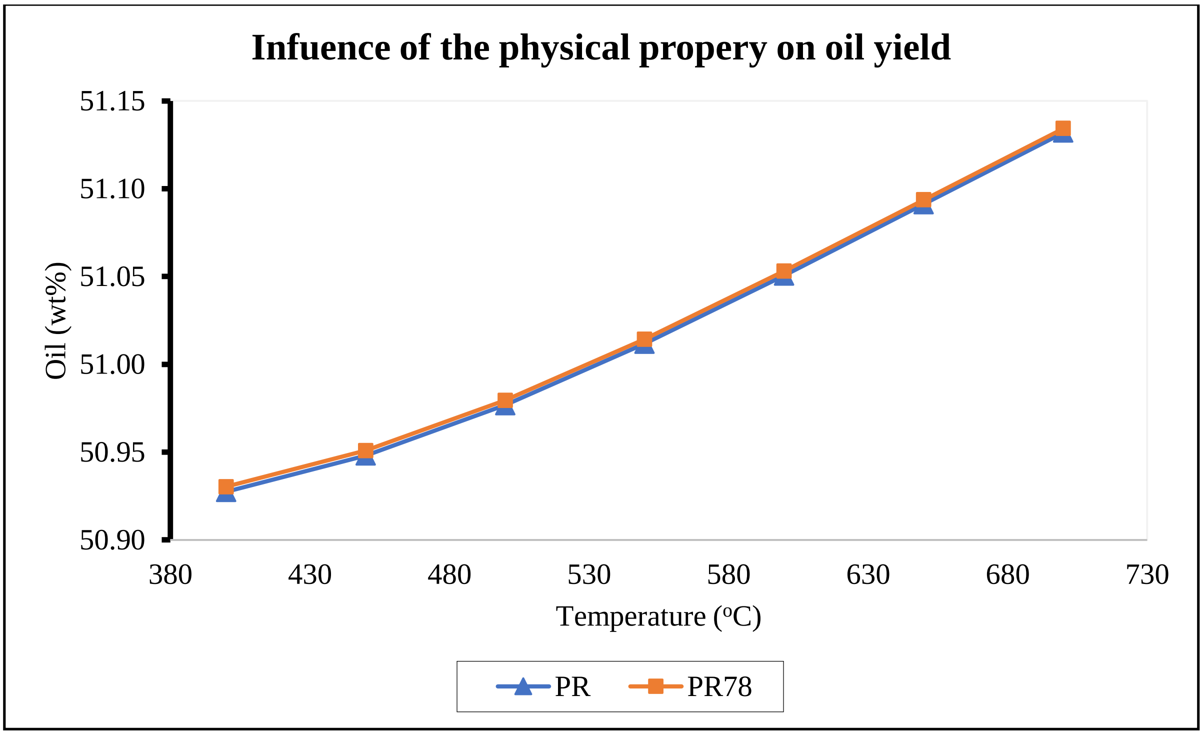


Figure 4.1: Impact of different equation of state *(wt.% are by weight of the waste tyre)*

4.3. Sensitivity analysis: Impact of reactor type and temperature

Figure 4.2 below show the impact of pyrolysis operating temperature and reactor type on the products yield. Figure 4.2 only focuses on the CSTR and PFR. It may be observed that as the temperature increases the oil yield increases from 50.93 % to 51.13 % and 44.02 to 44.13 on the CSTR and PFR respectively. According to the outcomes, it may be observed that the increase in the oil yield results in the decrease in char generated. This implies that with increase in temperature, more carbon in reacted with H_2 to form more pyrotic gases which subsequently condenses into more oil products. It may be observed that the mixing in the CSTR generally favours higher yield as opposed to the PFR reactor.

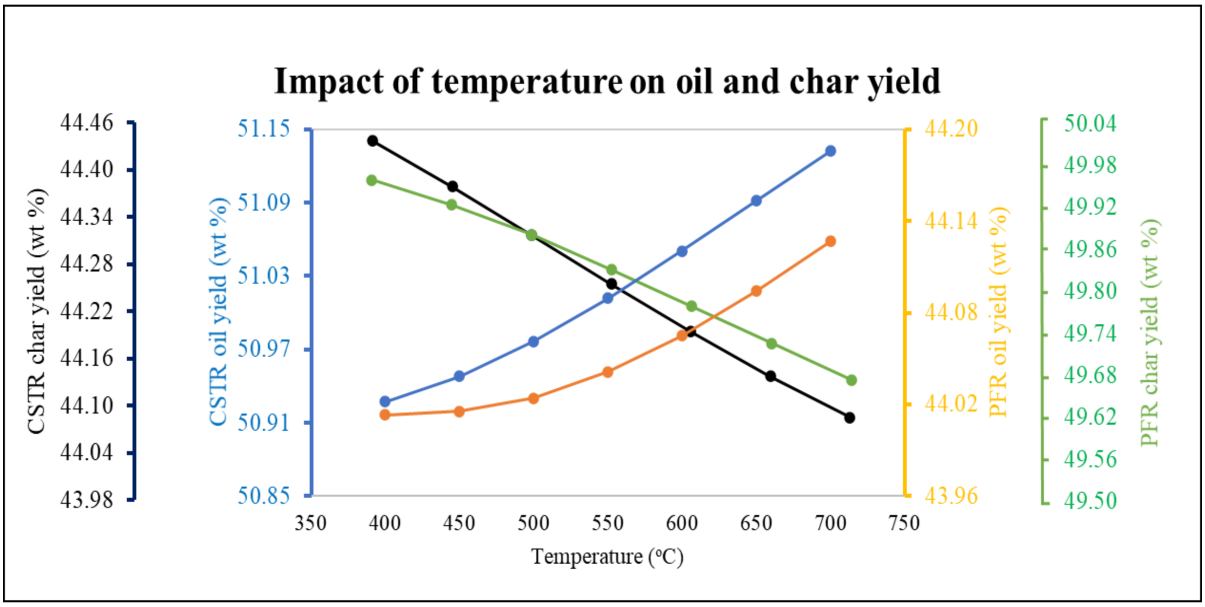


Figure 4.2: Influence of temperature on oil and char yield for the CSTR and PFR *(wt.% are by weight of the waste tyre)*

A similar trend as that observed in the oil yield as a function of temperature is observed on the gas generated, more non-condensable gases are generated as the reactor temperature increases (Figure 4.3). It may be observed that in terms of gas generated, the PFR reactor favours higher gas generated when compared to CSTR which favours higher oil generated than non-condensable gases. The non-condensable gases are mainly composed of C1-C4 hydrocarbons (Laresgoiti, et al., 2000).

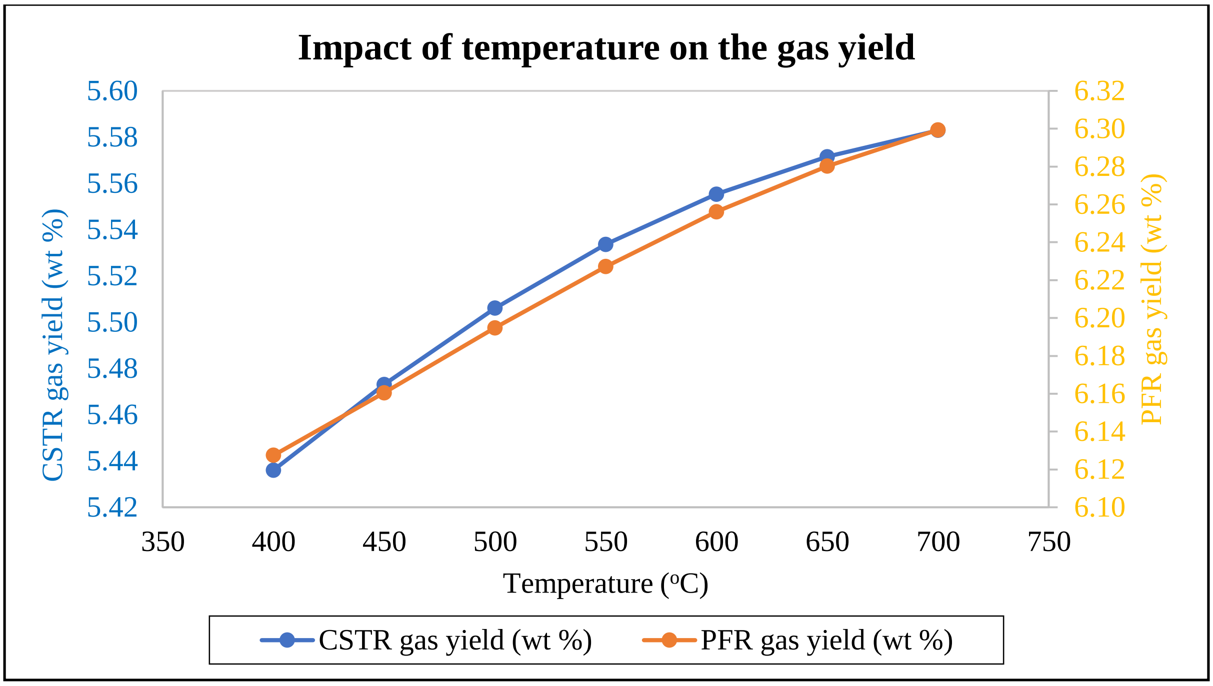


Figure 4.3: Effect of temperature on the gas yield for the CSTR and PFR *(wt.% are by weight of the waste tyre)*

4.4. Sensitivity analysis: Impact of reactor type at 550 °C

A kiln reactor was simulated using 3 CSTR reactors operating at different temperatures to aid mixing on each phase. Temperature profile studies done in Figure 4.2 and 4.3 for CSTR and PFR were not feasible with the kiln reactor. This in effect would have resulted in varying more than one parameter on the kiln reactor as different combinations of the 3 reactor temperatures would have been required. Hence, the consideration of kiln reactor against the CSTR and PFR was studied using a comparison at a constant temperature of 550 °C. The results showed that CSTR shows the highest oil yield of 51.01 %, followed by kiln reactor at 50.93 % while PFR showed lowest oil yield of 44.09 %. It may be observed that the char was highest on the PFR compared to the CSTR and kiln reactor. This implies that less carbon was reacted to form gases in the PFR and hence resulted in more char. The PFR also displayed highest non-condensable gases than the CSTR and kiln reactor. The poor performance of the PFR may be attribute to the fact that the PFR does not aid as much mixing as achieved from the CSTR and kiln reactor.

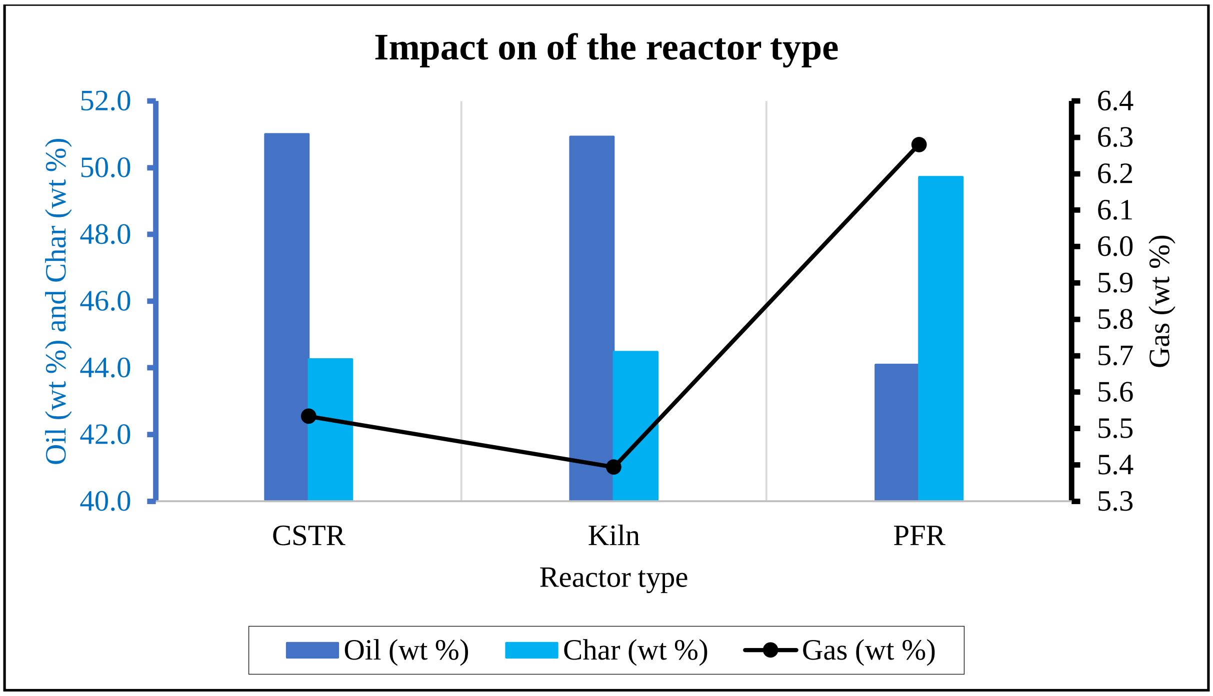


Figure 4.4: Comparisons between CSTR, Kiln reactor and PFR on products yield *(all wt.% are by weight of the waste tyre)*

The RGibbs reactor was also considered in the reactor type investigation, the RGibbs outcomes showed to result in higher oil yield which showed to be odd one out as per the expected results from literature studies. Evidently a figure of 67 % oil yield was attained from the RGibbs reactor of which was not used in the comparative studies. The RGibbs used a principle of achieving all the components as presented in Appendix B. As outlined, in addition to odd results from RGibbs there are limited studies that have done tyre pyrolysis to the level of individual components depicted in Appendix A and B.

4.5. Sensitivity analysis: Impact of residence time and reactor size

Figure 4.5 below presents the results of the influence of PFR length, PFR diameter and CSTR residence time. An increase in the PFR length show to have a slight positive impact on the oil yield, the increase was not as significant as that observed with temperature. The length was varied between 1 and 5 m and the oil yield increased from 44.08 % to 44.10 %. When the PFR diameter was increased from 0.1 to 2 m, the oil yield increased sharply between 0.1 and 1 m by 0.05 % points, beyond the 1 m mark the yield reduced to 44.09 % and remained relatively constant to a 2 m diameter mark. The CSTR showed an increase with the increase in the residence time, an increase of 0.04 % points was noted when the residence time was increased from 0.1 to 1 hr. The PFR length, PFR diameter, CSTR residence time, all these parameters have limitations as they have a direct impact on the equipment cost and thereby influencing capital cost. There are also space limitations associated with the improvements that come from equipment size while the residence time may negatively influence the production turnaround time. Hence the residence time and reactor size parameters present with them limited benefits.

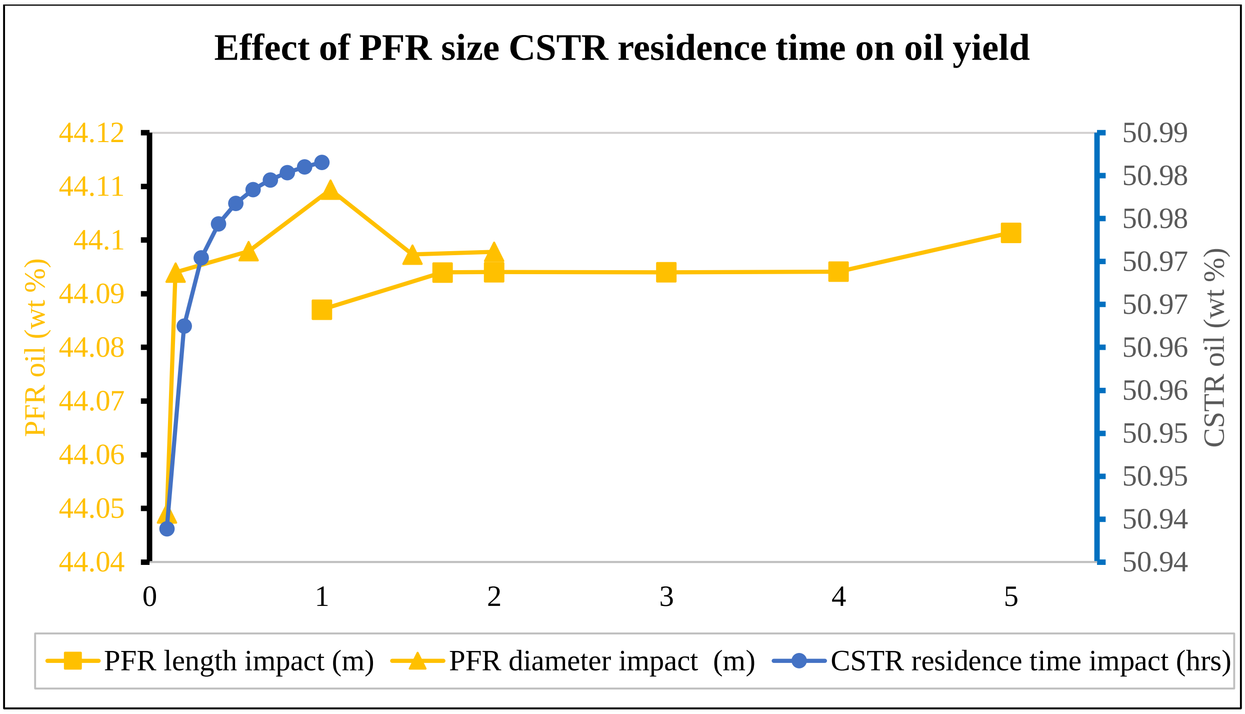


Figure 4.5: Effect of PFR size and CSTR residence time on the pyrolysis oil *(wt.% are by weight of the waste tyre)*

4.6. Sensitivity analysis: Impact of reactor pressure

Reactor operating pressure plays a crucial role in the oil yield from the pyrolysis of waste tyres. An investigation was conducted where the reactor pressure was varied from 0.1 to 1 atm, it was observed that the oil yield decreases with an increase in the operating pressure (Figure 4.6). As observed with case of temperature influence, it may be noted that the increase in the oil yield is as a result of a decrease in the char being generated. This implies that more carbon is reacted to form gaseous products and thereby resulting in less unreacted carbon which subsequently drives the char yield low.

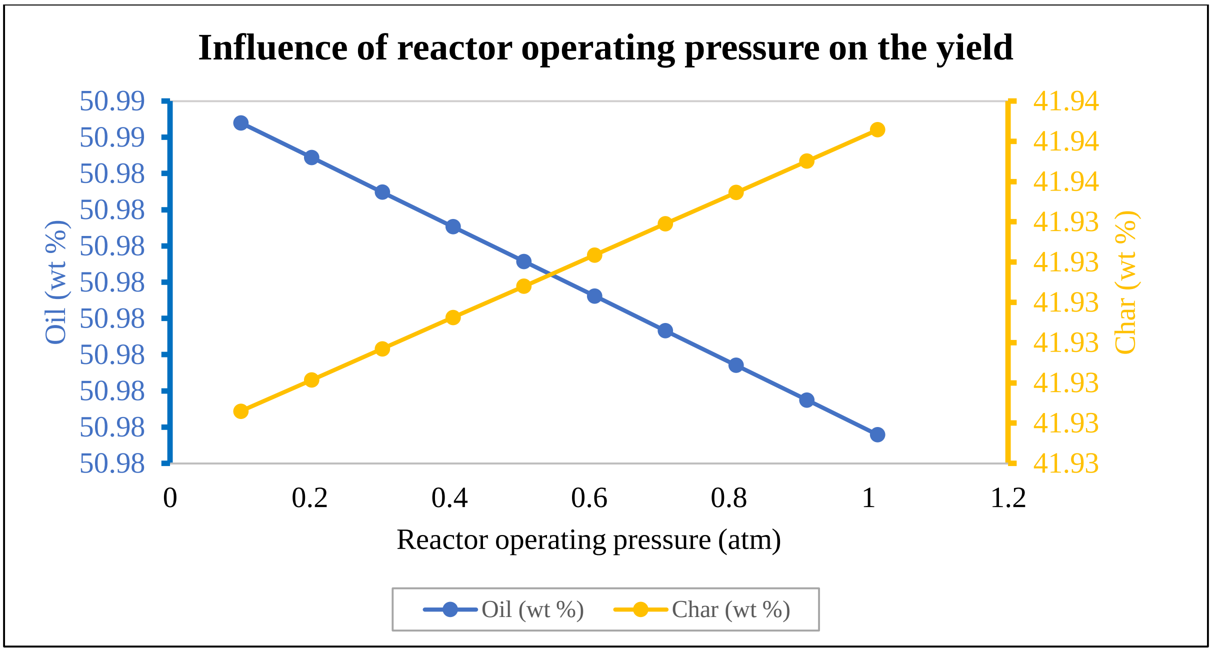


Figure 4.6: Reactor pressure impact on the oil *yield (wt.% are by weight of the waste tyre)*

4.7. Sensitivity analysis: Impact of reactor heating rate

Figure 4.7 below show the impact of the heating rate on the oil yield, the results show that higher heating rate results in higher oil yield. It may however be observed that the increase in oil yield as a function of heating rate show to decrease at heating rate above 15 K/min. Heating rate is also a parameter that negatively drives the operation cost of the pyrolysis plant. Hence presents limited benefits.

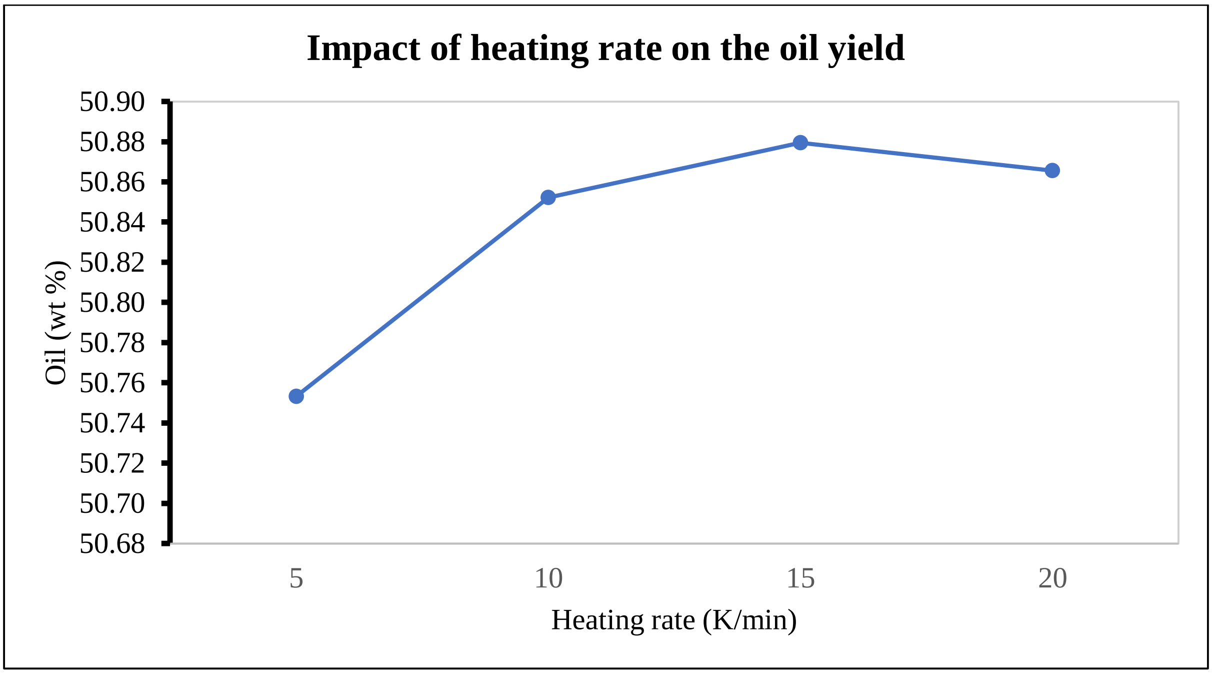


Figure 4.7: Effect of reactor heating rate on the pyrolysis oil *(wt.% are by weight of the waste tyre)*

4.8. Sensitivity analysis: Impact of the presence of the catalyst

In an investigation where the impact of a presence of catalyst was investigated, it was observed that the presence of a catalyst has a huge impact on the oil yield, Figure 4.8 below show that the presence of a catalyst results in 1.8 % points increase in the oil yield.

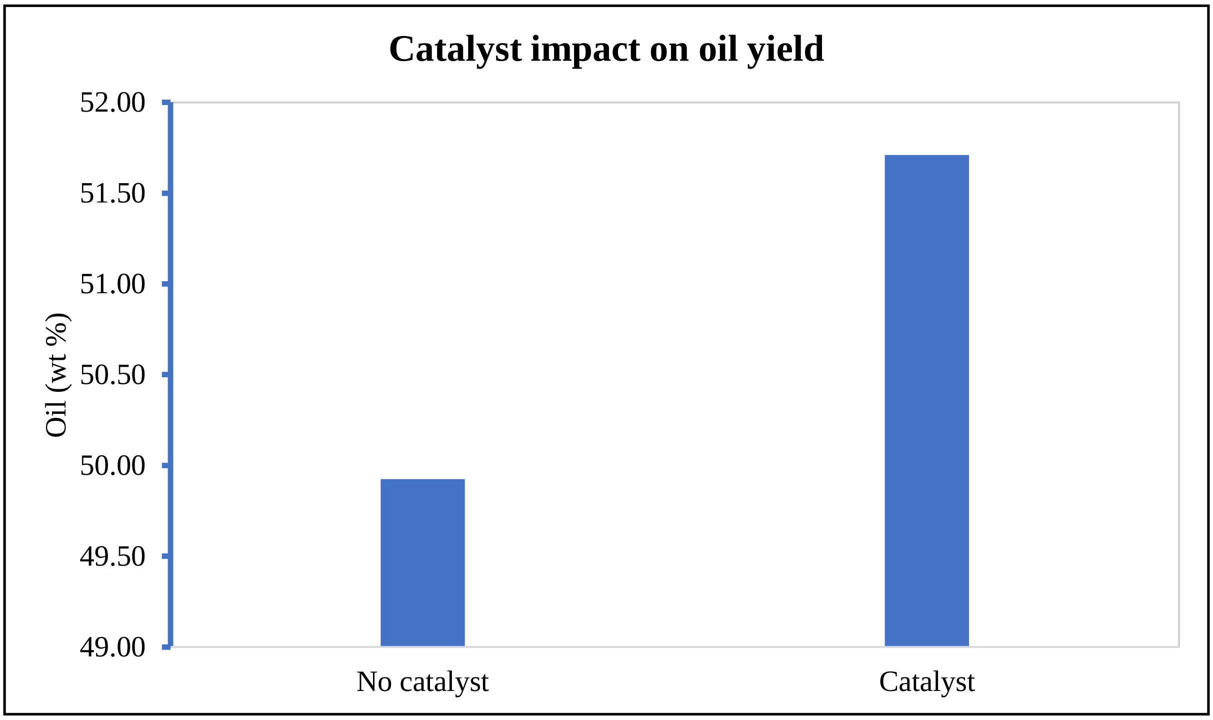


Figure 4.8: Impact of the presence of the catalyst on the oil yield *(wt.% are by weight of the waste tyre)*

4.9. Sensitivity analysis: Impact of tyre particle size

In the investigation of the particle size, two particle size classes were investigated, the 0.1-0.8 mm and a 0.8-4 mm class. The two classes were investigated at the same temperature range, the results showed that the lower particle size results in generally higher the oil yield (Figure 4.9).

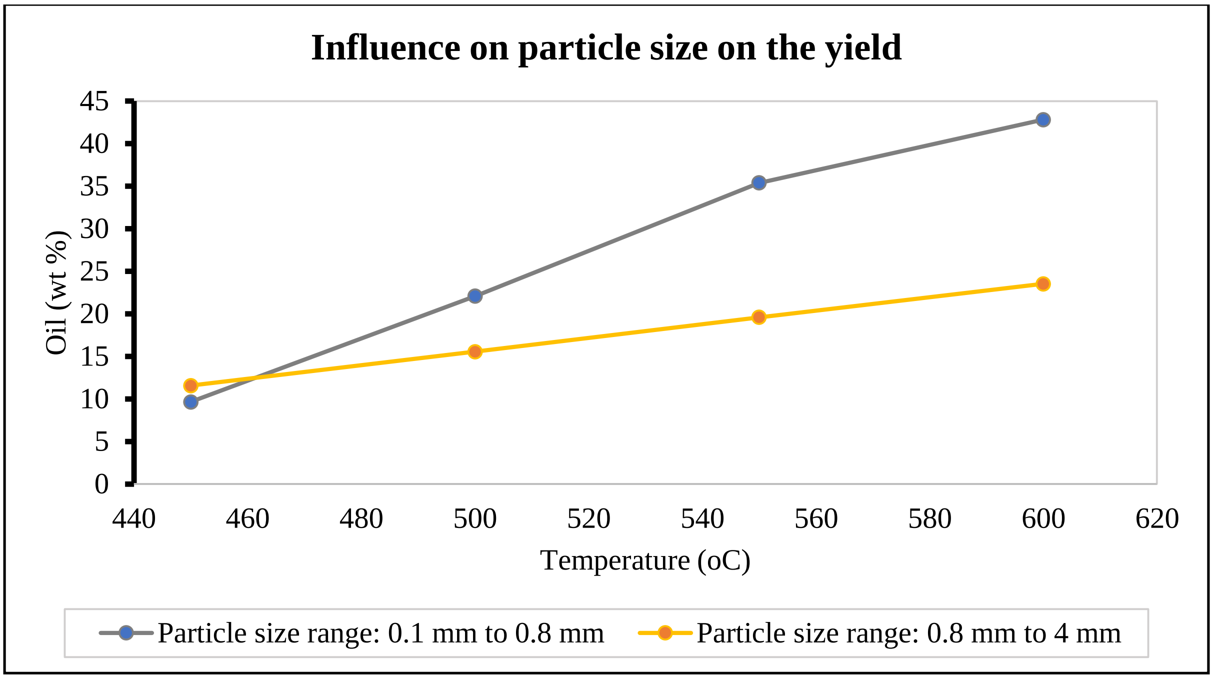


Figure 4.9: Tyre particle size impact on the oil yield *(wt.% are by weight of the waste tyre)*

4.10. Optimized numerical approach

The results below show the results from the optimized model using numerical equations developed by Raj, et al. (2013). The basecase for the oil yield from the Raj, et al. (2013) studies were from a relatively lower oil yield of 26.30 % while the maximum yield achieved was 47.90 % at a temperature of 400 ^{o}C, particle size of 1.0 mm and a feed rate of 0.78 kg/hr. The developed model was in this case based on a small-scale production, however it may be observed that the findings are following similar observations from the ASPEN Plus simulation. The increase in the temperature in the numerical findings results in an increase in oil yield as observed in the simulation results. The particle size is within the similar range as that of higher yield from the simulation, 0.1 – 0.8 mm size class in Figure 4.9.

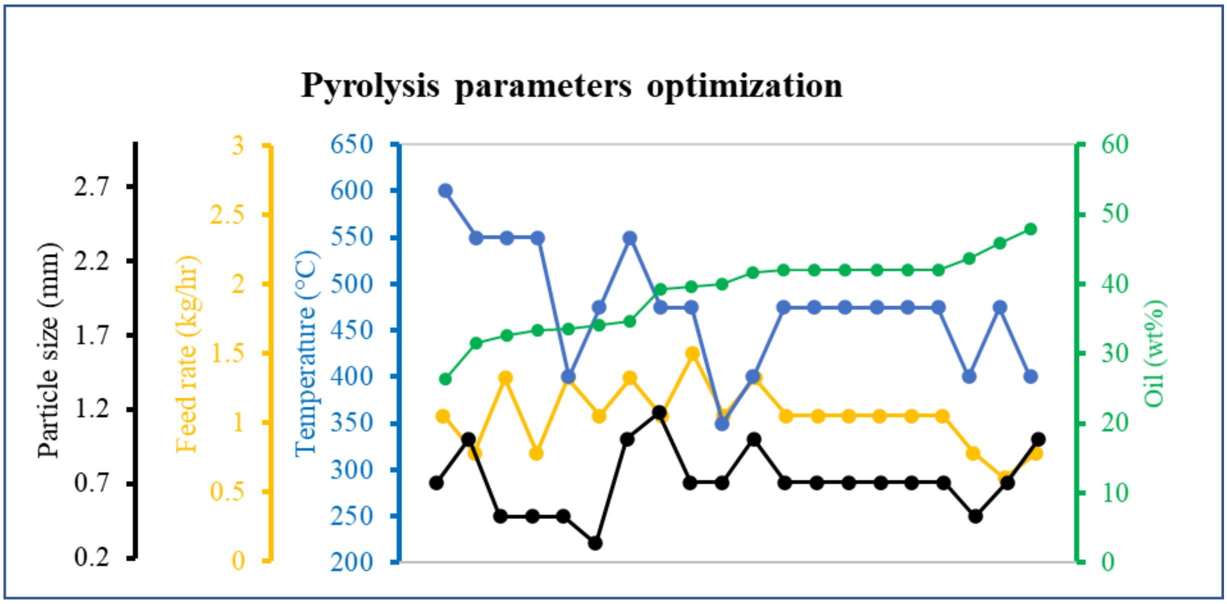


Figure 4.10: Optimization of Particle, feed rate and temperature for maximum oil yield *(wt.% are by weight of the waste tyre)*

4.11. Economic evaluation

The economic evaluation for this study was conducted based on the pricing from three sources reported in Table 3.27. All the investigations were done based on the return of investment. The results presented are based on the outcomes from analysis findings that spans over few years, this was done to understand the period after which the operation starts yielding positive returns (ROI) to the business. In all the three pricing used, it may be observed that on year zero of the investment the ROI figures were negative. This was expected as at this point no return would have been made hence entails no profit is made at this stage. In the graphs below all the negative ROI figures were not reported, only positive figures are shown.

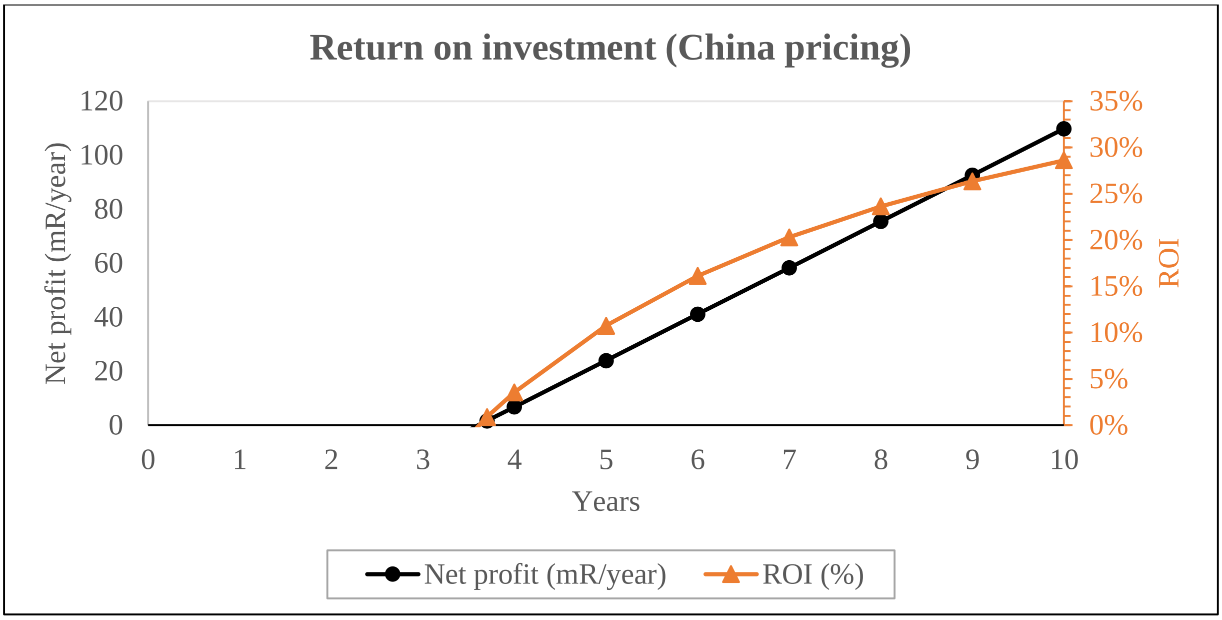


Figure 4.11: ROI findings based on China pricing

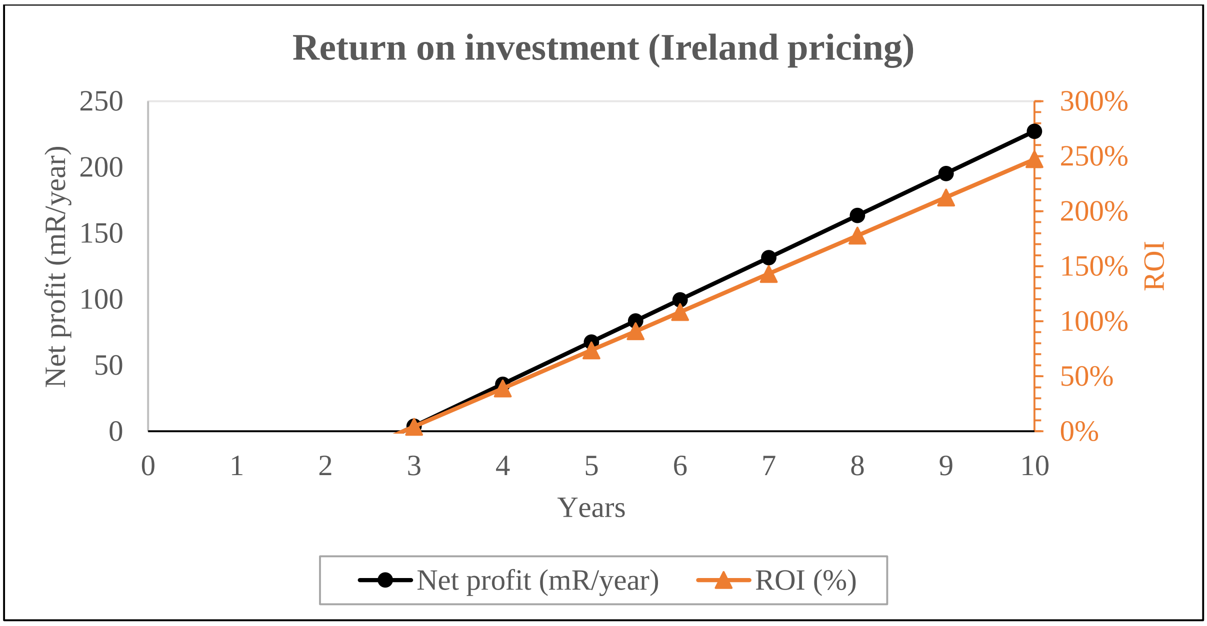


Figure 4.12: ROI findings based on Europe (Ireland) pricing

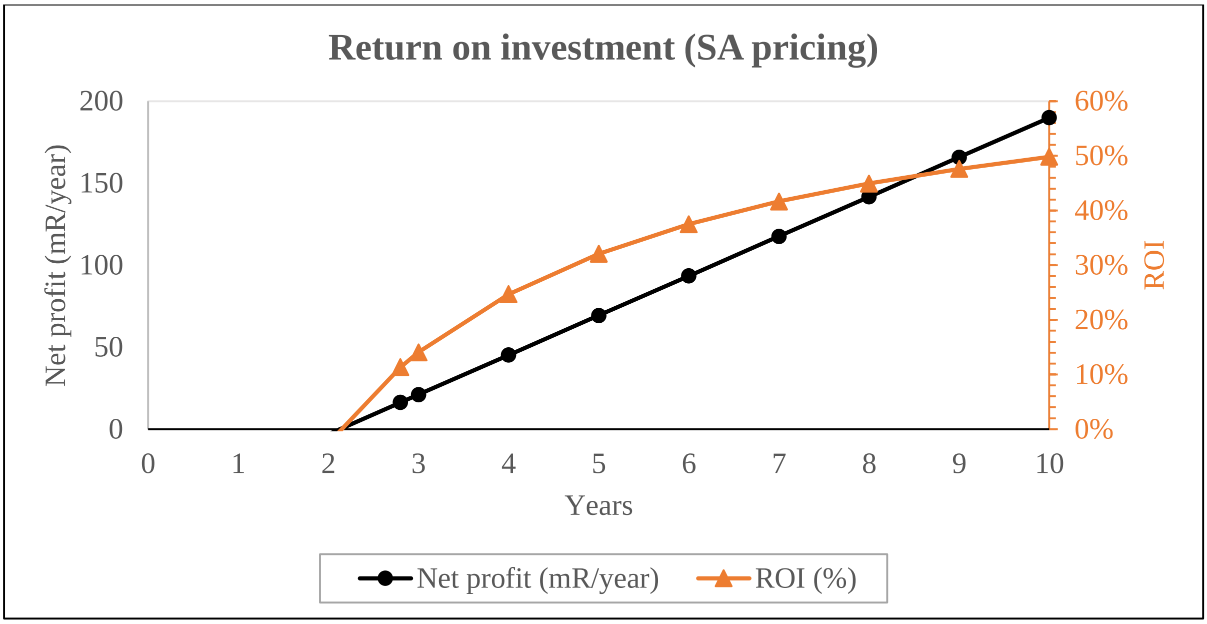


Figure 4.13: ROI findings based on South African pricing

CHAPTER 5: Discussions

Upon the development of a working tyre pyrolysis model, different ASPEN Plus property methods were evaluated for a suitable global equation of state to use. The selection criteria for the suitable property method was based on the literature oil yield results (Table 2.8 and Table 2.9). Based on the outcomes, the suitable global method was found to be the PR-BM and PR-BM78 modification (Figure 4.1). The investigations of various operation parameters through sensitivity analysis and kinetics were all based on the base model PR-BM.

A number of reaction kinetics were fitted into the tyre pyrolysis simulation developed. The kinetics differed depending on the scenario to be investigated and each scenario had a different basecase kinetics from which a basis was established. The comparative studies done from the scenarios developed were based on the impact of temperature, the influence of reactor type, the effect of the dimensions of the reactor and residence time, influence of reactor operating pressure, impact of heating rate, impact of the presence of the catalyst, and the influence of the particle size. Waste tyre pyrolysis key investigation product of interest was the oil yield due its vast energy applications. Among other tyre derived oil energy application, tyre pyrolysis oil may be used to substitute diesel. The non-condensable gases and char also have uses but their value is not as high as that of the oil. Hence in all the investigation carried out in this study oil yield is considered the main driving factor for the investigations. In principle the best scenario required in the investigations conducted is a case where the char and non-condensable gases production is minimised, and oil yield is maximised.

5.1. Impact of reactor type and temperature on pyrolysis yield

The temperature investigation on the oil yield was carried out together with the impact of the reactor type. Two reactor types were investigating together with temperature impact, viz. CSTR and PFR, three main products were presented for each of the reactor type case study, viz. oil, char and gas yield. Figure 4.2 and Figure 4.3 show that for both reactors, tyre derived oil and non-condensable gas yield increases as the temperature increases. The trend observed from the simulation displayed similar outcomes as those observed from literature studies. The main driving factor for the oil and non-condensable gases to increase with reactor operating temperature is due to the fact that higher temperatures favours cracking of higher carbon chains into smaller chains thereby reducing the amount of carbon residual. This phenomenon evidently manifests as lower char yield at higher temperatures. In the simulation results, the main change in terms of the char components is the residual carbon, the other components contained in the char product is the ash which remains constant as it does not form part in the reaction. As such, ash is not in any way influenced by any process parameters. Hence the key driving component relative to the change in temperature for the char product is the residual unreacted solid carbon. Thus, the unreacted solid carbon in effect changes the char yield and subsequently influence the gases and oil formed.

Different reactor types may be used in the tyre pyrolysis process. Depending on the requirements, different reactor types present different benefits and with them their associated limitations. Three main reactors were investigated in this study, viz. CSTR, PFR and kiln reactor. The CSTRs are typically instrumental in achieving fast pyrolysis (milliseconds to seconds reaction time), generally carried out using relatively small particle size. The CSTR can in effect process higher throughput. PFR generally aid slow pyrolysis with reaction time ranging between minutes to hours. PFRs are ran at low heating rates and they have limited accessibility to the catalyst surface area for catalytic pyrolysis processes. Another kind of reactor used in tyre pyrolysis is the kiln reactor, usually inclined between 1^{o} -$10^{o.}$ A number of parameters may be varied in the kiln reactor, viz. speed, filling degree and particle size. Kiln reactors can accommodate a wider particle sizes range. The CSTR and Kiln reactor have mixing benefit which is not achieved in the PFR. The mixing benefit evidently aid better oil yield, Figure 4.2 show that the CSTR has relatively higher oil yield when compared with PFR. In the CSTR the oil yield increases with temperature from 50.93 % to 51.13 % while in the PFR the increase is from 44.02 to 44.13 % for the similar temperature range. Both reactors were investigated for the temperature range between 400 and 700 ^{o}C. As such, the decrease in the char yield as the temperature increases is lower on the PFR when compared to the CSTR (Figure 4.2).

The temperature sensitively analysis could not be carried out on the kiln reactor, the limitation in the kiln was caused by the manner in which the kiln was simulated in comparison to the CSTR and PFR. The CSTR and PFR were simulated as one reactor with one operating temperature which may be varied when undertaking sensitivity studies. Kiln reactor was simulated differently, since kiln is a mixed reactor operating at different temperature zones, to attain a similar operation in the simulation environment, three different mixed reactors operating at different temperatures were simulated in series. Kiln reactor simulation set up made it difficult to run sensitivity analysis as three different reactor temperatures were going to have to be varied. This was going to introduce an inconsistent approach when doing the comparisons with the CSTR and PFR operations. Hence to alleviate this problem, one set of temperatures were used in the kiln reactor. The last mixed reactor temperature in the kiln series was set to be similar to the PFR and CSTR (550 ^{o}C) to achieve a sound comparison. The outcomes from the comparison were undertaken in terms of the oil yield. Figure 4.4 showed that the mixing has a positive impact on the oil yield, it may be observed that CSTR and kiln reactor have relatively higher oil yield when compared with PFR. The CSTR and kiln have 51.01 % and 50.93 % respectively while PFR resulted in the oil yield of only 44.09 % at 550 ^{o}C. Figure 4.4 also showed the char yield, it may be observed that lower carbon was reacted to gaseous products on the PFR compared with CSTR and kiln reactor. The levels of carbon reacted may be observed from higher char generated in the PFR compared with CSTR and kiln reactor. This observation in effect is an indication of the residual carbon being favoured more on the PFR than in the mixed reactors (Figure 4.4). RGibbs reactor showed odd results which presented relatively higher oil yield (67 % relative to the weight of waste tyres), this was considered the odd result relative to the expected oil yield as per the literature studies. The simulation basis for the RGibbs was centred around a rigorous approach aimed at achieving the comprehensive waste tyre pyrolysis products depicted in Appendix A and B. The limitation for simulating the comprehensive product's components is that there are few studies that have done tyre pyrolysis product studies to this level. As such there is limited literature studies against which the simulation findings may be validated. Hence the RGibbs results were discarded from the comparative studies of the investigations.

5.2. Impact of reactor size and residence time

The residence time is generally dependent of the flow rate, size of the reactor and the particle size. Generally, the large particle size requires larger reactor size to achieve longer residence time for achieving complete volatilization of the entire mass. In this study a sensitivity analysis on the reactor size and residence time was investigated. PFR and CSTR was investigated for this analysis. PFR showed that larger diameter and longer length of the reactor had a positive impact on the oil yield. However, it was observed that the impact of diameter showed to reach a point where no further improvements may be realised, this observation was noted at levels above 1m (Figure 4.5). For the CSTR, the results showed to present no further improvement at residence time above 1 hour. Figure 4.5 observations are crucial in the development of the economic studies from the equipment sizing point of view as these learnings determines the operating limits in terms of the reactor sizing.

5.3. Impact of reactor operating pressure on pyrolysis yield

Operating the pyrolysis reactor at lower pressure reduces the occurrence of the secondary reaction in the gaseous phase. Occurrence of secondary gas reactions are detrimental in the oil yields as they result in gas depositions onto the char. This phenomenon in effect improves the value of solid char but reduces the oil yield. Since this study is dominantly cantered around maximising the oil yield, it is thus critical to investigate the impact of operating pressure on the oil yield. The phenomenon caused by operating pressure was observed in the simulation results Figure 4.6. The findings showed that as the operating pressure increases from 0.1 atm to 1 atm, the oil yield decreases from 50.98 to 50.97 % while resulting in the increase in char yield, these changes from pressure variations showed to be insignificant.

5.4. Impact of reactor heating rate

The heating rate plays a critical role in the decomposition of tyres in the pyrolysis reactors since it has a direct influence on the rate of approaching the temperature at which volatilization occurs. However, increasing the heating rate significantly may have negative impacts as it may results in the secondary reactions which in effect lowers the oil yield and increases the char yield. When the studies were conducted in the simulation, it was observed that the oil yield increases with an increase in the heating rete. Figure 4.7 showed that when the oil yield was increased from 5 to 15 K/min the oil yield increased from 50.75 to 50.89 %. When the heating rate was increased to 20 K/min, the oil yield showed to decrease to 50.87 %. The outcomes presented in Figure 4.7 showed to be in line with the literature study theory. Hence the results implied that there is a limitation associated with how much heating rate may be beneficial to the oil yield before secondary reactions starts taking effect.

5.5. Impact of the presence of the catalyst

The use of the catalyst generally has a positive impact on the yield and the quality of the oil generated. The investigation conducted on this study was focused on the general impact of the catalyst use on the oil yield. Two kinetics were used for this investigation, the first being for the basecase while the second kinetics were for the presence of the catalyst. Based on Figure 4.8, it was observed that the presence of the catalyst resulted in an increase of the oil yield from 49.92 to 51.7 %. The use of the catalyst requires costing to be taken into account, specifically from the perspective of benefits derived versus the cost associated with using the catalyst.

5.6. Impact tyre particle size

The smaller particle size generally results in fast conversion of tyres to gaseous products while the larger particle size is associated with slower heat penetration and thereby slower pyrolysis. Depending on the temperature and the residence time, the large particle size may result in the interior of the particles not being heated. Thus, this may cause some parts of the tyre to remain unreacted and hence causing it to contribute more to unreacted carbon and in effect favouring more char production. This in effect means that the smaller the particle size the higher the chances of volatilizing the entire mass into gaseous products. Thus, smaller particle size results in more oil generation compared to the char products. In this study an investigation on the impact of the particle size was investigated. Two size classes were considered, viz. 0.1 mm – 0.8 mm and 0.8 mm – 4 mm. The results presented in Figure 4.9 showed that the lower size range class (0.1 mm – 0.8 mm) displayed higher oil yield when compared with the higher size class. The observations from the particle size investigations showed to be consistent for the temperature range studied.

5.7. Optimized numerical model

The simulation studies undertaken showed to be useful in understanding the impact of the various operating parameters of the tyre pyrolysis process. As much as the undertaken simulation’s one variable investigations provide useful information, in the process environment it goes without saying that a consolidated model that encompasses different operating parameters is more useful. To close this gap identified, a numerical model from literature was used in this study to understand the optimization of the different parameters. The numerical model used included temperature, particle size, and feed rate. It was observed that the optimum parameters identified from this model were a combination of 400 ºC, 1.0 mm and 0.78 kg/hr for temperature, particle size and feed rate respectively. These results were for a laboratory scale investigation, under the said optimum conditions the optimum oil yield of 47.90 % was achieved. The reference oil yield for the un-optimised numerical investigation was reported to be 26.3 % (Figure 4.10). The numerical approach has an added advantage as it combines various parameters into a single working model. While the numerical investigations provide a comprehensive optimum parameter, ASPEN Plus results are as important in understanding the influence of individual parameter and in running quick scenario analysis.

5.8. Economic evaluation

In the economic evaluation studies undertaken, three pricing from different locations were used, viz. China, Europe and South Africa. The key consideration for the economic evaluations of this study was the return on investment. ROI is a tool used to undertake business analysis, this tool is used to understand if the business will make profit. ROI may be used to understand after how long a period post commissioning will the operation start yielding returns. As such, since at only positive ROI values does a business start yielding benefits, only years after which positive ROI figures are realised were reported in the investigations. In the case where China pricing was used, it was observed that the positive ROI may only be realised after 3.7 of operation (Figure 4.11), while in the case where Ireland (Europe) pricing was used, a positive ROI may be realised after 3.4 years of operation (Figure 4.12). In the South African pricing case study, the positive ROI was observed to be only achievable after 2.8 years of operation (Figure 4.13).

CHAPTER 6: Conclusions and recommendations

A model was developed for the waste tyre pyrolysis process using ASPEN Plus computer simulation software. Using the developed simulation, a number of investigations were undertaken to understand the impact of the key process operating parameters on the tyre derived oil yield. Investigations conducted were on the operating temperature, reactor type, dimension of the reactor and residence time, reactor operating pressure, heating rate, presence of the catalyst and tyre particle size

The reactor type investigation showed that the reactors with some level of mixing generally produce higher oil yield results. In the temperature range investigated for the CSTR and PFR, the CSTR showed to yield higher oil results. The CSTR presented oil yield increase from a level 50.93 % to 51.13 % while the PFR showed only to present an increase from 44.02 to 44.13 %. Both reactors were investigated for the temperature range between 400 and 700 ^oC. At 550 ^oC, a CSTR and kiln reactor showed higher oil yields than PFR, the three reactors showed oil yields of 51.01 %, 50.93 % and 44.09 % respectively.

An increase in the size of the reactor showed positive results on the oil yield, however there were limitations associated with the maximum attainable yields. For the PFR, no further improvements on the yield were noticed at the diameter above 1m, while the CSTR showed the yield to remain constant above a 1 hour residence time. The operating pressure investigation done on the CSTR showed a decrease in oil yield with an increase in the operating pressure. When the pressure was increased from 0.1 atm to 1 atm, the CSTR oil yield decreases from 50.98 % to 50.97 %.

The impact of heating rate showed to display a positive impact on the oil yield, an increase from 50.75 to 50.89 % was realised when the heating rate was increased from 5 to 15 K/min. Above the 15 K/min heating rate the yield showed a decrease to a 50.87 % level. The incorporation of the catalyst presented an increase of the oil yield from 49.92 % to 51.7 %. In the particle size investigation, two size classes were considered, viz. 0.1 mm – 0.8 mm and 0.8 mm – 4 mm. The results presented showed that the lower size range class (0.1 mm – 0.8 mm) result in higher oil yield across the temperature range investigated.

A numerical model from literature study based on laboratory studies incorporated particle size, temperature and feed rate was used to attain the optimum operating conditions for the maximum oil yield. The un-optimised conditions of the model showed an oil yield of 26.3 %. Optimum conditions identified from the model was a temperature of 400 ^oC, particle size of 1.0 mm and a feed rate 0.78 kg/hr. The said optimum conditions resulted in a 47.90 % oil yield.

Based on the results of this study it may be concluded that the optimum oil yield is obtainable from the CSTR operated at a temperature range between 400 ^oC and 550 ^oC, tyre particle size less than 1 mm, operating pressure below 1 atm, heating rate between 10-15 K/min and residence time of less than 1 hour. In the worst case, the findings from the economical investigations undertaken showed that overall a tyre pyrolysis plant only starts yielding a positive ROI after 3.7 years of operating. The attained ROI is relatively acceptable pertaining to the investment decision making.

Based on the study learning, it may be concluded that the simulation is useful in yielding calculated, quick and cost-effective optimization investigations. The simulation can also be used as a troubleshooting guide for the working tyre pyrolysis plant.

Based on the learnings from this study, the following future studies are recommended:

- A study to develop a regression tyre derived products model that encompasses temperature, heating rate, particle size, mass of the catalyst, flow rate and operating pressure for different reactor types.
- A rigorous investigation that encompasses kinetics for individual components of the tyre derived products presented in Appendix A and B.
- A study on sulphur levels removal on the tyre derived oil to mimic those of diesel and undertake an updated economic evaluation with added unit operations.
- Steam incorporation investigations.

REFERENCES

Akbas, A. & Tyhana, N. Y., 2021. Recyling of Rubber Wastes as Fuel and Its Additives. *Recyling,* 6(78), pp. 1-14.

Alsaleh, A. & Sattler, M. L., 2014. Waste Tyre Pyrolysis: Influential Parameters and Product Properties. *Current Sustainable/Renewable Energy Reports,* pp. 129-135.

Altayeb, R. K., 2015. *Liquid Fuel Production From Pyrolysis of Waste Tyres: Process Simulaton, Exergetic Analysis,* American University of Sharjah: Shrjah.

American tyre distributors, 2019. *American tyre distributors.* [Online] Available at: https://americantyredistributors.medium.com/tyres-101-the-structure-of-a-tyre-34808e929064
[Accessed 05 January 2022].

Aslan, D. I., Parthasarathy, P., Goldfarb, J. L. & Ceylan, S., 2017. Pyrolysis reeaction models of waste tyres: Application of Master-Plots method for energy conversion via devolatilization. *Waste Management,* Volume 68, pp. 405-411.

aspentech, 2022. *A history of innovation.* [Online] Available at: https://www.aspentech.com/en/about-aspentech/35-years-of-innovation
[Accessed 12 April 2022].

Aydin, H. & Ilkılıc, C., 2012. Optimization of fuel production from waste vehicle tyres by pyrolysis and resembling of diesel fuel by various desulfurization methods. *Fuel,* Volume 102, pp. 605-612.

Aydin, H. & Lilkilic, C., 2012. Optimization of Fuel Production from Waste Vehicle Tyres by Pyrolysis and Resembling to Diesel Fuel by Various Desulfurization Methods. *Fuel,* Volume 102, pp. 605-612.

Aylon, E. et al., 2008. Waste Tyre Pyrolysis: Comparison between Fixed Bed Reactor and Moving Bed Reactor. *Industrial & Engineering Chemistry Research,* Volume 47, pp. 4029-4033.

Banar, M. et al., 2012. Characterization of pyrolytic oil obtained from pyrolysis of TDF (Tyre Derived Fuel). *Energy COnversion and Management,* Volume 62, pp. 22-30.

Barberousse, A., Franceschelli, S. & Imbert, C., 2009. Computer Simulations as Experiments. *Synthese,* pp. 557-574.

Conesa, J. A., Martin-Gullon, I., Font, R. & Jaunianinen, J., 2004. Complete Study of the Pyrolysis and Gasificatin of Scrap Tyres in a Pilot Plant Reactor. *Environmental Science & Technology* , Volume 38, pp. 3189-3194.

Cunliffe, A. M. & Williams, P. T., 1998. Composition of oils derived from the batch pyrolysis of tyres. *Analytical and Applied Pyrolysis,* Volume 44, pp. 131-152.

Dai, X. et al., 2001. Pyrolysis of waste tyres in a circulating fluidized-bed reactor. *Energy,* Volume 26, pp. 385-399.

Danon, B., Van Der Gryp, P., Schwarz, C. E. & Görgens, J. F., 2015. A review of dipentene (dl-limonene) production from waste tyre pyrolysis. *Journal of Analytical and Applied Pyrolysis,* pp. 1-13.

Dogan, O., Bahattin, M. & Ozdalyan, B., 2012. The Effect of Tyre Derived Fuel/ Diesel Fuel Blends Utilization on Diesel Engine Perfomance and Emssions. *Fuel,* Volume 95, pp. 340-346.

Evans, A. & Evans, R., 2006. The Composition of a Tyre: Typical Components. *The Waste & Resources Action Programme.*

Fels, M. & Pegg, M., 2018. A TECHNO-ECONOMIC AND ENVIRONEMENTAL ASSESSMENT OF A TYRE PYROLYSIS PLANT. *Chemical ENgineering, Dalhousie University.*

Foo, D. C., Selvan, M. & McGuire, M. L., 2005. Integrate process simulation and process synthesis. *Chemical engineering progress,* 101(10), pp. 25-29.

Galvagno, S. et al., 2002. Pyrolysis process for the treatment of scrap tyres: preliminary experimental results. *Wast Management,* Volume 22, pp. 917-923.

Guala, F., 2002. “Models, Simulations, and Experiments.” In Model-based Reasoning: Values, edited by L. Magnani and N. J. Nersessian. *New York: Kluwer,* pp. 59-74.

Humphreys, P., 2004. Extending Ourselves: Computational Science, Empiricism, and Scientific Method. *New York: Oxford University Press.*

Islam, M. R. et al., 2011. Feasibility study for thermal treatment of solid tyre wastes in Bangladesh by using pyrolysis technology. *Waste management,* 3(9), pp. 2142-2149.

Ismail, H. Y., Abbas, A., Azizi, F. & Zeauter, J., 2016. Pyrolysis of waste tyres: A modelling and parameter estimation study using Aspen Plus. *Waste Management.*

Jebeile, J., 2019. Computer simulation, experimetn, and novelty.

Kaminsky, W., Mennerich, C. & Zhang, Z., 2009. Feedstock recyling of synthentic and natural rubber by pyrolysis in a fluidized bed. *Analytical and Applied Pyrolysis,* Volume 85, pp. 334-337.

Kar, Y., 2011. Catalytic pyrolysis of car tyre waste using expanded perlite. *Waste Management,* Volume 31, pp. 1772-1782.

Kar, Y., 2011. Catalytic pyrolysis of car tyre waste using expanded perlite. *Waste Management,* Volume 31, pp. 1772-1782.

Kordoghli, S. et al., 2014. Managing the environmental hazards of waste tyres. *Journal of ENgineering Studies and Research,* 20(4).

Laresgoiti, M. F. et al., 2004. Characterization of the liquid products obtained in tyre pyrolysis. *Analytical and Applied Pyrolysis,* Volume 71, pp. 917-934.

Leung , D. & Wang, C., 2003. Fluidized-Bed Gasification of Waste Tyre Powders. *Fuel Processing Technology,* 84(1-3), pp. 175-196.

Li, S. Q., Yao, Q., Yan, J. H. & Cen, K. F., 2004. Pilot-Scale Pyrolysis of Scrap Tyres in a Continuous Rotary Kiln Reactor. *Industrial & Engineering Chemistry Research* , Volume 43, pp. 5133-5145.

Lopez, G. et al., 2009. Kinetics of scrap tyre pyrolysis under vacuum conditions. *Wast Management,* Volume 29, pp. 2649-2655.

Martinez, J. D., Murillo, R., Carcia, T. & Veses, A., 2013. Demonstration of waste tyre pyrolyis process on pilot scale in a continous auger reactor. *Hazardous materials* , Volume 261, pp. 637-645.

Mazloom, G., Farhadi, F. & Khorasheh, F., 2009. Kinetic modelling of pyrolysis of scrap tyres. *Journal of Analytical and Applied Pyrolysis* , Volume 84, pp. 157-164.

Morgan, M. S., 2005. Experiments versus models: New phenomena, inference and suprise. *Economic methodology,* 12(2), pp. 317-329.

Mulaudzi, L., 2017. *Process modelling and economic evaluation of waste tyres to limonene via pyrolysis* , Stellenbosch : Stellenbosch University.

Olazar, M. et al., 2005. Kinetics of Scrap Tyre Pyrolysis in a Conical Spouted Bed Reactor. *Ind Eng Chem Res,* Volume 44, pp. 3918-3924.

Olazar, M. et al., 2008. Kinetic modelling of tyre pyrolysis in a conical spouted bed reactor. *Analytical and applied pyrolysis* , Volume 81, pp. 127-132.

Pilkington, B., 2021. *Tachling the global tie waste problem with pretred.* [Online] Available at: https://www.azocleantech.com/article.aspx?ArticleID=1227 [Accessed 11 May 2022].

Pilusa, J., Shukla, M. & Muzenda, E., 2014. Economic Assessment of Waste Tyres Pyrolysis Technology: A Case study for Gauteng Province, South Africa. *Research in Chemical, Metallurgical and Civil Engg,* Issue 1, pp. 2349-1450.

Raj, R. E., Kennedy, Z. R. & Pillai, B. C., 2013. Optimization of process parameters in flash pyrolysis of wste tyres to liquid and gaseous fuel in a fluidized reactor. *Energy Conversion and Management,* Volume 67, pp. 145-151.

REDISA, 2012. Integrated Industry Waste Tyre Management Plan. Government Gazette Staatskoerant. *Government Gazette*, 569 (35927), pp. 1-4.

Riedewald, F. & Sousa-Gallagher, M., 2016. *Technological and economical feasibility of a 40 000 t/ye tyre pyrolysis plant: results of H2020 SME Phase 1 study.* Ireland, s.n.

Sharma, R. K., Yang, J., Zondlo, J. W. & Dadyburjour, D. B., 1998. Effect of process condition on co-liquefaction kinetics of waste tyre and coal. *Catalysis today,* Volume 40, pp. 307-320.

SMITHERS, n.d. *Smithers.com.* [Online]
Available at: https://www.smithers.com/resources/2019/jun/global-tyre-manufacturing-output-to-grow-by-2024#:~:text=The%20global%20tyre%20industry%20is,22.75%20million%20tonnes%20in%202024.
[Accessed 18 June 2022].

Tsiryapkina, I., 2019. *Technology and economy analysis of waste truck tyres management,* s.l.: University 0f North Dakota.

Uzun, B. B. & Yamen, E., 2014. Thermogravimetric characteristics and kinetics of scrap tyre and Juglans regia shell co-pyrolysis. *Waste Management & Research* , Volume 32, pp. 961-970.

Williams, P. T., 2013. Pyrolysis of Waste Tyres: A Review. *Waste Management* , 33(8), pp. 1714-1728.

Williams, P. T., Besler, S. & Taylor, D. T., 1990. The pyrolysis of scrap automotive tyres. *Department of Fuel and Energy, The University of Leeds,* Volume 1474-1482.

Williams, P. T. & Brindle, A. J., 2003. Fluidised Bed Pyrolysis and Catalytic Pyrolysis of Scrap Tyres. *Environmental Technology,* Volume 24, pp. 921-929.

APPENDICES

APPENDIX A: Comprehensive tyre pyrolysis reactions

Table A.1: Waste tyre pyrolysis reactions (Ismail, et al., 2016)

Reaction #	Reaction	Product	A (S^{-1})	E (kJ/mol)	n
1	$C + 2H_2 \rightarrow CH_4$	Methane	4.877	23.01	0
2	$2C + 3H_2 \rightarrow C_2H_6$	Ethane	0.52	23.01	0
3	$2C + 2H_2 \rightarrow C_2H_4$	Ethene	2.386	23.01	0
4	$3C + 4H_2 \rightarrow C_3H_8$	Propane	0.277	23.01	0
5	$3C + 3H_2 \rightarrow C_3H_6$	Propene	0.446	23.01	0
6	$4C + 5H_2 \rightarrow C_4H_{10}$	Butane	0.122	23.01	0
7	$4C + 4H_2 \rightarrow C_4H_8$	Butene	0.144	23.01	0
8	$4C + 3H_2 \rightarrow C_4H_6$	Butalyne	0.981	23.01	0
9	$C + O2 \rightarrow CO2$	Carbon Dioxide	0.226	23.01	0
10	$C + 1\ O2 \rightarrow CO$	Carbon Monoxide	0.096	23.01	0
11	$H2 + S \rightarrow H2S$	Hydrogen Sulfide	Equilibrium	Equilibrium	0
12	$5C + 6H_2 \rightarrow C_5H_{12}$	Pentane	0.339	23.01	0
13	$5C + 4H_2 \rightarrow C_5H_8$	Pentalyne	0.066	23.01	0
14	$6C + 6H_2 \rightarrow C_6H_{12}$	Methylcyclopentene	0.009, 0.009	1.59	0
15	$8C + 7H_2 \rightarrow C_8H_{14}$	Methylhexadiene	0.016	1.59	0
16	$8C + 9H_2 \rightarrow C_8H_{18}$	Trimethylpentane	0.023, 0.019	1.59	0

17	$7C + 7H_2 \rightarrow C_7H_{14}$	Dimethylcyclopentane	0.015	1.59	0
18	$8C + 9H_2 \rightarrow C_8H_{18}$	Dimethylhexane	0.044	1.59	0
19	$7C + 7H_2 \rightarrow C_7H_{14}$	Ethylcyclopentane	0.008	1.59	0
20	$7C + 7H_2 \rightarrow C_7H_{14}$	Methylcyclohexene	0.045	1.59	0
21	$8C + 8H_2 \rightarrow C_8H_{16}$	Dimethylcyclohexane	0.01	1.59	0
22	$8C + 8H_2 \rightarrow C_8H_{16}$	Octene	0.007	1.59	0
23	$8C + 7H_2 \rightarrow C_8H_{14}$	Dimethylhexadiene	0.011	1.59	0
24	$8C + 8H_2 \rightarrow C_8H_{16}$	Ethylcyclohexane	0.054, 0.007	1.59	0
25	$9C + 9H_2 \rightarrow C_9H_{18}$	Trimethylcyclohexane	0.003	1.59	0
26	$9C + 9H_2 \rightarrow C_9H_{18}$	Nonene	0.017	1.59	0
27	$9C + 9H_2 \rightarrow C_9H_{18}$	Methylocatene	0.164	1.59	0
28	$10C + 8H_2 \rightarrow C_{10}H_{16}$	Dlimonene	0.035	1.59	0
29	$10C + 8H_2 \rightarrow C_{10}H_{16}$	Pinene	0.064	1.59	0
30	$10C + 8H_2 \rightarrow C_{10}H_{16}$	Limonene	0.619	1.59	0
31	$6C + 3H_2 \rightarrow C_6H_6$	Benzene	1.654	33.89	0
32	$7C + 4H_2 \rightarrow C_7H_8$	Toluene	7.305	33.89	0
33	$8C + 5H_2 \rightarrow C_8H_{10}$	Ethylbenzene	4.708	33.89	0
34	$8C + 5H_2 \rightarrow C_8H_{10}$	Xylene	4.476	33.89	0
35	$8C + 4H_2 \rightarrow C_8H_8$	Styrenetyrene	4.049	33.89	0
36	$8C + 5H_2 \rightarrow C_8H_{10}$	Dimethylbenzene	1.084	33.89	0
37	$9C + 6H_2 \rightarrow C_9H_{12}$	Cumene	1.07	33.89	0
38	$9C + 5H_2 \rightarrow C_9H_{10}$	Ethylmethylbenzene	0.5	33.89	0
39	$9C + 6H_2 \rightarrow C_9H_{12}$	Propylbenzene	1.117	33.89	0

40	$9C + 6H_2 \rightarrow C_9H_{12}$	Ethylbenzene	1.189, 2.128	33.89	0
41	$9C + 6H_2 \rightarrow C_9H_{12}$	Trimethylbenzene	0.424	33.89	0
42	$6C + 3H_2 + O \rightarrow C_6H_6O$	Phenol	0.497	33.89	0
43	$9C + 5H_2 \rightarrow C_9H_{10}$	Methylethenylbenzene	1.532, 0.634, 0.344	33.89	0
44	$7C + 2.5H_2 + N \rightarrow C_7H_5N$	Benzonitrile	0.528	33.89	0
45	$9C + 5H_2 \rightarrow C_9H_{10}$	Propenylbenzene	0.567	33.89	0
46	$9C + 6H_2 \rightarrow C_9H_{12}$	C_3-benzene	1.808	33.89	0
47	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Isopropyltoluene	3.85	33.89	0
48	$9C + 6H_2 \rightarrow C_9H_{12}$	C_3-benzene	0.392	33.89	0
49	$9C + 5H_2 \rightarrow C_9H_{10}$	Dihydro-1H-indene	0.922	33.89	0
50	$9C + 4H_2 \rightarrow C_9H_8$	1H-indene	1.278	33.89	0
51	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Butylbenzene	1.058	33.89	0
52	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Ethyldimethylbenzene	0.338	33.89	0
53	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Isopropylmethylbenzene	0.769, 0.678	33.89	0
54	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Ethyldimethylbenzene	0.397	33.89	0
55	$9C + 5H_2 \rightarrow C_9H_{10}$	Dihydromethyl-1H-indene	0.516, 0.759, 3.694, 0.433	33.89	0
56	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Tetramethylbenzene	0.383	33.89	0
57	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Tetramethylbenzene	0.4	33.89	0
58	$10C + 7H_2 \rightarrow C_{10}H_{14}$	Ethylisopropylbenzene	0.198	33.89	0
59	$8C + 5H_2 + 0.5O_2 \rightarrow C_8H_{10}O$	Dimethylphenol	0.316	33.89	0
60	$7C + 3H_2 + O_2 \rightarrow C_7H_6O_2$	Benzoic acid	0.549	33.89	0
61	$10C + 5H_2 \rightarrow C_{10}H_{10}$	Methyl-1H-indene	0.539	33.89	0
62	$10C + 6H_2 \rightarrow C_{10}H_{12}$	Tetrahydronaphalene	0.562	33.89	0

63	$10C + 7H_2 \rightarrow C_{10}H_{14}$	C_4-benzene	0.165	33.89	0
64	$10C + 4H_2 \rightarrow C_{10}H_8$	Naphthalene	0.979	33.89	0
65	$10C + 7H_2 + 0.5O_2 \rightarrow C_{10}H_{14}O$	Isopropylphenol	0.056	33.89	0
66	$7C + 2.5H_2 + 0.5N_2 + 2S \rightarrow C_7H_5NS_2$	Benzothiazole	1.2	33.89	0
67	$12C + 8H_2 \rightarrow C_{12}H_{16}$	Tetrahydroethylnaphthalene	47.264	6.3	-1.089
68	$12C + 9H_2 \rightarrow C_{12}H_{18}$	C_6-benzene	47.815	6.3	-1.089
69	$11C + 5H_2 \rightarrow C_{11}H_{10}$	Methylnaphthalene	125.001, 156.807	6.3	-1.089
70	$12C + 7H_2 \rightarrow C_{12}H_{14}$	Trimethylindene	9.307, 95.891	6.3	-1.089
71	$12C + 5H_2 \rightarrow C_{12}H_{10}$	Diphenyl	142.201	6.3	-1.089
72	$12C + 6H_2 \rightarrow C_{12}H_{12}$	Ethylnaphthalene	97.289, 37.367	6.3	-1.089
73	$12C + 6H_2 \rightarrow C_{12}H_{12}$	Dimethylnaphthalene	85.169, 83.486, 119.843	6.3	-1.089
74	$10C + 4.5H_2 + 0.5N_2 \rightarrow C_{10}H_9N$	Ethylquinoline	184.356	6.3	-1.089
75	$14C + 14H_2 \rightarrow C_{14}H_{28}$	n-C_{14}	118.294	6.3	-1.089
76	$12C + 5H_2 \rightarrow C_{12}H_{10}$	Acenaphthene	36.147	6.3	-1.089
77	$15C + 16H_2 \rightarrow C_{15}H_{32}$	n-C_{15}	56.974	6.3	-1.089
78	$15C + 9H_2 \rightarrow C_{15}H_{18}$	Trimethylnaphthalene	88.852, 31.429, 29.175	6.3	-1.089
79	$13C + 5H_2 \rightarrow C_{13}H_{10}$	Fluorene	47.77	6.3	-1.089
80	$15C + 8H_2 \rightarrow C_{15}H_{16}$	Dimethyldiphenyl	60.554, 11.521	6.3	-1.089
81	$15C + 15H_2 \rightarrow C_{15}H_{30}$	Pentadecene	17.88	6.3	-1.089
82	$16C + 17H_2 \rightarrow C_{16}H_{34}$	n-C_{16}	46.822	6.3	-1.089
83	$14C + 5H_2 \rightarrow C_{14}H_{10}$	Phenanthrene	34.666	6.3	-1.089
84	$14C + 5H_2 \rightarrow C_{14}H_{10}$	Anthracene	38.059	6.3	-1.089
85	$15C + 6H_2 \rightarrow C_{15}H_{12}$	Methylphenanthrene	36.925	6.3	-1.089

86	$15C + 15H_2 + O_2 \rightarrow C_{15}H_{30}O_2$	Pentadecanoic acid	64.017	6.3	-1.089
87	$15C + 6H_2 \rightarrow C_{15}H_{12}$	Methylphenanthrene	41.028, 46.908, 82.056	6.3	-1.089
88	$19C + 20H_2 \rightarrow C_{19}H_{40}$	n-C_{19}	12.247	6.3	-1.089
89	$19C + 8H_2 \rightarrow C_{19}H_{16}$	Trimethylphenanthrene	22.599	6.3	-1.089
90	$19C + 19H_2 \rightarrow C_{19}H_{38}$	Isopropylmethylphenanthrene	51.627	6.3	-1.089
91	$20C + 21H_2 \rightarrow C_{20}H_{42}$	n-C_{20}	13.594	6.3	-1.089
92	$21C + 22H_2 \rightarrow C_{21}H_{44}$	n-C_{21}	15.524	6.3	-1.089
93	$22C + 23H_2 \rightarrow C_{22}H_{46}$	n-C_{22}	12.028	6.3	-1.089
94	$23C + 24H_2 \rightarrow C_{23}H_{48}$	n-C_{23}	15.641	6.3	-1.089
95	$24C + 25H_2 \rightarrow C_{24}H_{50}$	n-C_{24}	3.029	6.3	-1.089
96	$24C + 25H_2 \rightarrow C_{24}H_{50}$	n-C_{11}	35.684	6.3	-1.089

APPENDIX B: ASPEN plus components

Table B.1: ASPEN components

Component ID	**Type**	**Component name**	**Alias**
TYRES	Nonconventional	-	-
WATER	Conventional	WATER	H2O
N2	Conventional	NITROGEN	N2
H2	Conventional	HYDROGEN	H2
S	Conventional	SULFUR	S
CARBON	Solid	CARBON-GRAPHITE	C
ASH	Nonconventional	-	-
CH4	Conventional	METHANE	CH4
CO2	Conventional	CARBON-DIOXIDE	CO2
CO	Conventional	CARBON-MONOXIDE	CO
H2S	Conventional	HYDROGEN-SULFIDE	H2S
NO	Conventional	NITRIC-OXIDE	NO
ETHYL-01	Conventional	ETHYLENE	C2H4
ETHAN-01	Conventional	ETHANE	C2H6
PROPA-01	Conventional	PROPANE	C3H8
OXYGE-01	Conventional	OXYGEN	O2
TOLUE-01	Conventional	TOLUENE	C7H8
N-BUT-01	Conventional	N-BUTANE	C4H10-1

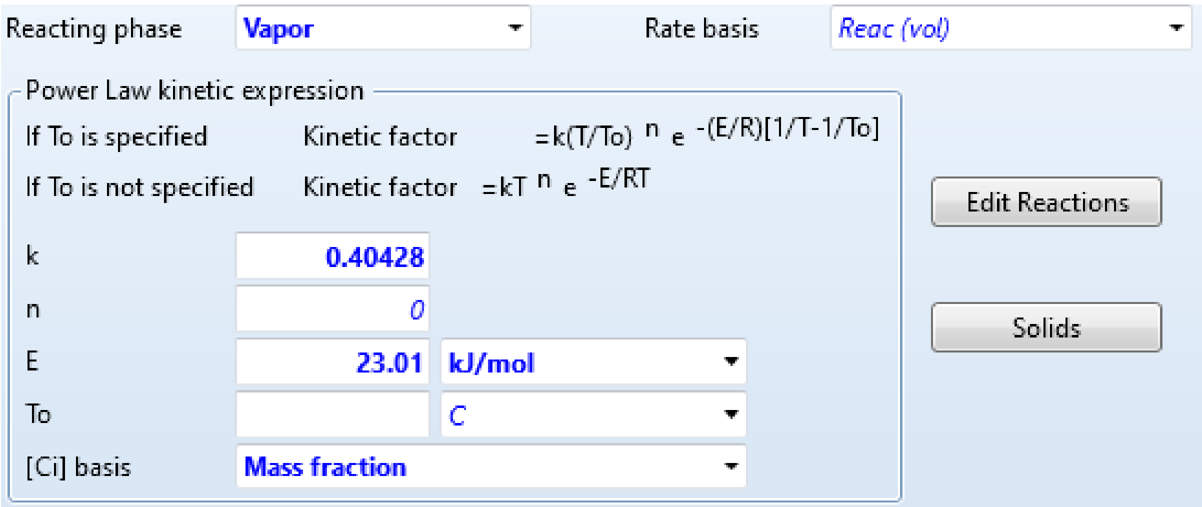
N-PEN-01	Conventional	N-PENTANE	C5H12-1
1-NON-01	Conventional	1-NONENE	C9H18-3
1-MET-01	Conventional	1-METHYLCYCLOPENTENE	C6H10-D1
01-Oct-01	Conventional	1-OCTENE	C8H16-16
PROPY-01	Conventional	PROPYLENE	C3H6-2
1-BUT-01	Conventional	1-BUTENE	C4H8-1
1-BUT-02	Conventional	1-BUTYNE	C4H6-1
1-PEN-01	Conventional	1-PENTYNE	C5H8-5
2:2:3-01	Conventional	2,2,3-TRIMETHYLPENTANE	C8H18-12
1:1-D-01	Conventional	1,1-DIMETHYLCYCLOPENTANE	C7H14-2
2:3-D-01	Conventional	2,3-DIMETHYLHEXANE	C8H18-6
ETHYL-02	Conventional	ETHYLCYCLOPENTANE	C7H14-5
METHY-01	Conventional	METHYLCYCLOHEXANE	C7H14-6
1:1-D-02	Conventional	1,1-DIMETHYLCYCLOHEXANE	C8H16-1
2:5-D-01	Conventional	2,5-DIMETHYL-1,5-HEXADIENE	C8H14-D2
ETHYL-03	Conventional	ETHYLCYCLOHEXANE	C8H16-8
1:1:3-01	Conventional	1,1,3-TRIMETHYLCYCLOHEXANE	C9H18-N26
D-LIM-01	Conventional	D-LIMONENE	C10H16-D1
BENZE-01	Conventional	BENZENE	C6H6
ETHYL-04	Conventional	ETHYLBENZENE	C8H10-4
N-PRO-01	Conventional	N-PROPYLBENZENE	C9H12-1
PHENO-01	Conventional	PHENOL	C6H6O
BENZO-01	Conventional	BENZONITRILE	C7H5N

1-MET-02	Conventional	1-METHYL-2-ISOPROPYLBENZENE	C10H14-5
BENZO-02	Conventional	BENZOIC-ACID	C7H6O2
N-TET-01	Conventional	N-TETRACOSANE	C24H50
N-UND-01	Conventional	N-UNDECANE	C11H24
N-TRI-01	Conventional	N-TRICOSANE	C23H48
N-DOC-01	Conventional	N-DOCOSANE	C22H46
N-HEN-01	Conventional	N-HENEICOSANE	C21H44
N-EIC-01	Conventional	N-EICOSANE	C20H42
N-NON-01	Conventional	N-NONADECANE	C19H40
PENTA-01	Conventional	PENTADECANOIC-ACID	C15H30O2
4-MET-01	Conventional	4-METHYLPHENANTHRENE	C15H12-D1
ANTHR-01	Conventional	ANTHRACENE	C14H10-1
PHENA-01	Conventional	PHENANTHRENE	C14H10-2
N-HEX-01	Conventional	N-HEXADECANE	C16H34
1-PEN-02	Conventional	1-PENTADECENE	C15H30-2
FLUOR-01	Conventional	FLUORENE	C13H10
N-PEN-02	Conventional	N-PENTADECANE	C15H32
ACENA-01	Conventional	ACENAPHTHENE	C12H10-D0
QUINA-01	Conventional	QUINALDINE	C10H9N
2-MER-01	Conventional	2-MERCAPTOBENZOTHIAZOLE	C7H5NS2
N-BUT-02	Conventional	N-BUTYLBENZENE	C10H14-1
1-ETH-01	Conventional	1-ETHYLNAPHTHALENE	C12H12-E3
2-ISO-01	Conventional	2-ISOPROPYLPHENOL	C9H12O-N1

INDEN-01	Conventional	INDENE	C9H8
ISOPR-01	Conventional	ISOPROPYLBENZENE	C9H12-2
INDAN-01	Conventional	INDANE	C9H10-E1
2:6-D-01	Conventional	2,6-DIMETHYLNAPHTHALENE	C12H12-E1
2:3-X-01	Conventional	2,3-XYLENOL	C8H10O-5
DIPHE-01	Conventional	DIPHENYL	C12H10
1:5-D-01	Conventional	1,5-DIMETHYL-4-(1-METHYLETHYL)NAPHTHALENE	C15H18-N13
1:2:3-01	Conventional	1,2,3-TRIMETHYLINDENE	C12H14
1:2:3-02	Conventional	1,2,3-TRIMETHYLBENZENE	C9H12-6
1:2:3-03	Conventional	1,2,3,4-TETRAMETHYL-BENZENE	C10H14-E7
1:2:3-04	Conventional	1,2,3,5-TETRAMETHYL-BENZENE	C10H14-E6
1:2:3-05	Conventional	1,2,3,4-TETRAHYDRONAPHTHALENE	C10H12
STYRE-01	Conventional	STYRENE	C8H8
PINAN-01	Conventional	PINANE	C10H18-N5
NAPHT-01	Conventional	NAPHTHALENE	C10H8
4-MET-02	Conventional	4-METHYLPHENANTHRENE	C15H12-D1
1-MET-03	Conventional	1-METHYLNAPHTHALENE	C11H10-1
1-MET-04	Conventional	1-METHYLINDENE	C10H10-D2
LIMON-01	Conventional	D-LIMONENE	C10H16-D1
1-MET-05	Conventional	1-METHYL-4-ISOPROPYLBENZENE	C10H14-7
BETA-01	Conventional	BETA-METHYLSTYRENE	C9H10-N2
1-TET-01	Conventional	1-TETRADECENE	C14H28-2
3-MET-01	Conventional	3-METHYL-1,2-HEXADIENE	C7H12-N43

1-MET-06	Conventional	1-METHYL-2-ETHYLBENZENE	C9H12-3

APPENDIX C: Developing kinetics into ASPEN software

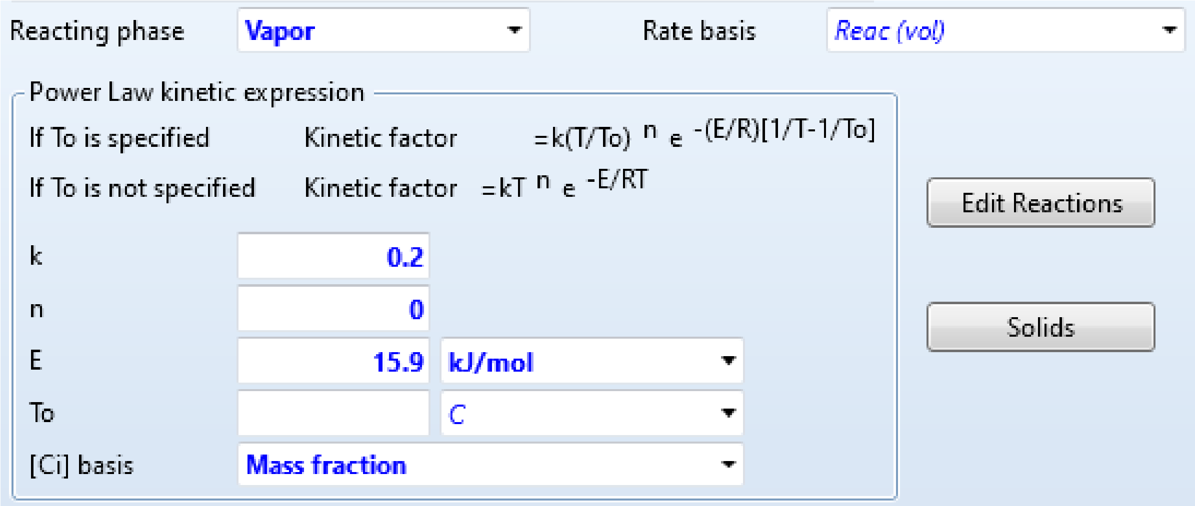


Reacting phase: Vapor
Rate basis: Reac (vol)

Power Law kinetic expression
If To is specified Kinetic factor $=k(T/To)^{n} e^{-(E/R)[1/T-1/To]}$
If To is not specified Kinetic factor $=kT^{n} e^{-E/RT}$

k: 0.40428
n: 0
E: 23.01 kJ/mol
To: C
[Ci] basis: Mass fraction

Figure 0.1: Non-condensable gas kinetics

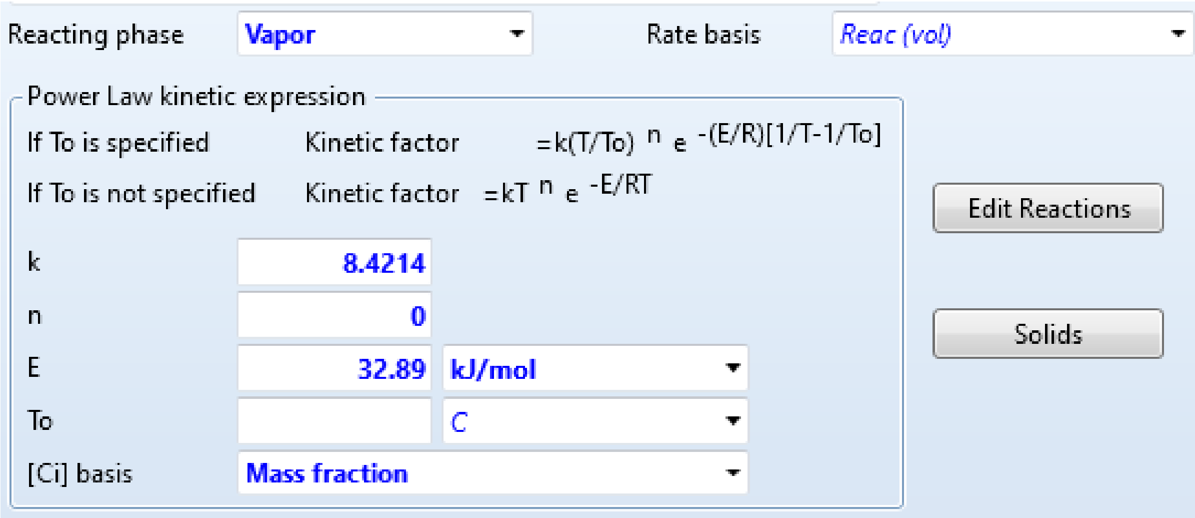


Reacting phase: Vapor
Rate basis: Reac (vol)

Power Law kinetic expression
If To is specified Kinetic factor $=k(T/To)^{n} e^{-(E/R)[1/T-1/To]}$
If To is not specified Kinetic factor $=kT^{n} e^{-E/RT}$

k: 0.2
n: 0
E: 15.9 kJ/mol
To: C
[Ci] basis: Mass fraction

Figure 0.2: Non-aromatics oil kinetics



Reacting phase: Vapor

Rate basis: Reac (vol)

Power Law kinetic expression

If To is specified Kinetic factor $=k(T/To)^{n} e^{-(E/R)[1/T-1/To]}$

If To is not specified Kinetic factor $=kT^{n} e^{-E/RT}$

k: 8.4214

n: 0

E: 32.89 kJ/mol

To: C

[Ci] basis: Mass fraction

Figure 0.3: Aromatic oil kinetics

APPENDIX D: Simulation data

CSTR simulation streams

Table D.28: CSTR streams

Parameter	**Units**	**TYRES**	**DRFEED**	**INFLASH**	**VAPOUR**	**DRYTYRES**	**N2**	**RFEED**	**ROUT**	**S30**
From			HX-1	DRYER	MOIST	MOIST		MIXER-1	DECOMP	H2S-EQUL
To		HX-1	DRYER	MOIST		MIXER-1	MIXER-1	DECOMP	H2S-EQUL	MIXER-2
Stream Class		MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC
Temperature	ºC	30.0	550.0	550.0	550.0	550.0	30.0	550.0	550.0	550.0
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Vapor Fraction		0.0	0.0	0.0	1.0	0.0	1.0	0.0	0.1	1.0
Mass Liquid Fraction		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Solid Fraction		1.0	1.0	1.0	0.0	1.0	0.0	1.0	0.9	0.0
Mass Flows	kg/hr	100.0	100.0	100.0	0.8	99.2	1.6	100.8	100.8	13.2

Table D.2: CSTR streams continued

Parameter	**Units**	**S29**	**S31**	**S25**	**CHAR**	**PRODUCT**	**COOLED**	**OIL**	**GAS**
From		H2S-EQUL	MIXER-2	CSTR	Sep-01	Sep-01	COOLER	Sep-02	Sep-02
To		MIXER-2	B1	Sep-01		COOLER	Sep-02		MIXER-3
Stream Class		MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC
Temperature	ºC	550.0	550.0	550.0	550.0	550.0	30.0	30.0	30.0
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Vapor Fraction		0.0	0.1	0.6	0.0	1.0	0.1	0.0	1.0
Mass Liquid Fraction		0.0	0.0	0.0	0.0	0.0	0.9	1.0	0.0
Mass Solid Fraction		1.0	0.9	0.4	1.0	0.0	0.0	0.0	0.0
Mass Flows	kg/hr	87.6	100.8	100.8	44.3	56.5	56.5	51.0	5.5

PFR simulation streams

Table D.3: PFR streams

Parameter	**Units**	**TYRES**	**DRFEED**	**INFLASH**	**VAPOUR**	**DRYTYRES**	**N2**	**RFEED**	**ROUT**	**S30**
From			HX-1	DRYER	MOIST	MOIST		MIXER-1	DECOMP	H2S-EQUL
To		HX-1	DRYER	MOIST		MIXER-1	MIXER-1	DECOMP	H2S-EQUL	MIXER-2
Stream Class		MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC
Temperature	ºC	30.0	550.0	550.0	550.0	550.0	30.0	550.0	550	550
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Vapor Fraction		0.0	0.0	0.0	1.0	0.0	1.0	0.0	0.1	1.0
Mass Liquid Fraction		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Solid Fraction		1.0	1.0	1.0	0.0	1.0	0.0	1.0	0.9	0.0
Mass Flows	kg/hr	100.0	100.0	100.0	1.5	98.5	1.6	100.1	100.1	12.9

Table D.4: PFR streams continued

Parameter	**Units**	**S30**	**S29**	**S31**	**CHAR**	**PRODUCT**	**COOLED**	**OIL**	**GAS**
From		H2S-EQUL	H2S-EQUL	MIXER-2	Sep-01	Sep-01	COOLER	Sep-02	Sep-02
To		MIXER-2	MIXER-2	B1		COOLER	Sep-02		MIXER-3
Stream Class		MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC
Temperature	ºC	550.0	550.0	550.0	550.0	550.0	30.0	30.0	30.0
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Vapor Fraction		1.0	0.0	0.1	0.0	1.0	0.1	0.0	1.0
Mass Liquid Fraction		0.0	0.0	0.0	0.0	0.0	0.9	1.0	0.0
Mass Solid Fraction		0.0	1.0	0.9	1.0	0.0	0.0	0.0	0.0
Mass Flows	kg/hr	12.9	87.2	100.1	49.7	50.4	50.4	44.1	6.3

Kiln Reactor simulations streams

Table D.5: Kiln reactor streams

Parameter	Units	TYRES	DRFEED	INFLASH	VAPOUR	DRYTYRES	N2	RFEED	ROUT	S30	S29
From			HX-1	DRYER	MOIST	MOIST		MIXER-1	DECOMP	H2S-EQUL	H2S-EQUL
To		HX-1	DRYER	MOIST		MIXER-1	MIXER-1	DECOMP	H2S-EQUL	MIXER-2	MIXER-2
Stream Class		MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC
Temperature	ºC	30.0	350.0	350.0	350.0	350.0	30.0	350.0	350.0	350	350
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Vapor Fraction		0.0	0.0	0.0	1.0	0.0	1.0	0.0	0.1	1.0	0.0
Mass Liquid Fraction		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Solid Fraction		1.0	1.0	1.0	0.0	1.0	0.0	1.0	0.9	0.0	1.0
Mass Flows	kg/hr	100.0	100.0	100.0	0.8	99.2	1.6	100.8	100.8	13.2	87.6

Table D.6: Kiln reactor streams continued

Parameter	**Units**	**S31**	**S25**	**S1**	**S2**	**CHAR**	**PRODUCT**	**COOLED**	**OIL**	**GAS**
From		MIXER-2	CSTR	B5	B6	Sep-01	Sep-01	COOLER	Sep-02	Sep-02
To		B1	B5	B6	Sep-01		COOLER	Sep-02		MIXER-3
Stream Class		MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC	MIXCINC
Temperature	ºC	350	350.0	450.0	550.0	550.0	550.0	30.0	30.0	30.0
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Vapor Fraction		0.1	0.6	0.6	0.6	0.0	1.0	0.1	0.0	1.0
Mass Liquid Fraction		0.0	0.0	0.0	0.0	0.0	0.0	0.9	1.0	0.0
Mass Solid Fraction		0.9	0.4	0.4	0.4	1.0	0.0	0.0	0.0	0.0
Mass Flows	kg/hr	100.8	100.8	100.8	100.8	44.5	56.3	56.3	50.9	5.4

APPENDIX E : Numerical model

Table 0.1: Numerical model parameters

T (°C)	Particle size (mm)	Feed rate (kg/hr)	A	B	C	AB	AC	BC	A^2	B^2	C^2	Oil (wt. %)	Char (wt. %)	Gas (wt. %)
600	0.71	1.05	600	0.71	17.5	426	10500	12.425	360000	0.5041	306.25	26.3	36.3	37.4
550	1	0.78	550	1	13	550	7150	13	302500	1	169	31.5	30.5	38.0
550	0.48	1.32	550	0.48	22	264	12100	10.56	302500	0.2304	484	32.7	46.6	20.8
550	0.48	0.78	550	0.48	13	264	7150	6.24	302500	0.2304	169	33.4	29.6	37.0
400	0.48	1.32	400	0.48	22	192	8800	10.56	160000	0.2304	484	33.5	44.7	21.8
475	0.3	1.05	475	0.3	17.5	142.5	8312.5	5.25	225625	0.09	306.25	34.0	44.6	21.3
550	1	1.32	550	1	22	550	12100	22	302500	1	484	34.6	30.5	34.9
475	1.18	1.05	475	1.18	17.5	560.5	8312.5	20.65	225625	1.3924	306.25	39.3	31.2	29.5
475	0.71	1.5	475	0.71	25	337.25	11875	17.75	225625	0.5041	625	39.6	34.0	26.4
350	0.71	1.05	350	0.71	17.5	248.5	6125	12.425	122500	0.5041	306.25	40.1	42.8	17.2
400	1	1.32	400	1	22	400	8800	22	160000	1	484	41.6	27.9	30.5
475	0.71	1.05	475	0.71	17.5	337.25	8312.5	12.425	225625	0.5041	306.25	42.1	31.2	26.7
475	0.71	1.05	475	0.71	17.5	337.25	8312.5	12.425	225625	0.5041	306.25	42.1	31.2	26.7
475	0.71	1.05	475	0.71	17.5	337.25	8312.5	12.425	225625	0.5041	306.25	42.1	31.2	26.7
475	0.71	1.05	475	0.71	17.5	337.25	8312.5	12.425	225625	0.5041	306.25	42.1	31.2	26.7
475	0.71	1.05	475	0.71	17.5	337.25	8312.5	12.425	225625	0.5041	306.25	42.1	31.2	26.7
475	0.71	1.05	475	0.71	17.5	337.25	8312.5	12.425	225625	0.5041	306.25	42.1	31.2	26.7

400	0.48	0.78	400	0.48	13	192	5200	6.24	160000	0.2304	169	43.6	39.8	16.5
475	0.71	0.6	475	0.71	10	337.25	4750	7.1	225625	0.5041	100	45.8	28.3	25.8
400	1	0.78	400	1	13	400	5200	13	160000	1	169	47.9	40.0	12.1

APPENDIX F : Sensitivity analysis on the factors influencing waste tyre pyrolysis

Table 0.29: A comparison between PR-BM and PR-BM78 on the pyrolysis oil yield

Temperature (ºC)	Oil yield (wt. %)	
	PR-BM	PR-BM 78
400	50.93	50.93
450	50.95	50.95
500	50.98	50.98
550	51.01	51.01
600	51.05	51.05
650	51.09	51.09
700	51.13	51.13

Table 0.30: Sensitivity analysis of temperature on the pyrolysis products for CSTR and PFR

Temperature (ºC)	CSTR			PFR		
	Oil (wt. %)	Char (wt. %)	Gas (wt. %)	Oil (wt. %)	Char (wt. %)	Gas (wt. %)
400	50.93	44.44	5.44	44.01	49.96	6.13
450	50.95	44.38	5.47	44.02	49.92	6.16
500	50.98	44.32	5.51	44.02	49.88	6.19
550	51.01	44.25	5.53	44.04	49.83	6.23
600	51.05	44.19	5.56	44.06	49.78	6.26
650	51.09	44.14	5.57	44.09	49.73	6.28
700	51.13	44.09	5.58	44.13	49.67	6.30

Table 0.31: Impact of reactor type on oil yield for 550 ºC operating temperature

Reactor type	Oil (wt. %)	Char (wt. %)	Gas (wt. %)
CSTR	51.01	44.25	5.53
Kiln	50.93	44.47	5.39
PFR	44.09	49.73	6.28

Table 0.32: Sensitivity analysis of PFR length on oil yield

Length (m)	Oil (wt. %)
1.0	44.087
1.7	44.094
2.0	44.094
3.0	44.094
4.0	44.094
5.0	44.101

Table 0.33: Sensitivity analysis of PFR diameter on oil yield

Diameter (m)	Oil (wt. %)
0.10	44.049
0.15	44.094
0.58	44.098
1.05	44.109
1.53	44.097
2.00	44.098

Table 0.34: Sensitivity analysis of CSTR residence time on oil yield

Residence time (hr)	Oil (wt. %)
0.1	50.939
0.2	50.963
0.3	50.970
0.4	50.974
0.5	50.977
0.6	50.978
0.7	50.980
0.8	50.980
0.9	50.981
1	50.982

Table 0.35: Sensitivity analysis of CSTR operating pressure on oil yield

Pressure (atm)	**Oil (wt. %)**
0.10	50.985
0.20	50.984
0.30	50.983
0.41	50.983
0.51	50.982
0.61	50.981
0.71	50.980
0.81	50.979
0.91	50.978
1.01	50.977

Table 0.36: Sensitivity analysis of CSTR heating rate on oil yield

Heating rate (K/min)	**Oil (wt. %)**
5	50.753
10	50.852
15	50.880
20	50.866

Table 0.37: Impact of the catalyst on the CSTR oil yield

Catalyst	**Oil (wt. %)**
No catalyst	49.925
Catalyst	51.710

Table 0.38: Impact of particle size on the CSTR oil yield

Temperature (ºC)	**Oil (wt. %)** **d_p range : 0.1 - 0.8 mm**	**Oil (wt. %)** **d_p range : 0.8 - 4 mm**
450	9.65	11.57
500	22.08	15.55
550	35.38	19.59
600	42.81	23.52

APPENDIX G: Economic analysis

Table 0.39: Revenue breakdown according to China pricing

Revenue	t/year	$/t	m$/year	mR/year
Oil sales	4181	400	1.7	25.1
Carbon sales	2847	300	0.9	12.8
Steel sales	813	150	0.1	1.8
Tipping fee	8000	80	0.6	9.6
Total revenue	-	-	3.3	49.3

Table 0.40: Revenues breakdown according to the Ireland pricing

Revenue	t/year	$/t	m$/year	mR/year
Oil sales	4181	421	1.8	26.4
Carbon sales	2848	105	0.3	4.5
Steel sales	814	84	0.1	1.0
Tipping fee	8000	102	0.8	12.2
Total revenue	-	-	2.1	31.9

Table 0.41:Revenue breakdown according to the South African pricing

Revenue	t/year	$/t	m$/year	mR/year
Oil sales	4181	537	2.2	33.7
Carbon sales	2848	274	0.8	11.7
Steel sales	814	66.28	0.1	0.8
Tipping fee	8000	91	0.7	10.9
Total revenue	-	-	3.8	57.1

Table 0.42: Return on investment based on pricing from three different locations

Year	China	Ireland	South Africa
0	-100 %	-100 %	-100 %
1	-48 %	-65 %	-32 %
2	-22 %	-31 %	-3 %
3	-7 %	4 %	14 %
4	4 %	39 %	25 %
5	11 %	74 %	32 %
6	16 %	108 %	37 %
7	20 %	143 %	42 %
8	24 %	178 %	45 %
9	26 %	213 %	48 %
10	29 %	247 %	50 %