



WASTE TYRES VALORIZATION BY SOLVENT EXTRACTION PRE-TREATMENT AND PYROLYSIS

by

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December 2020

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Abstract

Solvent extraction was studied as a pre-treatment method to eliminate certain impurities such as additives, plasticizers and heteroatoms before pyrolysis of waste tyres. This approach is the starting point for the proposal of waste tyres treatment to increase the yield of the liquid fraction and the efficiency of the pyrolysis process's accuracy. Two solvents, DCM and DEE, were used during the pre-treatment process. The products from both the pre-treated and untreated waste tyres crumbs pyrolysis are compared in yield and characterized using various analysis such as TGA, FTIR, GCMS.

The results show that DCM is the best solvent for waste tyres pre-treatment due to its polarity and strength in the heteroatom removal. The optimum results were found at an extraction time of 150 min, a recovery of 14.15 wt.% for oil yield using waste tyres small size (0.5-1 mm) with a selectivity of 1.35. These results make DCM a suitable solvent in the waste tyres pre-treatment.

The GCMS results for TDO show the predominance of DL-Limonene and BTXE, while those from solvent extraction oil show a predominance of 4-Benzenediamine, N-1,3-dimethylbutyl-N. This compound is used during the tyres manufacturing process as a rubber accelerator. The FTIR results show a prevalence of alkane, alkene, aldehyde and halo-compound functional group. The waste tyres crumb pre-treated and untreated have conducted to the pyrolysis unit as a feedstock. The highest oil yield was 55.64 wt.% at 550 °C, with the nitrogen flow rate of 6.5 l min⁻¹ and 15 °C min⁻¹ heating rate using waste tyres treated with DCM, large particle size (4-5 mm).

The FTIR analysis shows a predominance of carbonyls C=O, aldehyde CHO and ketone RCOR. There is also some ester RCOOR, acid RCOOH, N-H bending amine with a strong bond in the wavenumber range between 1700-400 cm⁻¹. As can be seen from the results above-mentioned, the better way to deal with waste tyres is to pre-treat them with solvent extraction using DCM as a solvent and the particle size in the range of 1-5 mm before the pyrolysis process. This method showed an improvement in the oil yield with a significant decrease in impurities.

Preface

The experimental work described in this dissertation carried out at the University of KwaZulu-Natal in the College of Agriculture, Engineering and Science (CAES) at the Department of Chemical Engineering, Howard College Campus, Durban, from February 2019 to December 2020, under the supervision of Dr Malusi Mkhize and Dr Mbuyu Ntunka,

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Dedication

To my uncle, Dr Auguy Mwandwe Mufute.

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List of chemical formula

Name	Formula
Aluminium	Al
Cadmium	Cd
Calcium	Ca
Calcium carbide	CaC ₂
Calcium carbonate	CaCO ₃
Carbone monoxide	CO
Carbone dioxide	CO ₂
Chromium	Cr
Copper	Cu
Copper (II) nitrate	Cu (NO ₃) ₂
Fluoride	F ₂
Hydrogen	H ₂
Hydrogen chloride	HCl
Iron	Fe
Isoprene	2-methyl-1, 3 butadiene
Lead	Pb
Magnesium	Mg
Magnesium oxide	MgO
Nitrogen	N ₂
Nitrogen oxide	NO _x
Oxygen	O ₂
Silicon	Si
Sodium carbonate	Na ₂ CO ₃
Sodium hydroxide	NaOH
Sulphur	S ₂
Sulphur dioxide	SO ₂
Titanium dioxide	TiO ₂
Zinc	Zn
Zinc oxide	ZnO ₂

List of abbreviations

Abbreviation	Description
DCM	Dichloromethane
DEE	Diethyl Ether
TGA	Thermogravimetry Analysis
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetric
GCMS	Gas Chromatographic-Mass Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
mm	Millimetre
cm	Centimeter
NR	Natural Rubber
SBR	Synthetic Butadiene Rubber
wt. %	Weight percentage
min	Minute
s	Second
l	Liter
MJ	Mega Joule
Kg	Kilogram
REDISA	Recycling and Economic Development Initiative of South Africa
TDO	Tyres Derived Oil
PAHs	Polycyclic aromatic hydrocarbons
ASTM	America Society for Testing Materials
ISO	International Organisation for Standardization
Exp	Experiment
CRM	Customer Relationship Management
LP	Linear Programming
ID	Internal Diameter
BTXE	Benzene Toluene Xylene Ethylbenzene
R time	Retention time

1 Introduction

The decreasing of fossil energy and the rise in greenhouse gas emissions create a growing demand for renewable resources and waste valorization processes. One of the significant challenges facing today's modern society is the disposal and recycling of liquid and solid waste created by human activities (Rowhani and Rainey, 2016). The use of renewable resources and waste valorization processes has become the forefront in researching potential materials and energy sources.

Waste tyre disposal is a rising issue concern since waste tyres are bulky; hence they occupy a significant portion of landfill for a prolonged period due to their complex chemical nature that renders them resistant to biological degradation. This solution is not attractive because the high chemical compounds loss can lead to soil, air and water pollution if not manipulated carefully (Galvagno et al., 2002).

Due to the rise in the number of vehicles, there is a substantial increase in tyre demand. At least 1.5 billion scrap tyres are decommissioned worldwide per year, and approximately 4 billion tyres have been accumulated discarded (Krishnan et al., 2018). A tyre consists mainly of rubber with a high heating value (HHV) at 42.00 MJkg⁻¹ compared to the high-grade coal 32.08 MJkg⁻¹. These properties make tyres a suitable candidate for energy and chemicals through pyrolysis. The estimated waste tyres that are generated every year in South Africa is between 60 to 100 million.

Following the Recycling and Economic Development Initiative of South Africa (REDISA), most scrap tyres are incinerated to recover metal content, creating an environmental problem. Open burning of waste tyres releases many dangerous components such as dioxins and carbon monoxide (CO). Many methods have been developed to deal with tyres; the most common one is pyrolysis, which entails the thermal devolatilization of various matter at high temperature, particularly in the oxygen-free atmosphere, to obtain oil, char and gas. Pyrolysis of waste tyres has the benefit of finding a solution to the energy crisis, chemicals and materials recovery (Verma et al., 2019).

Several experiments have been carried out in the laboratory and on an industrial scale to study the pyrolysis of waste tyres in an inert atmosphere to produce valuable compounds and energy from oil, solid char and gas (Sharma et al., 2000). The oil obtained from pyrolysis can be easily stored until required where they are utilized. Usually, waste tyres contain fixed carbon, high

volatile matter and low ash with an HHV (42.00 MJ kg^{-1}) greater than coal (32.08 MJ kg^{-1}) (de Marco Rodriguez et al., 2001).

Tyre derived oil (TDO) contains various compounds such as limonene, benzene, and toluene suitable for multiple applications. Due to the presence of polar compounds, which usually contain sulphur (S_2), nitrogen (N_2), O_2 , zinc (Zn) etc. the recovery of the valuable chemicals and processing (distillation) of the TDO is challenging (the presence of S_2 and nitrous component in the distillation products do not facilitate the procedure). The tyre processing additives mainly comprise a mixture of rubbers, metal, processing additives and textiles (Sienkiewicz et al., 2012).

A potential to remove the polar compound prior to pyrolysis and associated benefits such as less complicated TDO and elimination of nitrous, sulphurous and O_2 compounds that attached prevent the processing of the TDO. It is known that the rubber fraction is the primary source of valuable chemicals, while the processing additives are the primary source of the polar compound (Zhang et al., 2016).

The processing additives are the primary source of the heteroatoms, which are undesirable during the pyrolysis process due to catalyst deactivation and gum formation. Therefore, it recommended that these heteroatoms be removed before the pyrolysis process. It reduces the complexity when recycling the waste tyres, improving the liquid fraction obtained during pyrolysis (Williams, 2013). Solvent extraction as pre-treatment before the pyrolysis process is the proposed method to remove heteroatoms.

1.1 Problem statement

The lack of awareness regarding the influence on the climate and wellness impacts caused by improper waste tyres control can significantly impact global warming. In South Africa, dumping and landfills were the primary practical ways to deal with and handle waste tyres (Shakya et al., 2006). However, the routine is rapidly declining due to the government initiatives, such as REDISA, policies mandating that tyres may not be dumped in the landfill because they are not biodegradable (Moo-Young et al., 2003). It noted that open dumping has many effects on the environment because tyres stockpiles are breeding grounds for venomous insect, snakes and mosquitoes (Karell and Blumenthal, 2001).

In addition to the emission of hazardous gases, accidental run-away fires from waste tyres are difficult to extinguish (Chen et al., 2010). Currently, South Africa integrates a formal waste tyre legislation act to deal with waste tyres' manufacturing and accumulation. The National

Environmental Management purpose: Waste Act 2008, act no. 59 of 2008 aims to regulate waste tyres management by issuing regulatory mechanisms that affect those dealing with tyres, including the manufacturers of waste tyres, owners of waste tyre stockpiles, and recyclers of tyres (Godfrey and Oelofse, 2017). An amount of 3,256.7 tons of waste tyres was disposed of in South Africa in 2018 (Sebola et al., 2018).

In South Africa, a tyre recycling company, the Mathe Group, located in Hammarsdale, KwaZulu-Natal, was established later in 2011. The Mathe Group recycle many of the post-consumer tyres and utilizes its manufactured products in fields such as sports surfaces, acoustic underlays and road surfacing (Muzenda, 2014). Effort regarding recycling waste tyres is compulsory for solving the problems associated with stockpiles of the used tyres (Cook and Kemm, 2004). Furthermore, many tyres recycling methods are used, such as gasification, incineration, and grinding (Jang et al., 1998). Pyrolysis, which has gained great publicity worldwide from many organizations, will be the perfect way to solve tyre waste problems (Demirbas, 2004).

As a treatment option to generate the TDO, recycling the waste tyre using pyrolysis has several advantages that can be used at once as fuels or blended into petroleum refinery feedstock (Lam and Chase, 2012). The pyrolysis gas (pyro-gas) is also economical as a fuel, and solid char is using after some processing, as carbon black or activated carbon (Williams et al., 1993).

Waste tyres have a high volatile quality, carbon contents, and HHV, making them a suitable material for energy recovery with the appropriate method such as pyrolysis (de Marco Rodriguez et al., 2001).

1.1.1 Research question

Is there any improvement in the TDO composition achieved when the tyre crumb is treated with the solvent to remove processing additives before pyrolysis? What are the essential factors that affect the solvent extraction extent and pyrolysis of the wastes tyres?

1.2 Aims and objectives

This project investigates if waste tyre pre-treatment by solvent extraction is a suitable method to obtain TDO through pyrolysis and to see the feasibility of processing the tyre-derived fuel to produce valuable chemicals and recover the energy. The study further focuses on the following objectives,

- to investigate the effect of solvent extraction type and extraction time on the heteroatoms removal from waste tyre crumbs,
- to produce liquid fuel by using waste tyre crumb prior and post solvent treatment,
- to characterize the TDO for their physical properties and chemical composition,
- to describe the solid residue using various analysis methods, i.e., proximate.

1.3 Thesis outline

This part describes different chapters in the thesis and briefly explain some subsections.

Chapter 1 presents the introduction; this chapter reviews the waste tyres problem that needs to be solved.

Chapter 2 presents the literature review; this chapter includes an overview of the available published works in waste tyre valorization. A general description of the waste tyre challenge and the various approaches used to deal with them.

Chapter 3 presents the materials and methods, this chapter will provide the characterization procedure for the untreated and treated waste tyres crumb and highlight the experimental approach for pyrolysis and the characterization of the liquid product and solid obtained by the pyrolysis process.

Chapter 4 presents the result and discussion part in explaining solvent extraction and pyrolysis of the untreated and treated tyres. The thermal decomposition and the characterization of oil were reported.

Chapter 5 presents the conclusion and future work. In this chapter, conclusive remarks are provided and highlighting significant observation from the experiments performed and offer some guidelines for further study.

2 Literature review

This chapter offers a detailed review of the research most closely related to the waste tyres problem, solvent extraction and thermochemical conversion methods. The research that some authors have done in waste tyres pre-treatment before pyrolysis are also presented in this chapter.

2.1 Waste tyres problem

The latest figures for producing waste tyres are 2.5 million tonnes each year in America, 2.0 million tonnes in Europe and 0.5 million tonnes in Japan (Scarlat et al., 2019). Excessive waste tyres have become a significant environmental concern at an exponential production growth. Improper disposal of waste tyres leads to an environmental problem and may bring about complications when inadequately treated (Jacob et al., 2014). Developing countries have focused on effectively utilizing waste tyres to reach ecological preservation, recycling and energy efficiency (Suhanya et al., 2013).

Stockpiling and storage of waste tyres stimulate the incursion of snakes and vermin. Moreover, it can result in uncontrolled risk fire, which causes damage to the environment due to the release of toxic compounds such as Dioxins into the atmosphere (Doğan et al., 2012). The hazard to the environment posed by waste tyres is substantial because they are not biodegradable and can last for many decades if there is no careful handling (Torretta et al., 2015). Tyres are highly resistant to physical, chemical and biological deterioration, which minimizes the potential for their mechanical and chemical reuse and recycling (Gupta et al., 2015). The energy content of waste tyres may be used for incineration. However, this correlates with the release of sulphur dioxide (SO₂), Nitrogen oxides (NO_x) and other harmful pollutants (Stratiev et al., 2013).

2.2 Waste tyres in South Africa

Currently, South Africa utilizes formal waste tyre legislation to deal with the manufacturing and accumulation of waste tyres (Sebola et al., 2018). The purpose of the national environmental management waste act no.59 of 2008 is to regulate waste tyres management by issuing regulatory mechanisms that affect waste tyre producers (Godfrey and Oelofse, 2017).

An approximate 60 to 100 million used tyres are in South Africa in stocks spread across the world, to which about 11 million waste tyres are added each year (Oboirien and North, 2017). Most of the waste tyres (about 80 %) are stockpiled or dumped across the country, which causes threats to the environment and human due to improper management of waste tyres (Wagan et al., 2017).

2.2.1 Human health problems

The stockpiled and stored waste tyres may shelter pests that carry various diseases. Breeding for mosquitoes may also be the stagnant water stored within casings (Sharma et al., 2000). It is known that the deadly illness transmitted mainly by mosquitoes is malaria (Reschner, 2008). The hazardous chemicals from burned tyres such as chromium (Cr), Zn and lead can also be dangerous to human health (Singh et al., 2009).

2.2.2 Environmental problems

Water, air, and soil contamination are listed below as environmental problems caused by waste tyres' combustion. The high toxic portion in the composition of the tyres that can lead to pollution is also highlighted.

2.2.2.1 Air pollution

Total combustion releases carbon dioxide (CO₂) and (SO₂) into the atmosphere as tyres are burnt, whereas incomplete combustion produces highly toxic chemical compounds. They cause the problem to the reproduction, growth and the immune system in the human body. They can also interact with hormones and cause cancer (Labaki and Jeguirim, 2017).

2.2.2.2 Soil pollution

Remaining residues, such as cadmium (Cd), Cr, Zn, copper (Cu) and lead (Pb), may pollute the soil immediately after burning the waste tyres by penetrating liquid products into the ground or by gradually leaching ash and unburned residues (Zhang et al., 2018). Soil pollution can lead to a disaster in the agriculture sector (Humphrey et al., 2000).

2.2.2.3 Water pollution

Consequently, pyrolysis of the rubber after combustion, the decomposed oil penetrates and leaches into the groundwater or can discharge into nearby ditches, streams, and waterways. The cause of water bond diseases may be water contamination (Maheswari et al., 2012). Figure

2.1 shows the waste tyres disposal in landfills. As can be seen, the waste tyres are stocked up for recycling or re-using for their rubber and other value components.



Figure 2.1: Waste tyres disposal in landfill (Pilusa et al., 2014).

2.3 Rubber tyres

In addition to the rubberized cloth with reinforcement textile strings and steel, rubber is a commodity with different applications and includes vulcanized rubber (Kruželák et al., 2016). Three major rubber types used for tyre compounding are natural rubber (NR), synthetic and reclaimed. The most common synthetic rubber used is styrene-butadiene copolymer (SBR), containing 25 wt.% styrenes (Mastral et al., 2000).

2.3.1 Natural rubber

The isoprene polymer (2-methyl-1, 3 butadiene) is the chemical formula of NR derived from the sap of the rubber tree. Diverse other plants, such as *ficus elastica*, a native of the Congo, and *guayule*, also produce rubber (Tekasakul and Tekasakul, 2006). *Hevea* is a native of the Amazon Basin, and until about 1910, the majority of natural rubber came from wild trees in this region (Pehlken and Mueller, 2009).

2.3.2 Synthetic rubber

Synthetic rubber is artificial rubber made from raw materials such as butadiene and styrene (Mostafa et al., 2009). SBR is made of styrene and butadiene monomers, which are necessary in petroleum (Kan et al., 2017). The bulk of all SBR produced goes into tyres, while the remainder goes to items (Choi, 2000).

Table 2.1 shows a typical composition of passenger and truck tyres.

Table 2.1: Composition of passenger and truck tyres.

Composition	Passenger tyre	Truck tyre
Natural rubber (wt.%)	14	27
Synthetic rubber (wt.%)	27	14
Carbon black (wt.%)	28	28
Steel (wt.%)	14-15	14-15
Fibre, fillers, accelerators, antiozonants, etc. (wt.%)	16-17	16-17
Average weight (Kg)	New 11 Scrap 9	New 54 Scrap 45

2.3.3 Reclaimed rubber

Reclaimed rubber is known as devulcanized rubber, and its viscosity and the properties of the original compound have been restored (Nevatia et al., 2002). The treatment of soil vulcanized scrap produces the recovered rubber from various waste rubber products through heat and chemical agents (Naima and Liazid, 2013). In contrast to natural rubber, recycled rubber has lower tensile strength, lower elasticity and lower wear resistance. (Kumnuantip and Sombatsompop, 2003).

2.4 Characteristics and chemical composition of waste tyres

Tyres are composed of a composite mixture of chemical compounds and materials to yield the characteristics they require, such as temperature resistance, strength and durability (Osayi et al., 2014).

The most substantial proportion of a tyre consists of rubber, which made up of NR, SBR and thermoset polymer (Lin et al., 2006). In pyrolysis conditions, tyres' rubber composition plays a critical role as each rubber has a different degradation temperature. In a typical car type, the blending is 45 wt.% NR and 55 wt.% SBR (Moo-Young et al., 2003). To reinforce the tyres and improve properties such as tensile strength, strength and abrasion, Fillers such as carbon

black and silica are used (Moulin et al., 2017). Silica also increases the tyres' rolling resistance. Process additives in the form of extender oil are applied during the manufacturing process to the rubber compounds to soften, strengthen, and promote rubber processing (Edil, 2005).

The manufacturing process softens, improve and facilitate the processing of rubber production. The tyres' manufacturing process involves a chemical vulcanization process, also known as cross-linking or curing, where the rubber heated with a sulphur accelerator and an activator at 140-160°C (Gieré et al., 2004).

The process constitutes an irreversible reaction between S₂ and other chemicals to achieve high tensile strength and elasticity by creating a cross-linked three-dimensional polymer network between the rubber molecules. Accelerators and activators such as S₂, carbon black, zinc dioxide (ZnO₂) and titanium dioxide (TiO₂) are used as facilitators during the vulcanization time and improve the tyre properties (Materne et al., 2004).

The accelerators and activators utilized to decrease the vulcanization time, reduce the temperature and improve the tyre properties. Various accelerators such as 2-mercaptobenzothiazole, 2,2- dithiobenzothiazole, N-cyclohexyl benzothiazole-2-sulfenamide are used addition to sulphur and intended to increase the reaction rate of the vulcanization process, hence reducing the reaction time.

Activators also reduce the reaction rate by developing chemical complexes with the accelerators (Heideman et al., 2004). The formation of such complexities during the vulcanization process and the addition of components such as steel fibres during the manufacturing process aid in the difficulty of recycling, reclamation and degradation of waste tyres (Sharma et al., 2000).

2.5 Tyres categories

Based on vehicle applications, there are many different tyres categories, which usually have different rubber composition. They are made for their use on vehicles instead of recycling industry feedstock due to their complex structure that makes them difficult to recycle. However, the most popular tyres categories are passenger car tyres, truck tyres and off-the-road tyres. These tyres consist of various rubber compounds, carbon black, fillers such as clay and silica, which are added to promote vulcanization. Table 2.2 shows the description and composition of passenger car tyres, off-the-road tyres, and truck tyres.

Table 2.2: Tyres Categories.

Type of tyres	Description	Composition	Authors
Passenger car and light truck tyres	They are using on passenger vehicles to carry people and goods.	Rubber/ elastomer (47 wt.%), carbon black (21.5 wt.%), metal (16.5 wt.%), and additives (7.5 wt.%)	(Sharma, 2013)
Heavy-duty truck tyres	They are using on bus and truck. The tread and belt for the truck tyres must be made in synthetic and natural rubber to ensure a low rolling resistance, good petrol mileage and optimum handling.	Elastomer (45 wt.%), steel (25 wt.%) and carbon black (22 wt.%)	(Sharma et al., 2000)
Off-the-road tyres	These tyres are mainly using wheel loaders, backhoes and construction vehicles.	Rubber/Elastomers (47 wt.%), carbon black (22 wt.%), metal (12 wt.%) and additives (6 wt.%).	(Singh et al., 2019)

2.6 Methods of recycling of tyres

At the end of a tyreing life, the residual material product would still be either recycling or re-using. There are various methods, such as retreading, reclaiming, pyrolysis, incineration, gasification, combustion, etc.

2.6.1 Retreading

Retread, also referred to as remoulding, involves only the casings of used tyres that have been tested and repaired (Dabić-Ostojić et al., 2014). Trust in product quality is a significant obstacle in the process, although it is economically beneficial (Simic and Dabic-Ostojic, 2017). The mould cure method and pre-cure process are two types of tyre retreading. The distinction is only in the series of operations between them and whether the tread application happens before or after its healing (Ferrer, 1997).

2.6.2 Mechanical or cryogenic recycling

Mechanical and cryogenic manufacturing of used tyres require milling of casings for the production of ground rubber of various particle sizes (Jonna and Lyons, 2005). Finely ground rubber is used in multiple applications, such as road asphalt additives (Kalia, 2010). However, the small product market and the high cost of running the operation are drawbacks (Aguado et al., 2002).

2.6.3 Reclaiming rubber

Reclaiming rubber is the method used to produce the reclaimed rubber by mixing the waste vulcanized rubber with the unvulcanized new rubber in a hot atmosphere for mastication (Bockstal et al., 2019). There are various rubber recovery methods and procedures for reclaiming rubber, and used tyres can be converted from a three-dimensional polymer with virgin rubber properties (Shi et al., 2013).

2.7 Pyrolysis process

The high process cost such as retreading and reclaiming, the consistency of the goods and the lack of industry awareness of rubber recycling as raw material are a setback to the process (Molanorouzi and Mohaved, 2016). Pyrolysis is one of the processes used to produce renewable fuels and chemicals in which the organic material is converted into usable energy at temperatures between 200-600 °C (Berrueco et al., 2005). Added products such as fuels or chemicals in solid, liquid or gas form are produced by this process (Frigo et al., 2014). The key advantages of pyrolysis, including easy machinery and high-energy conversion, is the TDO obtained is used as fuel in the engine and can be stored or utilize in situ (Murugan et al., 2008). However, the existence of compounds such as phenolic and polycyclic aromatic hydrocarbons (PAHs) results in high emissions and high maintenance (Kumaravel et al., 2016). Figure 2.2 shows the pyrolysis process for waste tyres crumb, leading to the production of oil, char and gas.

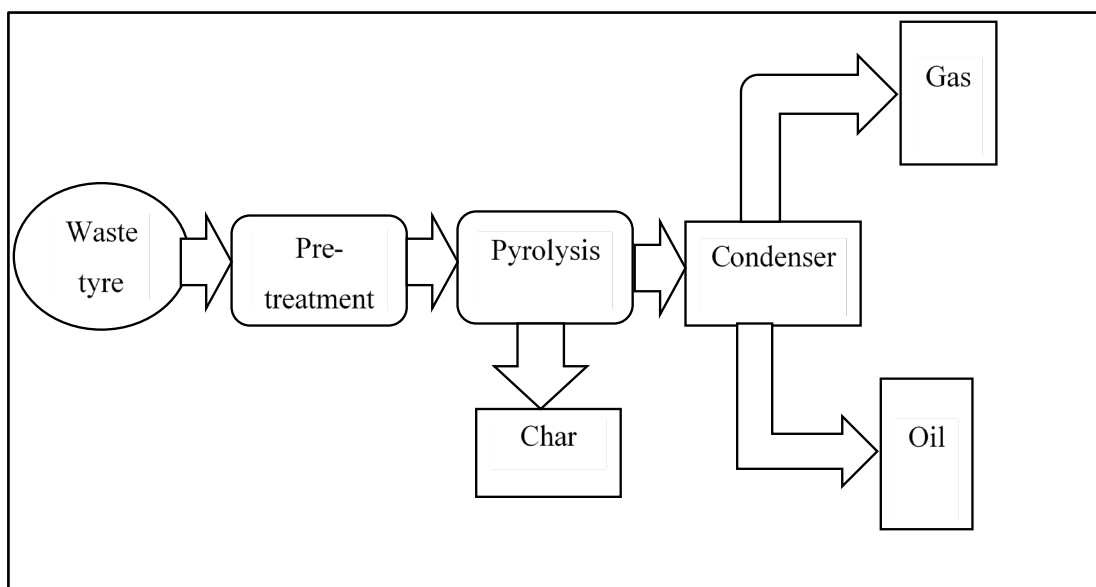


Figure 2.2: Waste tyres pyrolysis process.

2.7.1 Pyrolysis classification

Based on the operating conditions and product distributions, pyrolysis is divided into three main classes (slow, fast and flash pyrolysis) based on the working conditions and product distributions (Duman et al., 2011). Besides, the relative distribution of pyrolysis product is mainly affected by the reactor's temperature (Balat et al., 2009).

2.7.1.1 Slow pyrolysis

Slow pyrolysis has been used for thousands of years to increase char output at low temperatures and heating rate (Bruun et al., 2012). In this step, the vapour residence time is relatively more extended, and components begin to react with others in the vapour phase, resulting in solid char and oil formation (Onay and Kockar, 2003).

However, slow pyrolysis's technical limitations make it unlikely to be suitable for high-quality oil production (Pottmaier et al., 2013). In the slow pyrolysis process, cracking of the original product occurs due to prolonged residence time and may adversely affect oil yield and quality (Onay and Kockar, 2003). Besides, long residence time and low heat transfer require additional power inputs (Tippayawong et al., 2008).

2.7.1.2 Fast pyrolysis

In the quick pyrolysis process, waste tyres are heated to a high temperature in an inert atmosphere (Xue et al., 2015). Depending on the feedstock, fast pyrolysis generates 40 – 60 wt.% of oil products with 30 – 40 wt.% of solids and 10 – 20 wt.% of gaseous phase (Sanahuja-

Parejo et al., 2018). The fast pyrolysis process's significant characteristics are a high heating rate, short vapour residence time, and a rapid cooling system (Bridgwater et al., 1999).

In the development of TDO, the selection of speciality chemicals and commodities, fast pyrolysis is gaining enormous popularity (Brammer et al., 2006). Moreover, the quick pyrolysis method requires relatively low capital investment, particularly on a small scale, compared to other processes (Oasmaa et al., 2015).

2.7.1.3 Flash pyrolysis

This method is characterized by less than 0.5 s of residence time, a high heating rate of more than $200^{\circ}\text{C min}^{-1}$, a particle size of less than 0.2 mm and a high reaction temperature of more than 1000°C (Onay and Kockar, 2003).

2.7.1.4 Catalytic pyrolysis

A pyrolysis process that involves the use of a catalyst is called catalytic pyrolysis, and it helps by breaking down higher molecular weight hydrocarbon compounds into lighter hydrocarbon products (Carlson et al., 2009).

Several researchers have investigated the use of the catalyst in tyre pyrolysis systems. It has been found that the structure, consistency and yield of products can be significantly influenced by the catalyst (Williams and Brindle, 2003).

Sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), magnesium oxide (MgO), calcium carbonate (CaCO_3), perlite, calcium carbide CaC_2 , copper (II) nitrate $[\text{Cu}(\text{NO}_3)_2]$, etc., are some of the examples of catalysts used in pyrolysis (Shah et al., 2009).

2.7.2 Pyrolysis reactor

The subject of significant research has been on reactors, which focus on considerable research, innovation and growth to enhance the critical characteristics of high heating rates, moderate temperatures and short hot volatiles substance residence times for liquids (Stiles and Kandiyoti, 1989). At first, the pioneers of pyrolysis reactors had thought that the size of small waste tyres particles and the short time of residence would result in high oil yields (Boxiong et al., 2007). However, particle size and hot volatile residence time have little impact on the oil yield, while the heating rate and temperature have a significant effect on the composition of TDO (Wang et al., 2005).

Several reactor models were designed to optimize pyrolysis efficiency and generate high-quality oil (Yazdani et al., 2019). However, each reactor has its unique characteristics, oil yield

power, advantages and limitations (Hershkowitz et al., 2018). Among the pyrolysis reactors, the most popular used to recycle waste tyres are presented in the following sub-sections.

2.7.2.1 Fixed bed reactor

The gas refrigeration and cleaning reactor is part of the fixed bed pyrolysis system. Fixed bed reactor technology for fuels is fast, reliable and tested (Chopra and Jain, 2007). In this type of reactor, the solids travel down a vertical or horizontal shaft and contact the commodity gas stream's upward-moving counter-current (Aylón et al., 2008). The fixed bed reactors usually operate with carbon retention, long residence time and low gas velocity (Dixon and Nijemeisland, 2001). The biggest challenge with fixed bed reactors is removing tar, but recent developments in thermal and catalytic tar conversion have created viable options for tar removal (Yang et al., 2006).

2.7.2.2 Fluidized bed reactor

The stable mixture that exhibits specific properties consists of the fluidized bed reactor (Dai et al., 2001). In general, the pressurised fluid introduction usually achieves this through the solid particulate material (Rodríguez et al., 2019). They provide reasonable control for pyrolysis reaction and the residence time of hot volatile, extensive high surface contact between the fluid and reliable volume per unit bed volume (Nikoo and Mahinpey, 2008).

2.7.2.3 Vacuum pyrolysis reactor

The slow pyrolysis process is performed by vacuum reactors resulting in lower heat transfer rates and lower oil yields of 35 – 50 wt.% compared to 75 wt.% recorded with the fluidized bed technologies (Roy et al., 1997). The pyrolysis process using the vacuum reactor is very mechanically complex and involves high capital expenditure and maintenances costs (Lopez et al., 2010). However, vacuum reactors have the critical advantage of handling larger particles (up to 2-5 cm) of waste tyres than fluidized bed reactors (Ismadji et al., 2005).

2.7.2.4 Pyros reactor

Pyros pyrolysis is done in a single oil production unit with a cyclone reactor with an integrated hot gas filter (Brem and Bramer, 2007). The waste tyres and the inert heat carrier have been introduced as part of the cyclone, and recycled vapours transport the solids from the process (Bramer et al., 2004). The particles are forced downwards by the centrifugal force to the cyclone's periphery, and the scrap tyres are washed, heated and devolatilized during the transport. This reactor is relatively compact and low cost with 70 – 75 wt.% oil yield power (Lede, 2013).

2.7.2.5 Plasma reactor

Plasma pyrolysis reactors are usually made of a cylindrical quartz tube surrounded by two copper electrodes (Zenasni et al., 2003). To generate gas flows through the line with thermal energy, the electrodes are coupled to electrical power sources. Also, the oxygen is absorbed by an inert gas that is injected into the reactor (Mitarai, 1995). The inert gas is often used by a variable speed vacuum pump as a working gas to produce plasma and expel the gas from the reactor (Tang and Huang, 2005).

Moreover, in the pyrolysis of waste tyres, plasma reactors offer some specific advantages compared to conventional reactors., but they consume high electrical power and have high operating costs (Chen et al., 2003).

2.8 Gasification

Gasification is a method based on transforming a carbonaceous material into gas that contains mainly CO, CO₂, and light hydrocarbons (López et al., 2012). Gasification typically occurs at higher temperatures (700-1400°C) than pyrolysis and in the presences of a partially oxidative reactive atmosphere (Galvagno et al., 2006). The resulting gas mixture is a fuel capable of running gas turbine fuel cells. Gasification reactors are known as fixed beds, fluidized beds, or arched beds (Stiegel and Ramezan, 2006).

2.9 Liquefaction

Usually, liquefaction includes the processing of heavy molecular compounds from a stream of pyrolytic gas (Ruwona et al., 2019). Owing to its greater energy density, the upper edge of TDO over solid fuels and syngas is more accessible to transport and store than gaseous materials (Cao et al., 2009). TDO is the fuel oil used in engine, turbine and burner applications to be used as a substitute (Jena and Das, 2011).

When pyrolysis offers an alternative solution and is simplified because the solvent is not needed compared to the liquefaction due to the higher temperature (200-600°C), liquefaction provides a practical method for converting the organic matter into oils (200-600°C) (Li et al., 2015).

2.10 Incineration

Waste tyre incineration requires high-temperature burning of tyres to turn the fuel matter into energy and inert residue (Oriaku et al., 2013). Waste tyres incineration have been used in various applications such as cement furnaces, power plants and industrial boilers. (Lebreton and Tuma, 2006). There are numerous general public questions regarding incinerating waste streams' health risks (Shakya et al., 2008). Primary care is the emission of toxic substances such as dioxins, mercury (Hg), Cd, nitrous oxide, hydrogen chloride (HCl), fluorides (F₂) and particulates that can be inhaled and magnified or permanently reside in our lungs (Mahlangu, 2009). Among all the methods detailed above, pyrolysis showed a significant advantage in the pollution and pyrolysis products handled efficiently.

2.11 Solvent extraction

Solvent extraction is a method that has been made in a wide field of application such as extraction in wastewater treatment, in hydrometallurgy, in pyro-oil and biofuel separation (Rydberg, 2004). Nowadays, much research conducted using solvent has become a subject of interest because most of the solvent used in the laboratory and chemical industry is dangerous and unsafe from the environmental perspective (Reichardt and Welton, 2011).

To classify and evaluate the extractable component from tyres, several studies have been performed. A soxhlet extractor is generally used with an organic solvent such as dichloromethane, diethyl ether, acetone, chloroform, methanol, etc. Furthermore, it is a reflux condenser that may be used to remove component additives from waste tyres (Mangili et al., 2014).

2.12 Summary of previous work done in solvent extraction

Several research studies on the recycling and disposal of scrap tyres have been developed. These include landfill, reuse as construction material and thermal devolatilization to gas, liquid and solid fraction. Solvent and supercritical extractions are also studied as a promising method for extracting valuable compounds from disposal scrap tyres (Al-Rahbi and Williams, 2016).

Soxhlet extractor was used by Mangili et al. (2014), the amount of extractable fraction that can be extracted from waste tyres (Mangili et al., 2014). In addition, they used acetone and chloroform to eliminate plasticizers, accelerators and antioxidant. They received a quantity of 10 wt.% that is linked to the processing additives in the waste tyres crumb.

According to Funazukuri et al. (1987), 57 wt.% of tyres can be converted into oil at 380 °C and 5.2 MPa, using supercritical toluene (Funazukuri et al., 1987). On the other hand, according to Park and Gloyna (1997), 68 wt.% of waste tyres were converted by supercritical water extraction (Park and Gloyna, 1997). The oil yield obtained through supercritical ethanol extraction at low temperature is much lower than toluene, n-butanol and acetone. According to Kandah et al. (2017), after special chemical treatment for low temperature and atmospheric pressure, solvent extraction was used to extract oil from waste tyres. DCM, methanol and methanol/DCM mixture were used as a solvent, and it is indicated that the best conditions for extracting oil from waste tyres are the combination of polar and non-polar solvents.

According to Money and Harrison (1999), the TDO composition included phenanthrene, pyrene and their methyl derivatives from a batch pyrolysis unit. They suggested that the composition of the fuel extracted from the was not different from that of the liquefaction-produced coal liquid and that it could be used in the processing schemes, mainly to increase the solvent requirement (Money and Harrison, 1999).

According to Williams et al. (1990), the chemical distribution from TDO depends on the heating rate and retention time. They found that gas production enhanced the heating rate increasing (Williams et al., 1990). Table 2.3 shows the work done in the waste tyres process with solvent extraction as a method.

Table 2.3: Summarized work done in solvent extraction.

Authors (year)	Types of solvent	Reactor type	Temp range (°C)	Max oil yield (wt.%)
(Park and Gloyna, 1997)	Supercritical water	Batch reactor	400	68
(Kandah et al., 2017)	Acetone, hexane, DCM and chloroform	Soxhlet extractor	50	30
(Funazukuri et al., 1987)	n-pentane, toluene and N ₂ .	Autoclave	380	57

3 Research materials equipment and methodology

This chapter describes the approaches carried out to achieve the aims of this project. The acquisition and characterization of samples are detailed herein. To assess the waste tyres composition, Characterization and analysis tests, including TGA analysis, were carried out. The waste tyres were sieved and divided into three separate samples. Pyrolysis was conducted on the samples before and after they had been subjected to solvent extraction. A schematic of the operations carried out is shown in Figure 3.1.

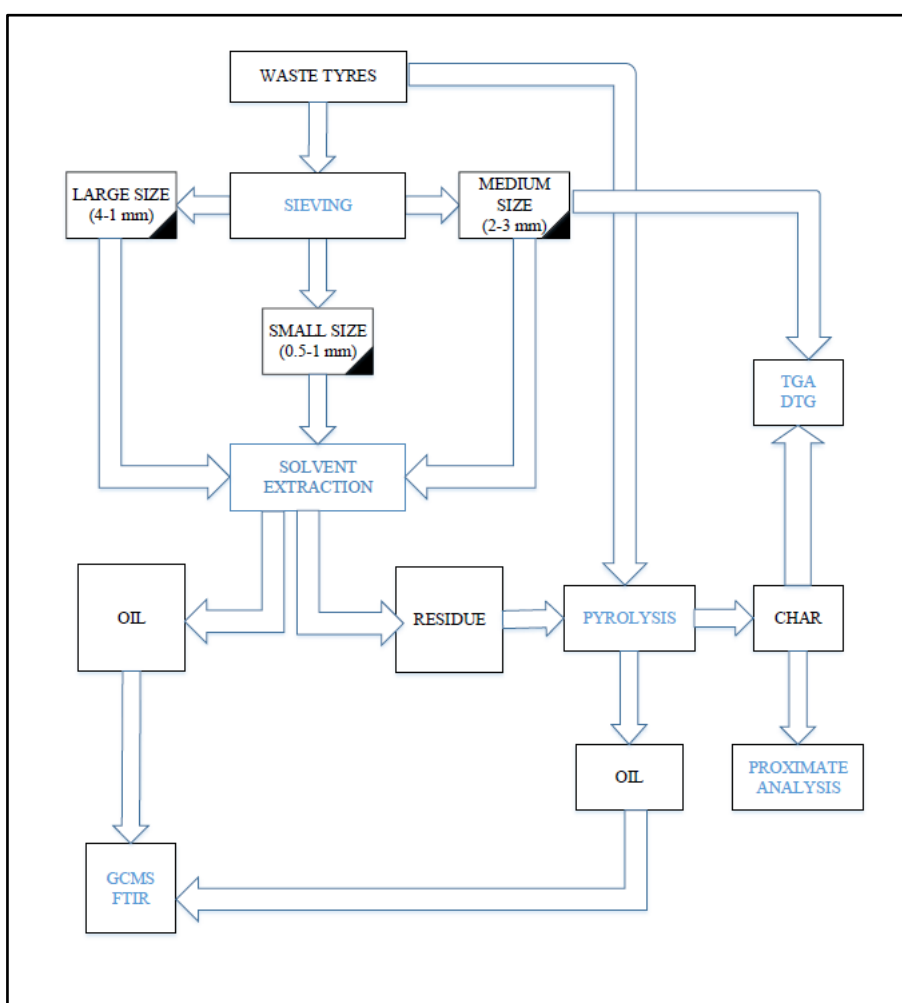


Figure 3.1: Schematic of waste tyres treatment methodology.

3.1 Sample acquisition and initial preparation

The three packets of truck waste tyres, each 2 kg, were collected from Mathe Group located in Hammarsdale, KwaZulu-Natal. These samples, shred tyres were cone and quartered and then sieved to give size passing 4-5 mm (large), 2-3 mm (medium) and 0.5-1 mm (small). The steel thread and textiles were removed from the tyre before sieving. The samples were sieved in the sieve series supplied by the Kingliest Laboratory Test Sieve at the school of chemical engineering to size 4-5 mm, 2-3 mm and 0.5-1 mm for solvent extraction, pyrolysis and practical analysis.

3.2 Characterization analysis

Since tyres contain more than 100 components, it is essential to provide a thorough analysis of characterization, identifying and predicting the most appropriate behaviours. Empirical research includes proximate and ultimate analysis, carried out using a thermogravimetry analysis (TGA), and the Leco carbon sulphur analyzer is more necessary.

3.2.1 Proximate analysis

The proximate analysis calculates the inherent moisture, volatile matter, ash and fixed carbon from waste tyres, coal and others matter. A series of standard methods American Society for Testing and Materials (ASTM), the International Organisation for Standardisation (ISO), the South African National Standards (SANS) and the South African Bureau of Standard (SABS) can be used as methods for analysis. Many forms of proximate tyre analysis are available, including ASTM D3172, ISO 1171, SANS 5925, SABS ISO 562 (Speight, 2005). However, ASTM-E1131 is a rapid process using a thermogravimetric analyzer. The DTG SHIMADZU was used for proximate analysis in this study.

The DTG SHIMADZU consists of a precision balance with a sample pan with a programmable temperature controller placed within the furnace.

The TGA measures the mass loss when a tyre sample is heated between 30-900°C under a nitrogen atmosphere, with a low heating rate (5-15 °C min⁻¹), followed by a switch to oxygen combustion. The sample sizes used were 15 mg of large (4-5 mm), medium (2-3 mm) and small (0.5-1 mm) size placed in the TGA alumina crucible.

The water content can be evaporated at 110°C, while the volatile material formed under nitrogen between 110-900°C. When the sample is kept at 900 °C, the fixed carbon combustion occurs, and the atmosphere is moved from N₂ to O₂.

The ash content is the residue that remains after the tyre has lost its humidity, volatile matter, and fixed carbon during O₂ combustion. The essential oxides of aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), and silicon (Si) are composed of ash.

3.2.2 Elemental analysis

The Leco SC 632 analyzer was used to evaluate the quantity of C, H, N, and S in the waste tyre sample. To obtain CO₂ and SO₂, a sample mass of 0.5 mm was combusted into pure O₂ to obtain CO₂ and SO₂ and then detected and quantified by infrared detection.

3.3 Solvent extraction

Solvent extraction is a process used to extract or eliminate impurities from a feed stream. Extraction may successfully remove the target solute from the sample. However, further separation is required to obtain the desired solute from the solvent employed, and this may facilitate using evaporation or filtration.

The solvents used were dichloromethane (DCM >99.50 wt.%) and diethyl ether (DEE >99.20 wt.%) obtained from LABOQUIP located in Durban South Africa.

3.3.1 Design of experiment

A full factorial design was used to measure the response of every combination of variable and their level. The experiment model considered the two variables of extraction, residence time and particles size. The volume of solvent was constant. Table 3.1 shows the design of the experiment for solvent extraction using DCM and DEE. As can be seen, nine tests conducted with a continual feedstock (40 g) and different particle size and the variable responses are wt.% yield and selectivity.

Table 3.1: Design of experiment for solvent extraction.

Experiment number	Factors				Responses	
N°	Extraction time (min)	Particles size (mm)	Extraction time (min)	Particles size (mm)	Oil yield wt. %	Selectivity
1	-	-	90	small (0.5-1)		
2	-	0	90	medium (2-3)		
3	-	+	90	large (4-5)		
4	0	-	120	small (0.5-1)		
5	0	0	120	medium (2-3)		
6	0	+	120	large (4-5)		
7	+	-	150	small (0.5-1)		
8	+	0	150	medium (2-3)		
9	+	+	150	large (4-5)		

Table 3.2 shows the number of parameters and their level. Level -1 represents the minimum level for the extraction time and the particles size. Level 0 offers the medium, and level 1 shows the maximum or large for the extraction time and particles size.

Table 3.2: Parameters and their level.

Factors		
Level	Extraction time	Particles size in mm
-1	minimum	Small (0.5-1)
0	intermediate	Medium (2-3)
+1	maximum	Large (4-5)

As shown in Figure 3.2, the waste tyres crumb was pre-treated by solvent extraction in the Soxhlet extractor. The oil obtained was separated with the solvent using the rotary evaporator.

Moreover, the residue from solvent extraction was conducted to the pyrolysis unit to obtain TDO, char and gas. The GCMS and FTIR analysis were used to characterize the composition of the oil. Figure 3.2 shows the experimental procedure for solvent extraction using DEE and DCM.

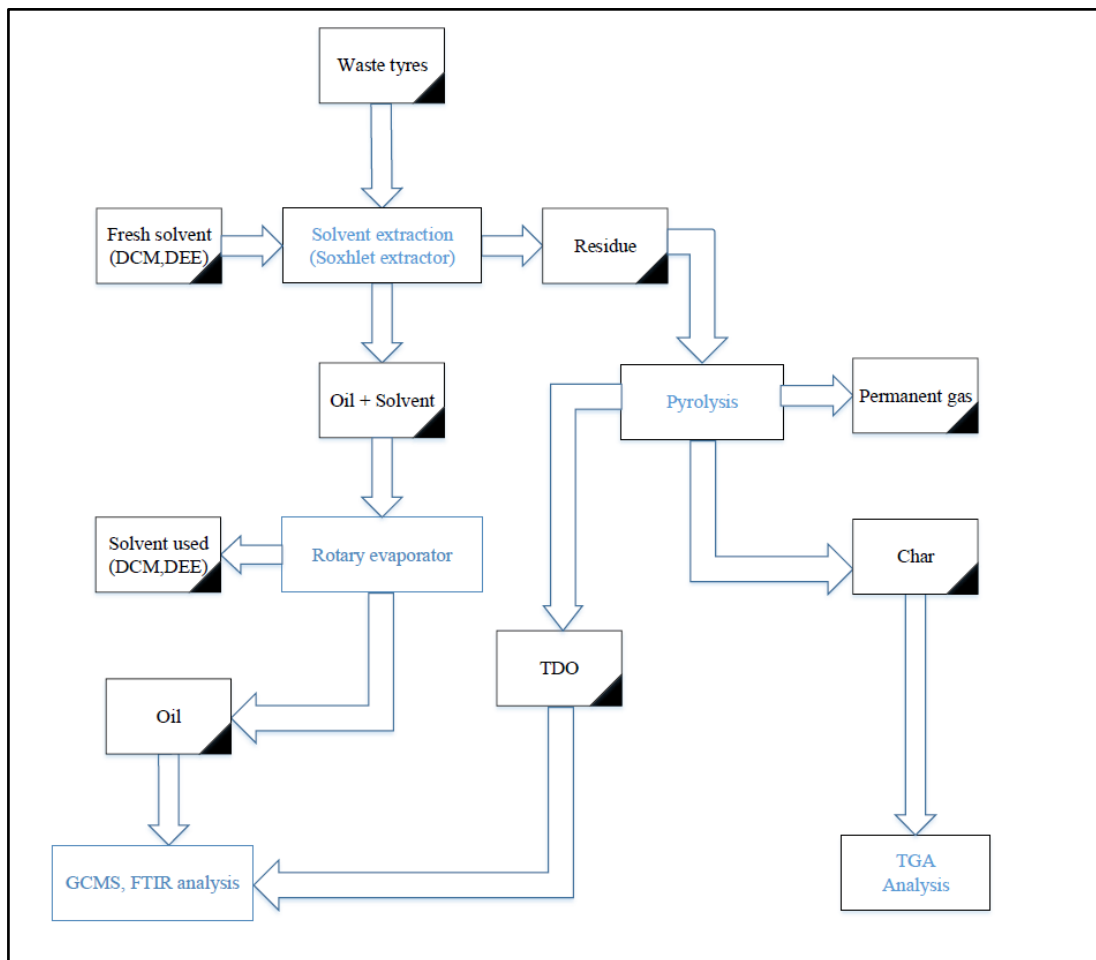


Figure 3.2: Experimental procedure for solvent extraction.

3.3.2 Soxhlet extractor

Soxhlet extractor is a type of solvent extraction unit designed for desired compounds with limited solubility in a solvent and where the impurity is insoluble in that solvent (Jensen, 2007).

A soxhlet extractor's essential operation involves the placement of the solid material containing the coveted compounds into a thimble, constructed from thick filter paper, usually made of cellulose and permeable to the solvent. It then positioned into the chamber of the Soxhlet apparatus. The soxhlet placed onto a round-bottom flask or still-pot that contains the

extraction solvent, and the condenser appeared to the upper part. The total reflux should be reached with a minimum extraction time of 60 min. This time has been found after some prior experiences. Figure 3.3 shows the soxhlet extractor with the boiling flask, thimble, extraction chamber and condenser.

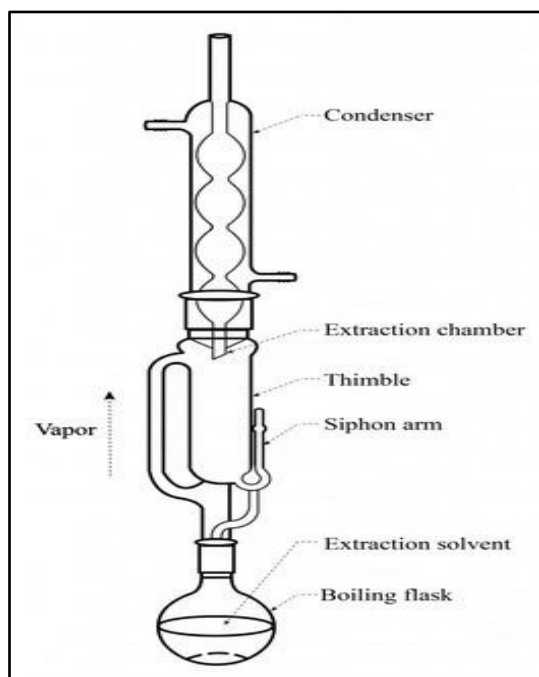


Figure 3.3: Soxhlet extractor apparatus (Dutta et al., 2014).

Usually, the total reflux observed after heating the solvent for more than an hour, and the solvent degradation can occur when the solvent extraction takes a while. The boiling point of DEE is lower than DCM, so the solvent degradation occurred earlier when DEE was used. The preliminary experiments were conducted between 90 min and 180 min. Table 3.3 shows the experimental conditions for solvent extraction.

Table 3.3: Experimental conditions for solvent extraction.

Parameters	Type of Solvent	
	Dichloromethane	Diethyl ether
Solvents	Dichloromethane	Diethyl ether
Duration min	90,120,150,180	90,120,150,180
The boiling point of solvents- Heating rates (°C)	39.6	34.6
Cooling water temperature (°C)	10	

3.3.3 Rotary evaporator

The rotary evaporator (Rotavap R215) is a distillation apparatus located in the engineering, chemical engineering department, made by Labotec with a vacuum pump V-700 and the vacuum controller V-855. The Rotavap is using heat, rotation and operates under vacuum conditions. It used to remove solvents from organic, inorganic and polymeric materials. The rotary vapour served at a lower temperature to remove only the solution from the mixture without affecting the oil component. Figure 3.4 shows the rotary evaporator apparatus.

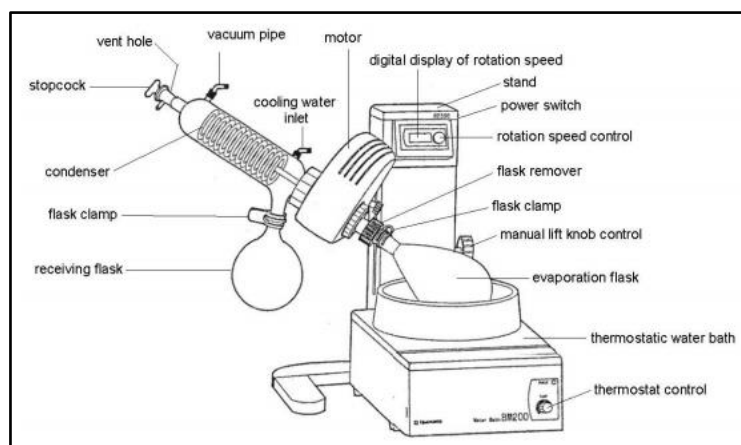


Figure 3.4: Rotary evaporation apparatus (Genser, 2006).

The rotary evaporation conditions were determined based on the manufacturer's guidelines. The oil bath was set to 60 °C while the vacuum was adjusted to yield a solvent boiling point of 40 °C. A standard table of solvents with corresponding pressure to produce a boiling point of 40 °C was made available by the manufacturer. Table 3.4 shows the common table of solvent DCM and DEE handled at atmospheric pressure.

Table 3.4: Standard characteristics of solvent.

Factors	Working conditions	
Solvents	Dichloromethane	Diethyl ether
Pressure (bar)	1.013	1.013
Oil bath temperature (°C)	60	
Cooling water temperature (°C)	25	

3.4 Semi-batch pyrolysis reactor

A semi-batch pyrolysis reactor made from Watford, Herts (Length -60.5 cm, 1.30 cm internal diameter and outer diameter-3.0 cm), stainless steel was used in pyrolysis experiments. The semi-batch reactor has a similarity with the batch reactor, but the removal of substance is not the same as that of a semi-batch reactor.

3.4.1 Pyrolysis setup

Figure 3.5 shows the pyrolysis unit representation created by an electric furnace and a reactor in which the temperature was kept constant using a temperature controller.

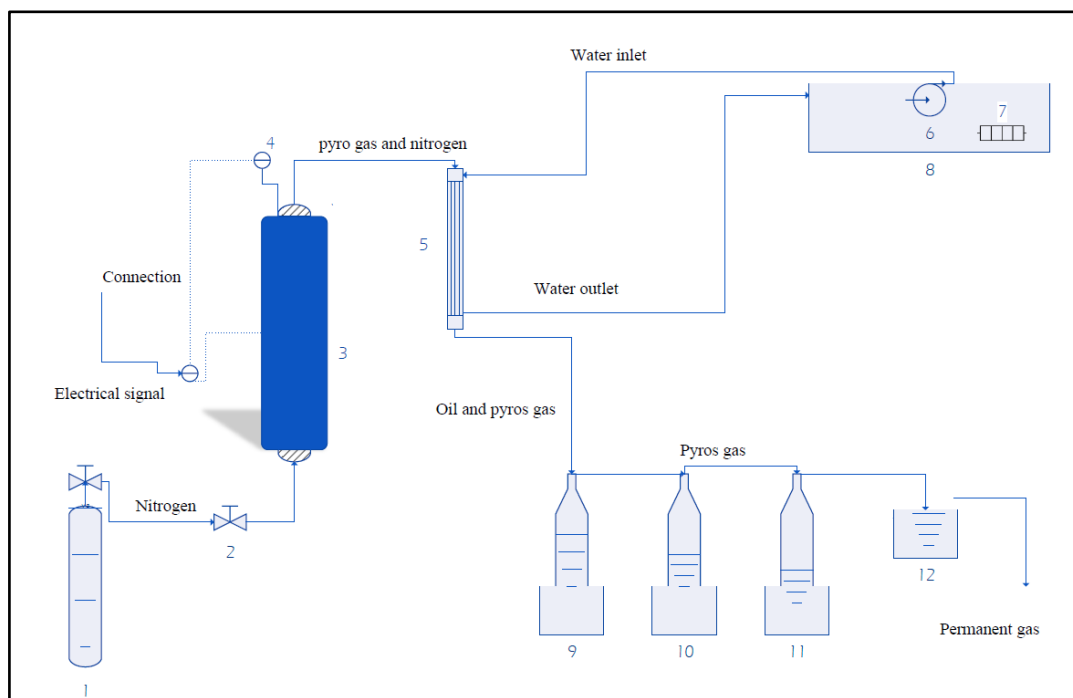


Figure 3.5: Pyrolysis setup.

1. Nitrogen cylinder 2. Flowmeter 3. Pyrolysis furnace 4. Control panel 5. Condenser 6. pump and temperature controller 7. Chiller 8. water bath 9. collector for heavy oil 10. Collector for light crude 11. Collector 12. Gas scrubber

3.4.2 Experimental procedure

By holding the heating rate and nitrogen pressure constant and increasing the pyrolysis temperature from 350 to 600 °C, some preliminary experiments were conducted. In the current study, from the TGA data, the heating rate was 15 °C min⁻¹ and the nitrogen flow rate at 6.5 l min⁻¹ from the TGA results and based on some works, which have been done in pyrolysis of waste tyres.

Restricted literature is available on the selective temperature condensation of waste tyres volatile matter from the pyrolysis reactor for oil processing. In particular, to create chemical interest in a given fraction, William and Brindle (2003) investigated step-wise condensation of the hot volatile produced in the fixed bed reactor from waste tyres pyrolysis (Williams and Brindle, 2003). The effect of maintaining the entire condensation unit at various temperatures and using the dry-ice acetone mixture has been investigated.

In this current study, the cooling system temperature was maintained between 2.0-2.5 which allowed a better water recirculation in the condenser followed by dry-ice use in the three collectors. Table 3.5 shows the pyrolysis design of the experiment by increasing the temperature in the range between 350 and 600°C.

Table 3.5: Pyrolysis preliminary experiments.

Pyrolysis Temperature (°C)	Cooling system temperature (°C)
350	2.5
400	2.3
450	2.4
500	2.2
550	2.3
600	2.0

An amount of 40 g of the waste tyre was placed in an electrically heated furnace for each run. The reactor performed pyrolysis experiments at temperatures ranging from 350°C to 600°C. The TGA shows that the tyre devolatilization starts at 350°C with a heating rate of 15°C min⁻¹.

In the water-cooled shell and tube heat exchanger condenser at 2°C and dry, the reactor's gas was condensed and dry ice were used. Permanent gases are emitted through an extraction fan into the atmosphere. The condensed oil was obtained from the condenser outlet in a series of three beakers and weighted. After the reactor is cooled, the remaining residue is collected and weighted. Permanent gas weight was determined by mass balance (the difference between the initial and final mass of pyrolysis products).

3.5 Chemical and physical characterization

Tyre characterization consists of two levels; physical and chemical. The gas chromatography/mass spectrometry (GCMS), while the Mettler Toledo and Brookfield Viscometer were used for the material characterization.

3.5.1 GCMS analysis

The GCMS system consists of a gas chromatographic coupled with a mass spectrometer to isolate, classify and quantify complex solutions (the GC component) at the molecular level (MS component). The GCMS GC-2010 plus the AOC-20I auto-injector and AOC-20S autosampler located in the engineering department, Howard college campus, were used in this study.

GCMS analyzed the composition of the extracted TDO. A gas chromatograph with a linear programming (LP) column, 30 m long, 0.25 mm internal diameter (ID) and 0.25 µm film thickness. The GC is fitted with a mass spectrometry detector and is facilitated by helium, as a carrier gas, of 99.99 % purity. A method developed for the GCMS analysis to guarantee that the solvent saturation does not occur. The procedure was done by running each solvent through the GCMS to identify the peaks and adjust the cut time solvent accordingly for the perspective analysis.

Table 3.6 showing the method used during the GCMS analysis.

Table 3.6: GCMS analysis method.

Parameter	Diethyl ether/ Dichloromethane
Injection temperature (°C)	250
Column Oven temperature (°C)	45
Injection mode	Split (40:1)
Injection volume	0.5 µL
Carrier gas flow	Helium at 36.2 cm/sec (linear flow)
Oven program	45°C (5 min) to 90°C at a rate of 5°C min ⁻¹ , 90°C to 180°C (2min) at 20°C min ⁻¹ and finally 180°C to 250°C (10 min) at a rate of 10°C min ⁻¹
Mass Spectrometer	
MS temperature °C	200 °C (ion source) 250 °C (interface)
Threshold	0
Solvent delay (cut-time) (min)	6
Duration (min)	6-39.5

3.5.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR IR prestige-21, SHIMADZU, located in the engineering school, Howard College campus, was used for the chemical characterization.

The FTIR was used to analyse the oil from solvent extraction and TDO. The FTIR spectra were obtained at a resolution of 4.0 in the range of 400-4000 cm⁻¹ and the number of scans was equivalent to 30. The FTIR imaging is completed using Perkin Elmer RX.

3.5.3 Viscosity and density of tyres derived oil

Using the Mettler Toledo Easy D40 and Brookfield Viscometer RV apparatus, respectively, physical properties such as density and Kinematic viscosity were determined. The apparatus was calibrated using distilled water and the Lovis method (Lovis temperature 20°C, sound velocity 1483.29 and apparent density 0.997430 g cm⁻³).

3.5.4 Characterization of pyrolytic char

The char characterized using the TGA/DTA 60 AH for proximate analysis. The initial temperature was 30°C, the heating rate 10°C min⁻¹, and the hold time was 10 min. The nitrogen flow rate was 25 ml min⁻¹, and the waste tyres sample mass was between 15-20 mg per run.

4 Results and Discussion

The results of the three different sample preparation techniques (tyres raw material, tyres treated with DCM and tyres treated with DEE) are described in this chapter and then discussed.

4.1 Solvent extraction results

The results of solvent extraction using DCM and DEE are summarized in Table 4.1 and Table 4.2. Nine runs were conducted for each solvent using 40 g of waste tyres as feedstock. Also, to have the highest possible precision, the experiments were conducted in duplicates. Two parameters were varied, extraction time and particles size; the responses were percentage oil yield and selectivity. Table 4.1 shows the solvent extraction results using DCM.

Table 4.1: DCM solvent extraction results.

Solvent extraction with DCM							
Exp	Factors		Response variable				
N°	Extraction time (min)	Particles size (range in mm)	Mass1 (g)	Mass2 (g)	Average mass (g)	Oil yield (wt.%)	Selectivity
1	90	small (0.5-1)	34.60	34.62	34.61	13.48	1.19
2	90	medium (2-3)	34.72	34.73	34.73	13.19	1.35
3	90	large (4-5)	35.02	34.66	34.84	12.90	1.30
4	120	small (0.5-1)	34.29	34.72	34.50	13.74	1.38
5	120	medium (2-3)	34.82	34.71	34.57	13.58	1.46
6	120	large (4-5)	34.88	34.72	34.80	13.00	1.35
7	150	small (0.5-1)	34.35	34.33	34.34	14.15	1.35
8	150	medium (2-3)	34.90	34.73	34.51	13.73	1.37
9	150	large (4-5)	34.63	34.65	34.64	13.40	1.35

Table 4.2 shows the solvent extraction results using DCM where two factors were varied, and the response variable was the oil yield in wt.% and the selectivity. The volume of solvent, type of solvent and sample mass remained constant.

Table 4.2: DEE solvent extraction results.

Solvent extraction with DEE							
Exp	Factors		Response variable				
N°	Extraction time (min)	Particles size (range in mm)	Mass1 (g)	Mass2 (g)	Average Mass (g)	Oil yield (wt.%)	Selectivity
1	90	small (0.5-1)	34.72	35.53	35.12	12.19	1.31
2	90	medium (2-3)	35.13	34.50	34.81	12.97	1.28
3	90	large (4-5)	34.87	34.73	34.80	13.00	1.24
4	120	small (0.5-1)	34.64	34.73	34.69	13.28	1.45
5	120	medium (2-3)	34.76	34.69	34.73	13.18	1.48
6	120	large (4-5)	34.71	34.78	34.75	13.14	1.43
7	150	small (0.5-1)	34.81	34.54	34.68	13.31	1.43
8	150	medium (2-3)	34.99	34.46	34.73	13.19	1.41
9	150	large (4-5)	34.73	34.76	34.75	13.14	1.31

The effect of extraction time was investigated on the percentage yield of oil. Figure 4.1 and Figure 4.2 present the results. As shown in Figure 4.1, the treatment of waste tyres using DCM showed a considerable improvement in oil extraction compared to those treated with DEE. During an extraction time of 150 min, the highest extraction oil was 14.15 wt.% from the tyres handled with the DCM using the small particles size. This result can be explained on the basis of Fick' law of diffusion, which is proportional to the larger surface area of the solid, which directly related to the concentration of the solute in the extraction solution (Burada et al., 2007). Figure 4.1 shows the solvent extraction results for waste tyres using DCM as a solvent.

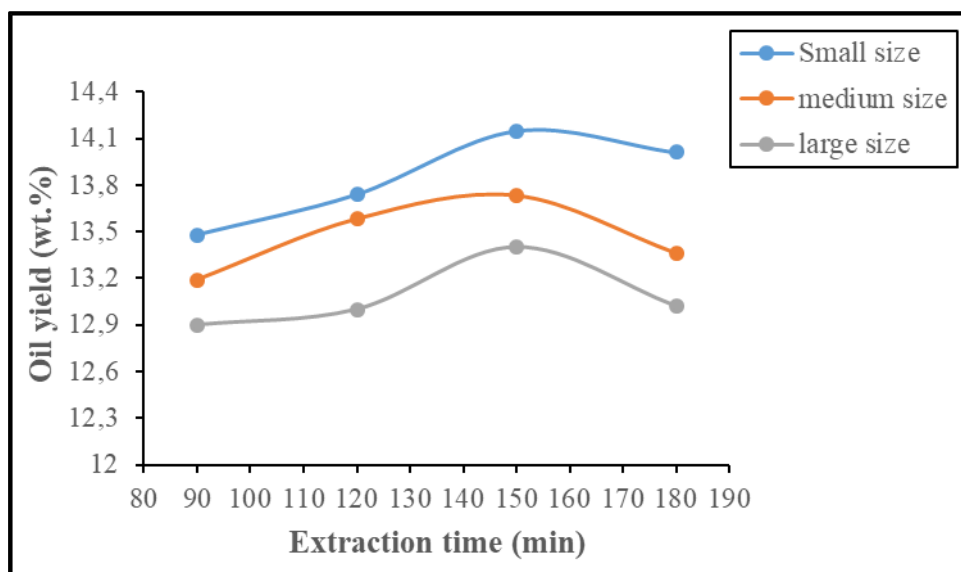


Figure 4.1: DCM solvent extraction result using waste tyres from different sizes.

As shown in Figure 4.2, there was a slight difference in the treatment of waste tyres with DEE relative to those treated with DCM. However, the small particle size treated with DEE above 150 produced 13.31 wt.% oil. There was an insignificant difference in the percentage yield oil of the Medium and large particles. The yield difference between small, medium and large particles size was respectively 0.05, 0.12 and 0.17. The shape of the curves (waste tyres treated with DCM and DEE) shows that the oil yield rises to an optimum of 150 min from the beginning of solvent extraction. However, due to the solvent saturation, the oil yield starts decreasing at 180 min. Figure 4.2 shows the solvent extraction results using DEE.

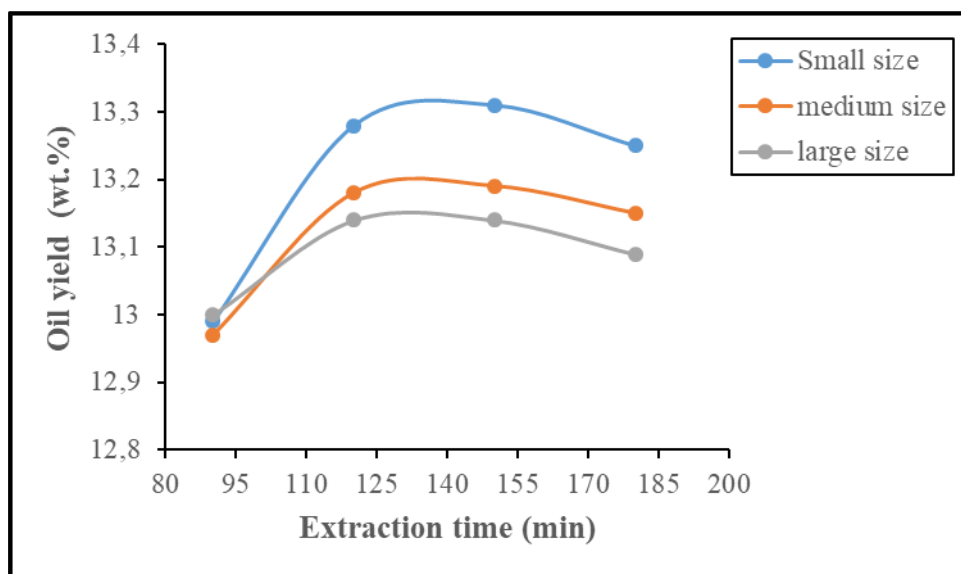


Figure 4.2: DEE solvent extraction results.

The solvent selectivity for tyres treated with DCM and DEE is shown in Figure 4.3 and Figure 4.4. The solvent's selectivity relates to its capacity to remove from a solution the desired compounds. It is the ratio of the compounds needed to the combinations that remain. As shown in Figure 4.3, the selectivity of 1.48 obtained at the extraction time of 120 min using waste tyres medium size is more efficient than those obtained at 90 and 150 min. However, the selectivity remains constant when the extraction time is increased regardless of the temperature but remain lower than 1.46. Figure 4.3 shows the solvent extraction results for waste tyres treated with DCM.

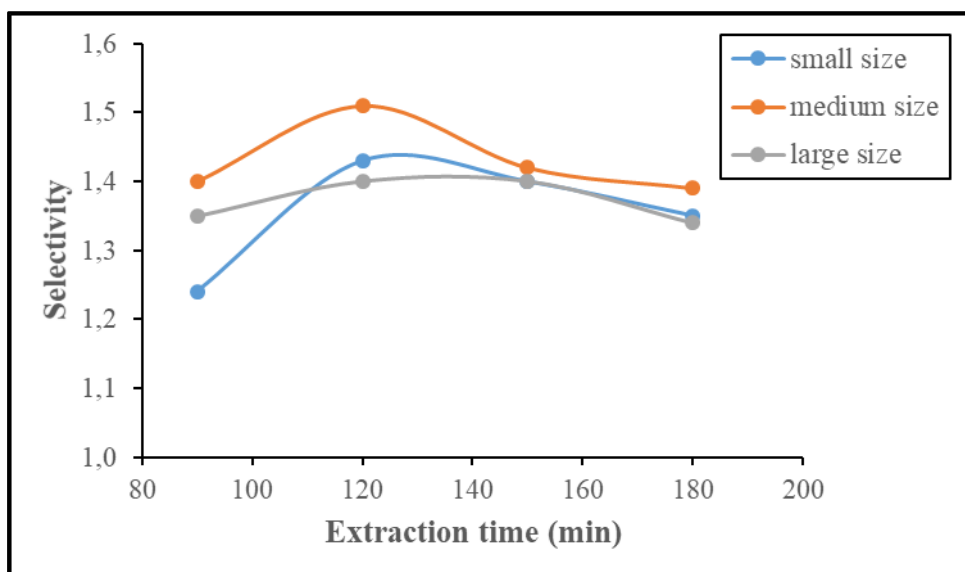


Figure 4.3: DCM selectivity results.

Figure 4.4 shows the increase of selectivity with the extraction time. The optimum was found at 120 min, similar to those treated with DCM. At 150 and 180 min, the shape of the curve starts decreasing due to the solvent degradation. This phenomenon occurred when the solvent is heated for a while during the solvent extraction.

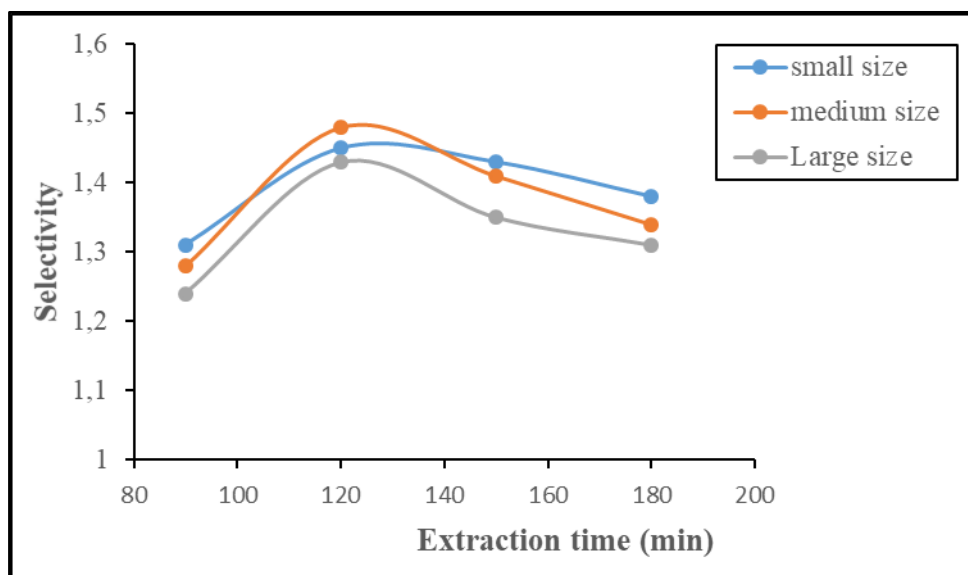


Figure 4.4: DEE selectivity results.

4.1.1 Analysis for extracted oil using The GCMS

The peaks, retention time (R time) and name of the components observed for the GCMS shown in Table 4.3, while Figure 4.5 showed the GCMS chromatogram for solvent extraction oil when the DCM was used. The result used in this section illustrates the highest oil yield wt.% obtained when DCM was used for solvent extraction. The GCMS results for other experiments are displayed in Appendix C.

Table 4.3 indicates all the component that can be separated when DCM is used in the tyre crumb by solvent extraction. Therefore, most of them contain such heteroatoms that can contaminate the TDO obtained during pyrolysis from the tyres manufacturing additive.

Table 4.3: Composition of oil from waste tyres treated with DCM for 150 min.

Peak N°	R time (s)	Area %	Name
1	17.30	1.94	Benzothiazole
2	17.78	1.15	Neodecanoic acid
3	20.21	0.87	Quinolone, 1-2-dihydro-2,2,4-trimethyl-
4	23.16	0.61	Oxalic acid, cyclohexylmethyl tridecyl ester
5	24.17	1.36	Nonadecane
6	25.20	0.55	Hexadecane
7	26.17	2.45	2-Methyl hexacosane
8	27.22	0.94	2-Methyltetracosane
9	27.51	0.86	Methyl stearate
10	27.93	2.29	Tetrapentacotane, 1,54-dibromo-
11	28.11	2.64	Pyrene
12	28.34	1.78	Heneicosane
13	28.47	1.24	1-Acetoxynonadecane
14	29.63	2.15	Heneicosane
15	30.79	9.32	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
16	31.01	8.32	Hexanedioic acid, bis (2-ethylhexyl) ester
17	31.27	0.86	1-Docosanol, acetate
18	32.56	3.42	Heneicosane
19	33.68	3.50	Hexatriacontane
20	33.87	2.98	Eicosane
21	34.17	3.02	Octanoic acid, morpholide
22	34.43	2.69	Acetic acid 4,4-acetylamino-phenylimino
23	34.81	7.56	Indole-3-carboxaldehyde 2,4-chlorophenyl
24	35.10	6.51	Hexacosane
25	35.27	1.76	1,4-Benzenediamine, N,N'-diphenyl

As can be seen from the GCMS production shown in Figure 4.5, there are several components from TDO. The predominance of 1, 4-Benzenediamine, N-(1,3-dimethylbutyl)-N is shown in the chromatogram study for oil from waste tyres treated with DCM for 150 min. This

component is used as a rubber accelerator during the process of producing tyres. The synthetic rubber uses n-Hexanedioic acid as a plasticizer. However, it is used in the food industry as a flavouring agent. Benzothiazole is the result of vulcanizing agent's degradation used during the tyre manufacturing process. It is considered to be the leading compound containing sulphur and nitrogen in TDO. In the medical field, It has alternative uses since it has a range of therapeutic applications (Mkhize et al., 2017). Figure 4.5 shows the chromatography of solvent extraction oil from waste tyres treated with DCM.

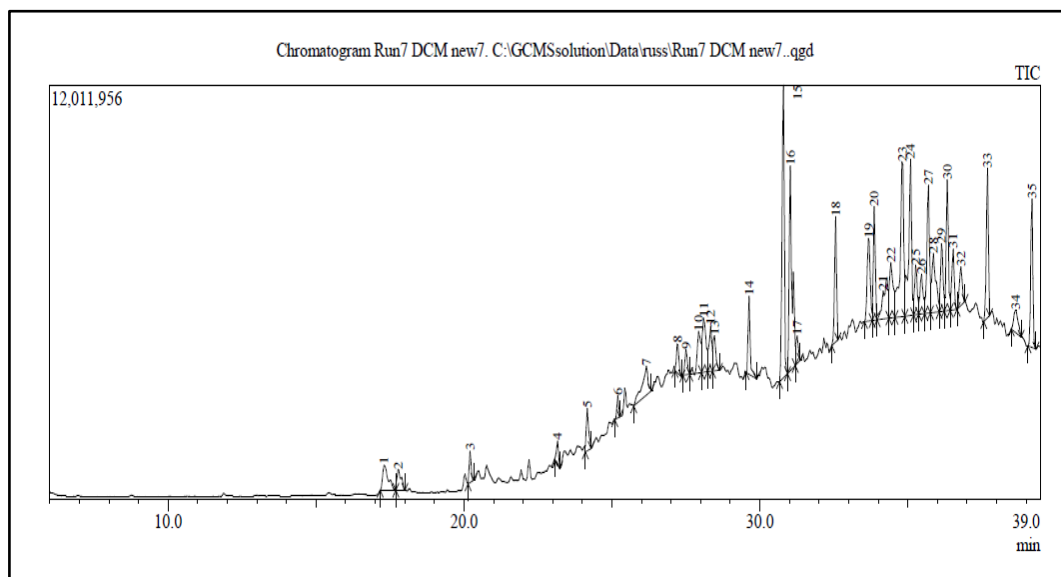


Figure 4.5: Chromatogram for oil from waste tyres treated with DCM for 150 min.

As shown in Table 4.4, which shows the list of components removed from the tyres crumb using DEE as a solvent, there is a vast difference in terms of components compared to the composition of oil obtained when DCM were used. The difference is due to the physical characteristics of DCM, such as polarity and boiling point, that is greater and better than DEE.

Table 4.4: Composition of oil from waste tyres treated with DEE for 150 min.

Peak N°	R time (min)	Area %	Name
1	20.87	1.42	Butylated hydroxytoluene
2	22.17	0.66	Phenol, 4-(1,1,3,3-tetramethylbutyl)
3	23.11	0.74	Heptadecane
4	25.17	1.15	Heneicosane
5	25.43	0.92	Hexadecanoic acid, methyl ester
6	25.97	1.73	1-Ascorbic acid 2,6-dihexadecanoate
7	26.16	1.00	octadecane
8	27.20	1.14	2-Methyltetracosane
9	27.50	0.77	Methyl stearate
10	28.34	2.70	Heneicosane
11	28.53	4.27	tetratetracontane
12	29.63	1.17	Heneicosane
13	30.79	7.84	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
14	31.03	5.17	Hexanodioic acid, bis(2-ethylhexyl) ester
15	32.56	2.58	2-Methyloctacosane
16	33.86	6.97	tetratetracontane
17	34.17	3.14	Octanoic acid, morpholide
18	34.43	2.24	Acetic acid 4-(4-acetylamino-phenylimino)-m
19	34.82	7.33	1,2,5-Oxadiazole-3-carboxamide, 4-amino-N
20	35.10	5.36	Heneicosane
21	35.27	3.51	1,4-Benzenediamine, N,N'-diphenyl
22	35.47	1.63	Octadecane , 1,1(1-methyl -1,2-ethanediyl)bis
23	35.70	4.27	N-Benzyl-N'-phenyl-p-phenylenediamine
24	35.88	4.18	Glutaric acid, 4-chloro-3-methylphenyl
25	36.16	3.00	1,4-Benzenediamine, N1,N1-bis(4-methylphenyl)

Figure 4.6 shows the chromatogram analysis for oil from waste tyres treated with DEE for 150 min. The chromatogram indicates a similarity with the predominance of 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N and n-Hexanedioic acid. As can be seen, the heteroatoms (compounds containing both nitrogen and sulphur atoms) used as vulcanizing agents during the tyre's manufacturing process were not detected. However, the chromatogram shows the Tetratetracontane, a long-chain alkane consisting of an unbranched chain of 44 carbon atoms with the chemical formula $C_{44}H_{90}$. This compound is used in medicine as a human metabolite (Tripathi et al., 2015). The polarity of DEE (2.8) is lower than that of DCM (3.1), which justifies the detection of heteroatoms removal when DCM were used while not detected when DEE solvent was used.

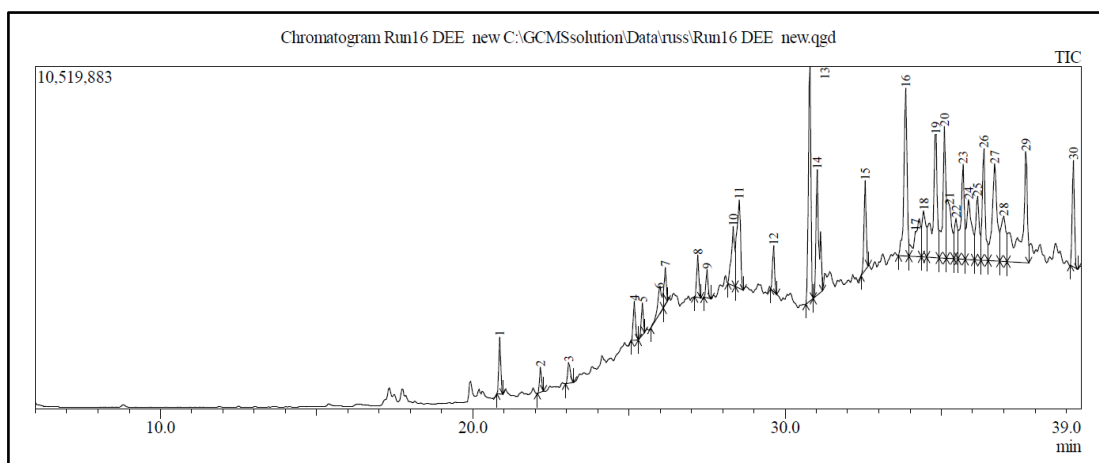


Figure 4.6: Chromatogram for oil from waste tyres treated with DEE for 150 min.

There is a correlation after comparing the oil obtained when the waste tyres were treated with DCM at 120 min and 150 min, respectively, as can be shown in Table 4.5. However, the greater the extraction time, the more components we expect to get due to the DCM's polarity and intensity in removing heteroatom.

Table 4.5: Composition of oil from waste tyres treated with DCM for 120 min.

Peak N°	R time (min)	Area %	Name
1	23.16	1.11	Tetracontane, 3,5,24-trimethyl
2	24.17	0.90	Eicosane
3	25.43	1.02	Hexadecanoic acid, methyl ester
4	26.16	1.44	Heneicosane
5	27.20	1.69	2-Methylhexacosane
6	27.50	1.22	Methyl stearate
7	27.92	4.05	2-Methylhexacosane
8	28.33	4.00	Heneicosane
9	29.63	2.18	heptadecane
10	30.78	12.01	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
11	31.00	4.48	Hexanedioic acid, bis (2-ethylhexyl) ester
12	31.13	2.72	Docosane
13	31.27	0.67	1-Acetoxynonadecane
14	32.55	3.10	Hexacosane
15	33.67	2.81	Hexatriacontane
16	33.87	4.01	heneicosane
17	34.27	7.56	Benza anthracene, 7-methyl
18	34.80	5.58	Indole-3-carboxaldehyde, 1,2,4-chlorophenol
19	35.08	6.24	tetratetracontane
20	35.27	1.68	1,4-Benzenediamine, N,N'-diphenyl
21	35.47	1.92	tritriacontane
22	35.68	4.07	N-Benzyl-N'-phenyl-p-phenylenediamine
23	35.86	3.30	15-Hydroxydehydroabietic acid, methyl ester
24	36.14	2.45	1,4-Benzenediamine, N1,N1-bis (4-methyphenol)
25	36.33	4.46	Hexatriacontane

Figure 4.7 shows the chromatogram from the highest selectivity result from the waste tyres treated with DCM. There is a predominance of 1,4-Benzenediamine, N-(1,3-dimethyl butyl)-N with an immense contribution, as shown in Figure 4.7, which comes from the highest selectivity using DCM in tyres pre-treated for 120 min. There is also a 7- Methylbenz anthracene with the chemical formula $C_{18}H_{12}$, which is a carcinogenic constituent of tobacco smoke (Wang et al., 2007).

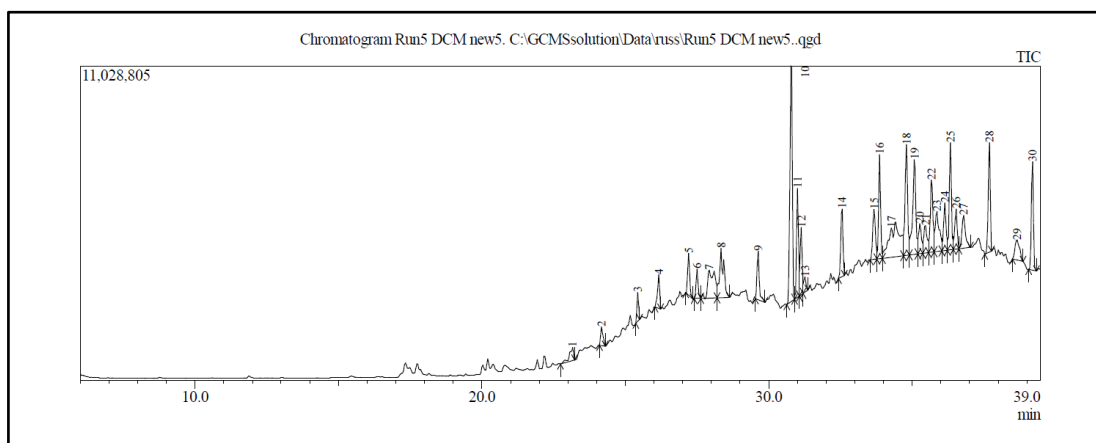


Figure 4.7: Chromatogram for oil from waste tyres treated with DCM for 120 min.

The components obtained after the GCMS analysis for oil from waste tyres after being pre-treated by DEE with a solvent extraction time of 120 min are shown in Table 4.6. The oil composition is slightly different from that of waste tyres treated with DEE for 150 min. It can be seen that the solvent extraction time has a significant influence on the composition of oil from waste tyres pre-treated by solvent extraction.

Table 4.6: Composition of oil from waste tyres treated with DEE for 120 min.

Peak N°	R time (s)	Area %	Name
1	17.29	1.03	Benzothiazole
2	20.87	1.10	Butylated Hydroxytoluene
3	22.17	1.00	Phenol, 4-(1,1,3,3-tetramethylbutyl)
4	23.16	0.61	Sulphurous acid, cyclohexylmethyl hexyl ester
5	24.17	1.08	Octadecane
6	25.20	1.13	Nonadecane
7	25.44	0.57	Hexadecanoic acid, methyl ester
8	26.07	2.28	n-Hexadecanoic acid
9	26.19	1.66	Hexadecane
10	27.23	1.42	2-Methyl tetracosane
11	27.53	0.71	Methyl stearate
12	28.11	0.69	Pyrene
13	28.37	6.84	Docosane
14	29.66	1.67	Heneicosane
15	30.82	8.53	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
16	31.06	6.46	Hexanedioc acid, bis (2-methylhexyl) ester
17	31.30	0.77	Undec-10-ynoic acid, octadecyl ester
18	32.59	3.38	hexacosane
19	32.87	3.79	Benza anthracene
20	33.89	7.61	Eicosane
21	34.20	3.43	Octanoic acid, morpholide
22	34.45	2.91	Acetic acid 4,4-acetylamino-phenylimino-m
23	34.84	6.81	Indole-3-carboxaldehyde, 1,2,4-chlorophenol
24	35.13	6.17	Heneicosane
25	35.30	2.63	1,4-Benzenediamine, N,N'-diphenyl

The chromatogram study for waste tyres treated with DEE for 120 min, shown in Figure 4.8, indicates a new component that appears after 1,4-Benzenediamine, N-(1,3-dimethyl butyl)-N, it is a chain alkane with 22 carbon atoms called docosane. Docosane is used in organic synthesis, calibration and temperature sensing equipment; it is a solid insoluble in water. The majority of the heteroatom compounds derived from tyre crumb samples have several applications, enabling their recovery and reuse for more practical purposes such as in the chemical, pharmaceuticals and cosmetic industries, thus facilitating their reclamation (Baer-Dubowska et al., 1996). Figure 4.8 shows the highest selectivity result for waste tyres treated with DEE.

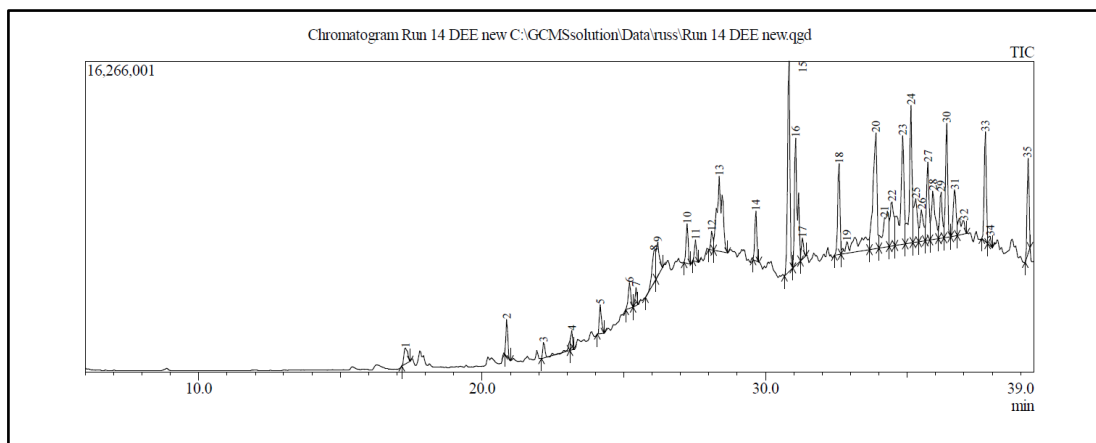


Figure 4.8: Chromatogram for oil from waste tyres treated with DEE for 120 min.

4.1.2 FTIR analysis for solvent extraction oil

The FTIR results are presented in Figure 4.9, illustrating spectra for oil from solvent extraction using waste tyres small size, medium size, and large size.

As can be seen from Figure 4.9, the FTIR spectrum of oil chemical compounds obtained after pre-treatment with small waste tyres shows that the sample contains a C-H stretching vibration chemical such as alkyne, alkene, aldehyde, and thiol. However, owing to C-Br functional groups' presence, which denotes the presence of halo compounds with a stretching vibration, the peak became wider at a frequency of 733 cm^{-1} . (Guo et al., 2015). Figure 4.9 shows the FTIR result from a waste tyre small size treated with DCM and DEE.

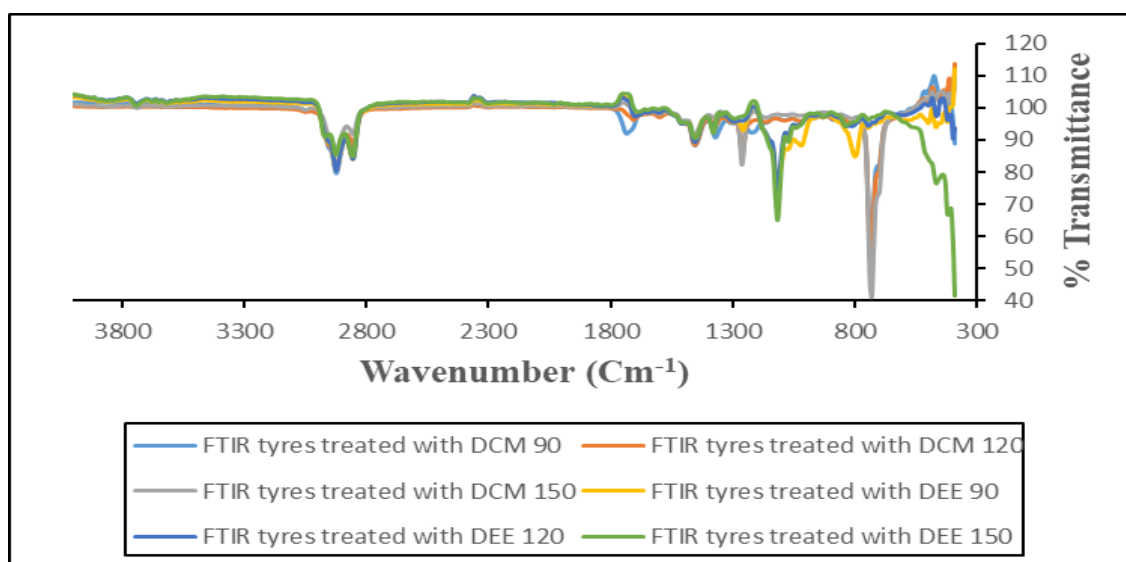


Figure 4.9: FTIR Spectrum for oil from waste tyres small size.

A similarity to the previous one is shown in Figure 4.10, and there is a stretching vibration around 1177 cm^{-1} in the processing of oil using medium size waste tyres due to the S=O

functional group, which implies the presence of sulfonic acid. There is a C-O active group at a frequency of 1055 cm^{-1} , with a stretching vibration that can be attributed to the presence of primary alcohol and anhydride. Figure 4.10 shows the FTIR results from solvent extraction using the medium particle size.

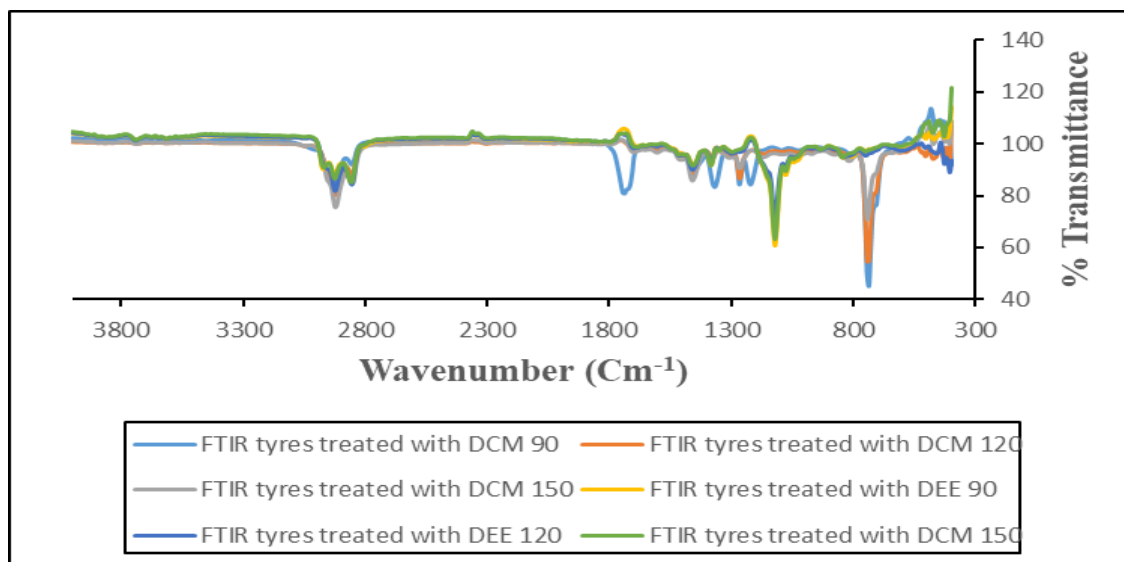


Figure 4.10: FTIR spectrum for oil from waste tyres medium size

Similar observations reported in Figure 4.11, but due to alcohol and a primary amine, there is some difference at a frequency of 3700 cm^{-1} in an O-H functional group. Aromatic C-H bending is assigned to the fingerprint region between 900 and 620 cm^{-1} (Ben and Ragauskas, 2012). Figure 4.11 shows the FTIR result from solvent extraction using large particle size.

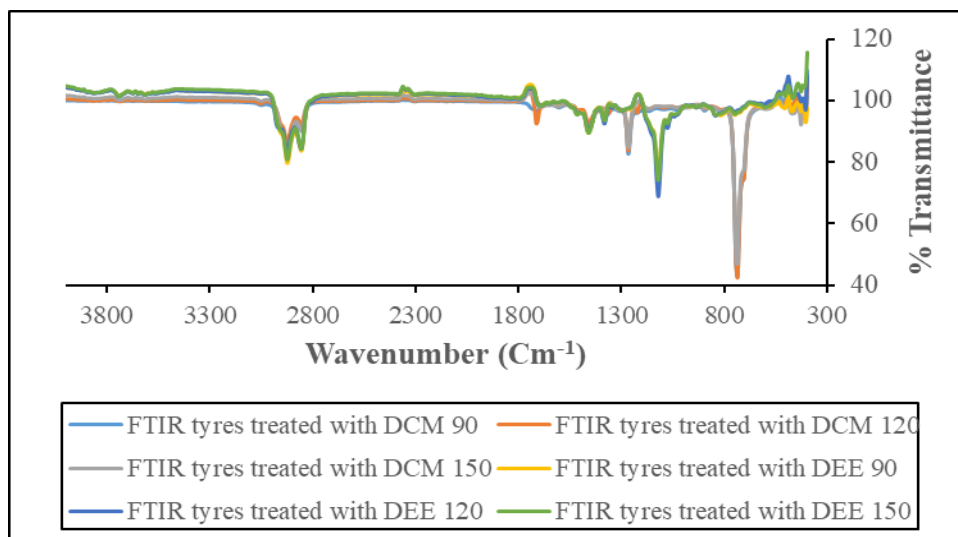


Figure 4.11: FTIR spectrum for oil from waste tyres large size.

4.2 Pyrolysis results

The pyrolysis results for waste tyres raw material, treated with DCM and DEE, are presented, including the proximate and ultimate analysis.

Gas, TDO, and pyro-char are the main products that can be obtained from waste tyres pyrolysis. The TDO yield can be greater than pyro-gas and pyro-char under certain conditions. Alternatively, waste tyres pyrolysis may be based on the proximate analysis results that display the moisture of waste tyres crumb, volatile matter (oil and rubber content processing) and non-volatile matter (fixed carbon and ash). Different researchers did most of the work involving the pre-treatment of waste tyres. Still, none of them studied the effect of pre-treatment of waste tyres on material recovery and chemicals development.

The following subsection shows the waste tyres pyrolysis results after pre-treatment compared to the untreated waste tyres.

4.2.1 Characterization of waste tyres

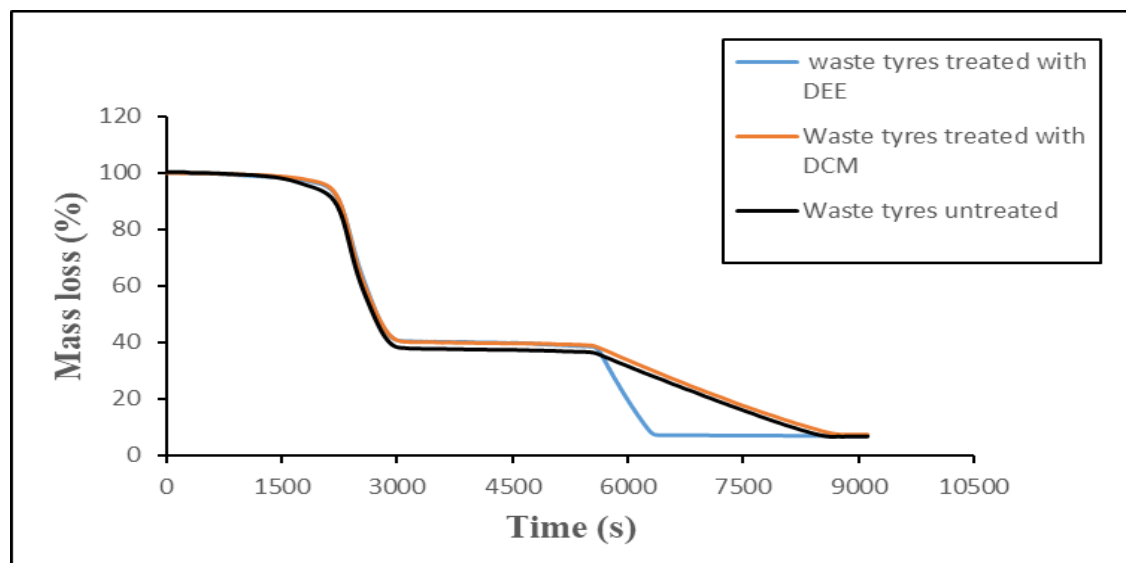
Data from chemical characterization analysis, including proximate analysis and elemental analysis, is shown in Table 4.7 and Figure 4.12.

The study of waste tyres in Table 4.7 shows that only 61.63 wt.% of the high volatile matter is seen in the waste tyres treated with DEE. In the entire study, the average moisture content was estimated at 0.5 wt.%. However, the sulphur content was around 2.6 wt.%, and the ash content was high, with an average of 7 wt.%. The quantity of fixed carbon was similar to those from the literature review (around 28 wt.%). Usually, due to the carbon black applied during tyres compounding, tyres contain more fixed carbon. Usually, during the waste tyres pyrolysis, the fixed carbon remains in the solid products (char). Table 4.7 shows the proximate and ultimate results for untreated and treated tyres.

Table 4.7: Proximate and Ultimate results.

Samples	Proximate analysis				Elemental analysis			
	Moisture content (%)	Volatile matter (%)	Fixed carbon (%)	Ash content (%)	C	H	S	N
Tyres raw material	0.38	64.05	28.69	6.88	84.46	6.93	2.62	0.35
Tyres treat with DCM	0.44	62.63	29.59	7.34	86.47	7.62	2.66	0.44
Tyres treat with DEE	0.63	61.63	30.62	7.12	82.11	6.88	2.57	0,30

The TGA profile corresponding to the waste tyre pyrolysis process is shown in Figure 4.12. As shown in Figure 4.12, the TGA analysis for waste tyres treated with DEE shows a decrease in fixed carbon and the massive amount of ash content. It seems that this behaviour is due to the effect of DEE on the waste tyres crumb. There is a similar characteristic between the tyres raw material and those treated with DCM in moisture content, high volatile matter, combustible material and ash. Figure 4.12 shows the proximate analysis results for untreated and treated waste tyres.

**Figure 4.12: Proximate analysis.**

4.2.2 Impact of particle size in the thermal degradation of tyres

The standard methods for researching the thermal degradation of waste tyre samples are TGA and DTG. The differences in weight loss (TGA) and mass- change derivative (DTG curves) versus temperature for three types of sampling (raw material, tyres treated with DEE and tyres treated with DCM) are shown in Figure 4.13.

As shown in Figure 4.13, the devolatilization of tyres raw material starts at low temperature by using the untreated tyres small size, which is due to moisture, dust, and other impurities. Small particles size usually has more significant surface areas; which can impact the reaction rate. However, we observed similar behaviour in tyres treated with DCM and DEE. The heteroatom removal, using some solvent such as DCM and DEE, can change the thermal devolatilization of tyres due to the change in tyre composition. Figure 4.13 shows the TGA results for waste tyres of small size.

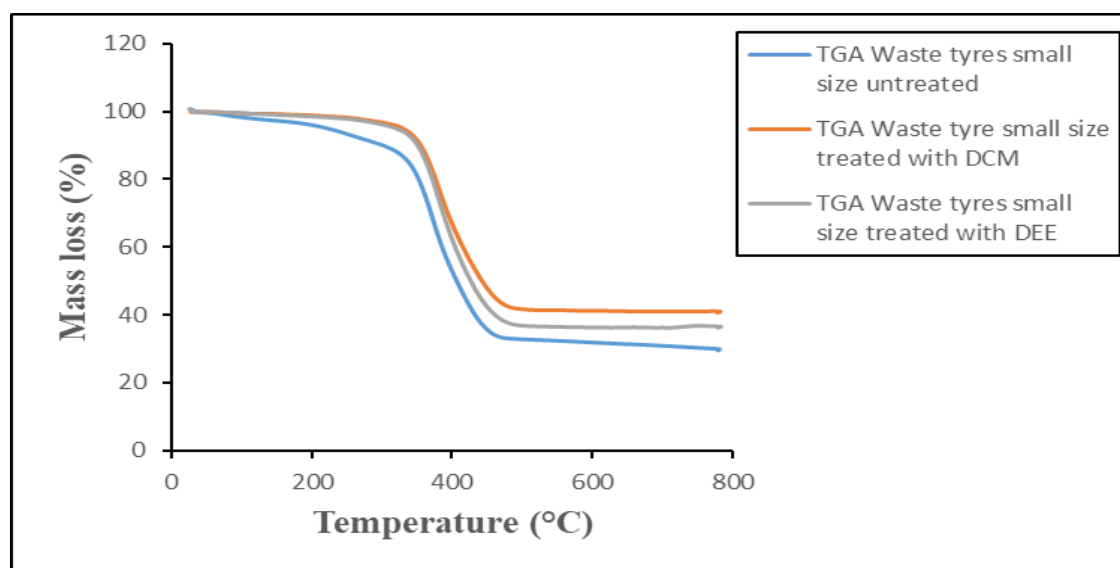


Figure 4.13: TGA Curve for waste tyres small size.

Figure 4.14 shows the first derivative thermogravimetry analysis (DTA) for tyres small-sized raw material, treated with DCM and DEE. There is a devolatilization at 70 °C due to the moisture content in the tyres raw material. This means the moisture in the tyres after solvent pre-treatment decreases due to the residue's drying in the oven for 24 hours. As can be observed in the temperature range of the organic material's devolatilization in waste tyres, pyrolysis starts at 200°C and finishes at 550°C. However, it was found there was different behaviour

between untreated tyres and treated tyres. Those treated with DEE and DCM need more energy because of the heteroatoms removal, and there is only one stage according to the DTG curve shapes. The DTG curves for untreated tyres shows two steps, one from 200-400°C and the second from 400-550°C. According to Leung and wang (1998), the first peak is due to the thermal devolatilization of the blend of oils, moisture, plasticizers and other additives (Leung and Wang, 1998). The second is the thermal decomposition of NR, butadiene rubber (BR) and SBR, which are the tyres' main components. Figure 4.14 shows the DTG result for waste tyres small size.

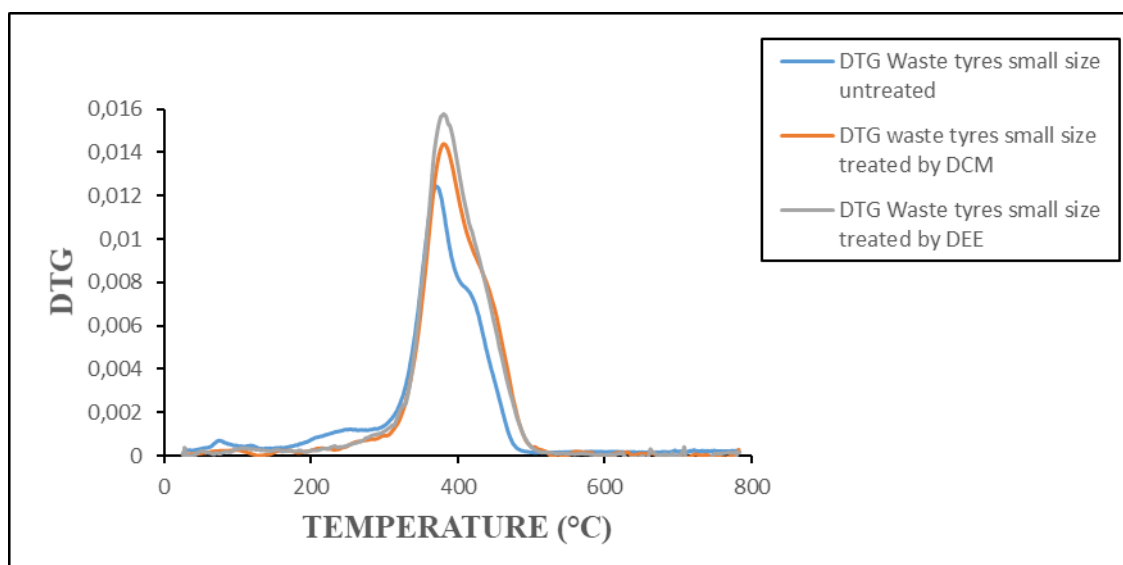


Figure 4.14: DTG Curve for waste tyres small size

Figure 4.15 shows the thermogravimetry profile corresponding to the pyrolysis of waste tyres medium size untreated, treated with DEE, and treated with DCM. The curves showed no substantial difference between the untreated tyres and those treated with DEE and DCM using the scrap tyres medium size. The mass loss was similar in the entire sample. This is due to the thermal devolatilization of NR and SBR. The specific areas in waste tyres medium size were smaller than the previous one, and the pyrolysis temperature was between 200-470°C from the shape curve. Figure 4.15 shows the TGA results for waste tyres Medium size.

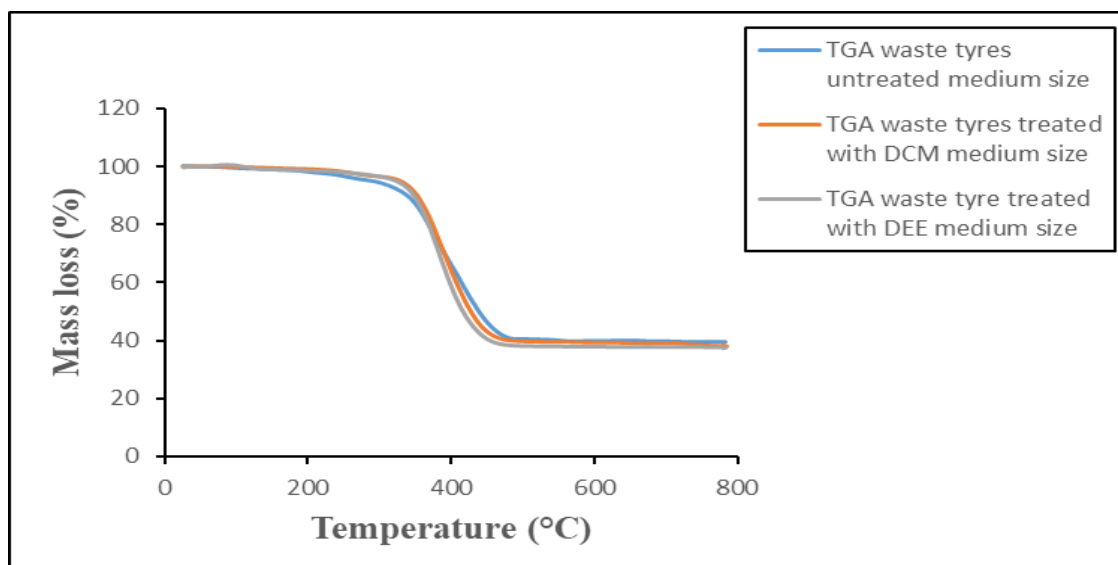


Figure 4.15: TGA result for waste tyres medium size.

Figure 4.16 shows the first derivative thermogravimetric analysis for tyres raw material, treated with DCM and treated with DEE. The curve profile showed that there is a significant difference between the untreated and treated tyres. From the figure for waste tyres untreated, two peaks are to be observed at 300 – 400°C and 400 – 500°C. The first stage shows that the devolatilization of NR and BR, and the second peak is attributed to the dissolution of SBR. However, there is a similar behaviour between those treated with DCM and DEE in terms of temperature range between 300 – 500°C. Nevertheless, it can be observed that a slight difference in the temperature between 100 – 140°C owing to the presence of moisture, plasticizers, and additives in the tyre treated with DEE. Figure 4.16 shows the DTG result for waste tyres medium size.

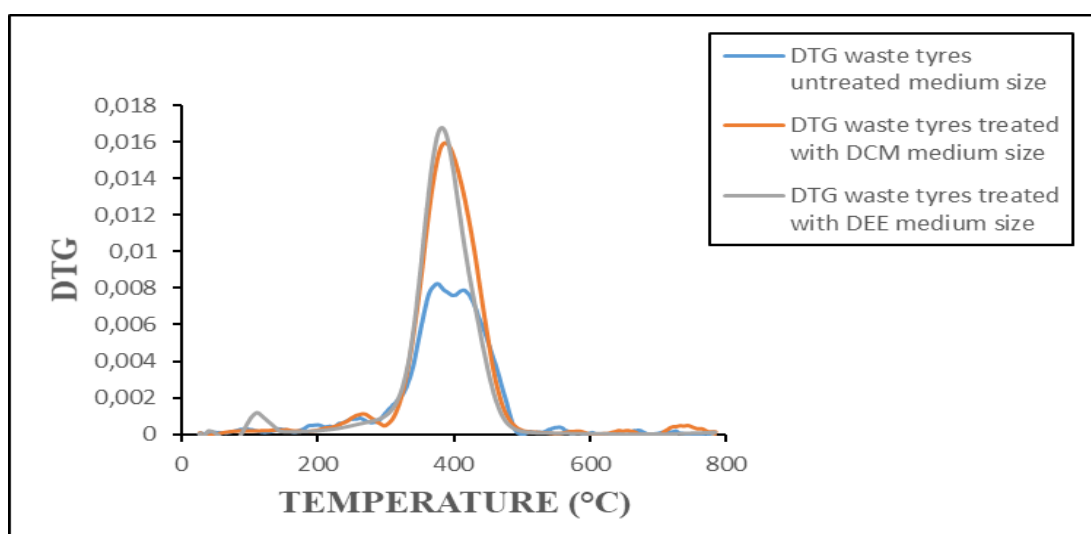


Figure 4.16: DTG result for waste tyres medium size.

Figure 4.17 shows the Thermogravimetry analysis for untreated, treated with DCM and DEE large size tyres. As shown from the curve's shape profile, there is a significant difference in terms of mass loss and temperature between the waste tyres untreated and treated. This is due to the impact of removing heteroatoms in the waste crumb tyres using DCM and DEE.

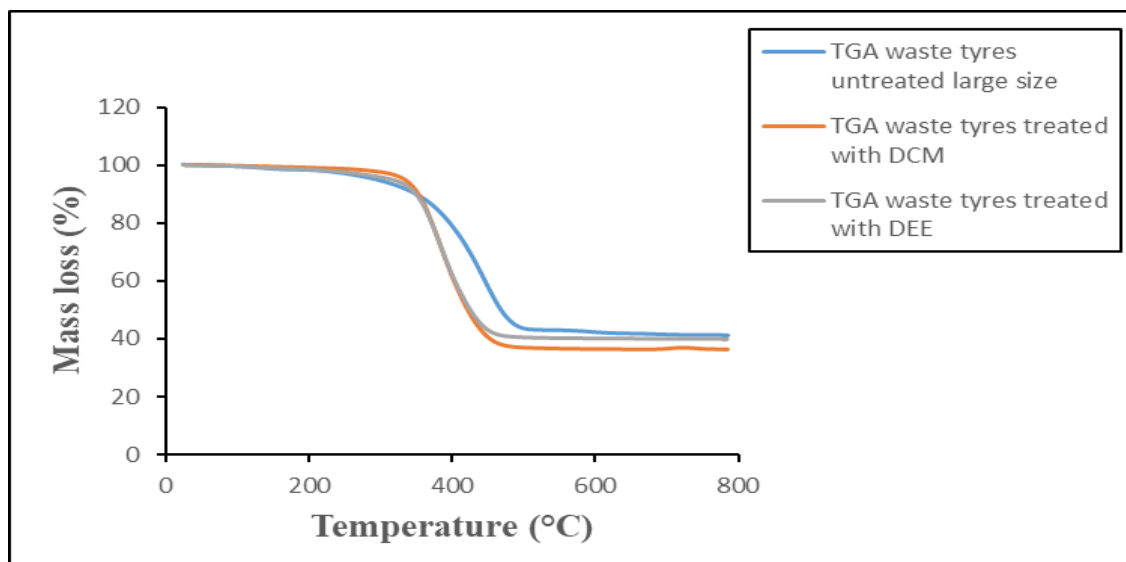


Figure 4.17: TGA result for waste tyres large size.

Figure 4.18 shows the first derivative thermogravimetry analysis for waste tyres and waste tyres treated with DEE and DCM. The curve profile revealed that the untreated and treated waste tyres vary significantly from each other in terms of thermal devolatilization using the large particle size. The treated waste tyres curves display a massive temperature difference compared to those not treated. This is due to the solvent's effect in the removal of a component such as polybutadiene, which requires more heat for their decomposition.

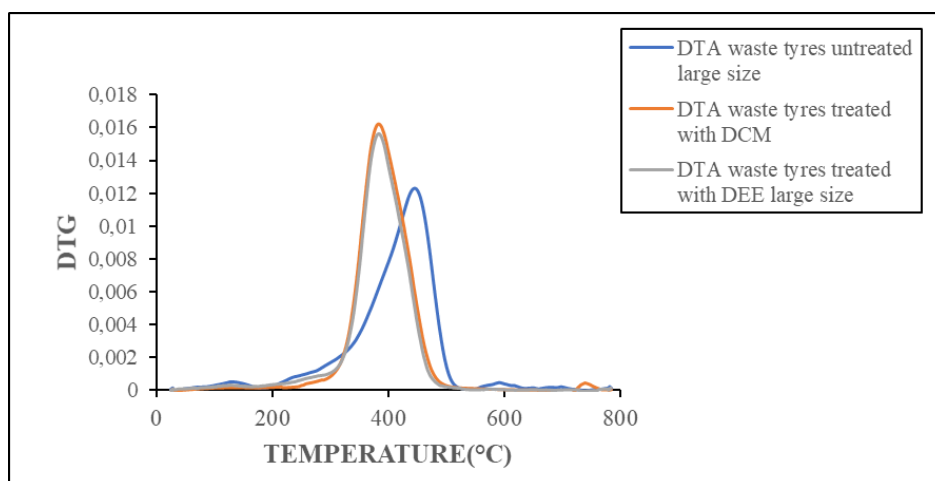


Figure 4.18: DTG result for waste tyre large size.

4.2.3 Pyrolysis oil results

Table 4.8 shows the preliminary experiment's pyrolysis result using the temperature range between 350 and 600°C. According to some researchers such as Quek and Balasubramanian (2013), there are three potential patterns in the case of pyrolysis temperature yield oil (Quek and Balasubramanian, 2013). Some researchers have found an increasing yield with the temperature (Rombaldo et al., 2008), while some found a decreasing product (Kaminsky and Mennerich, 2001). Several researchers have found either a maximum or minimum yield (Kyari et al., 2005). The TGA and DTG results revealed that the thermal devolatilization of truck tyres starts from 200°C to 600°C, reason why the table displays the temperature in that range. Table 4.8 shows the preliminary pyrolysis result by increasing the temperature, the optimum temperature was found at 550 °C due to the highest oil yield.

Table 4.8: Pyrolysis preliminary results.

Temperature (°C)	Oil Yield (wt.%)	Char (wt.%)	Gas (wt.%)
350	16.50	49.00	34.50
400	28.00	41.50	30.50
450	34.00	38.50	27.50
500	42.00	35.60	22.40
550	51.40	31.90	16.70
600	39.00	32.50	28.50

Figure 4.19 shows the pyrolysis preliminary experiment result by plotting temperature versus oil yield percentage. There is an increase in oil yield with the increase in temperature, as shown in shape. The maximum oil recovered was at 550°C. Meanwhile, a decrease in oil yield was observed due to the production of non-condensable gas such as CO, CO₂, methane, ethane and propane at high temperature after reaching the maximum oil yield (Asadullah et al., 2008). As can be seen in Table 4.8, the total amount of the oil yield in the initial run was 51.4 wt.% at 550°C, 16.7 wt.% for gas and 31.5 wt.% for char which contained more fixed carbon. The preliminary experiment's result facilitated the fix of all the parameters for the pyrolysis experiment to find a way that can help us deal with waste tyres. Figure 4.19 shows the preliminary pyrolysis results for waste tyres.

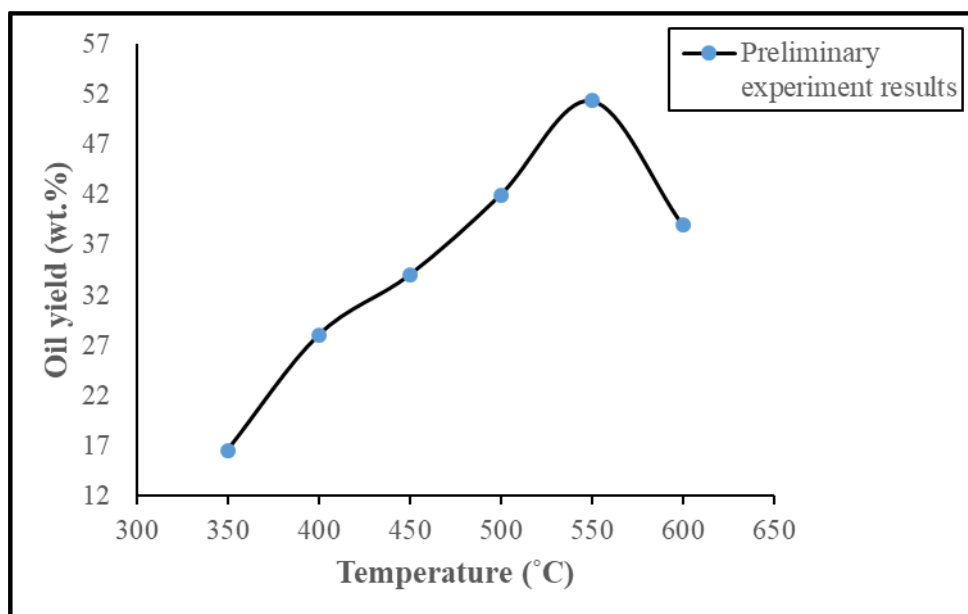


Figure 4.19: Pyrolysis preliminary experimental results.

The pyrolysis results from untreated, treated with DCM, and DEE waste tyres feedstock are presented respectively in Table 4.9, Table 4.10, and

Table 4.11. All the experiment conducted in the optimum conditions:

- ✓ Pyrolysis temperature: 550°C
- ✓ Nitrogen flow rate: 6 l min⁻¹
- ✓ Sample mass: 40 g
- ✓ Water bath temperature: 2.1/2.3°C
- ✓ Heating rate: 15°C min⁻¹

Table 4.9 summarized the result for the pyrolysis experiment using waste tyres treated with DCM. Nine tests were carried out at 550 °C in the same conditions using waste tyres treated with DCM at different extraction times and sizes. The table shows the amount of oil yield percentage, char and gas. Table 4.9 displays the pyrolysis results for waste tyres treated with DCM.

Table 4.9: Pyrolysis results for waste tyres treated with DCM at 550 °C.

N°	Sample name	Weight %		
		Oil	Char	Gas
1	Small size 90	38.25	40.62	21.13
2	Medium size 90	38.31	39.51	21.78
3	Large size 90	39.55	39.02	21.43
4	Small size 120	34.75	36.50	28.75
5	Medium size 120	34.25	39.00	26.75
6	Large size 120	43.19	33.68	23.13
7	Small size 150	34.78	40.17	25.05
8	Medium size 150	44.12	39.66	16.22
9	Large size 150	55.64	29.36	15.00

Figure 4.20 shows the pyrolysis oil from waste tyres treated with DCM. The curve shape revealed that there is an increase in oil yield with extraction time and particle size. At the extraction time of 90 min, no change occurred in terms of oil yield percentage using a small, medium or large size. At 120 min, the oil yield is the highest when the large particle size was used. However, the oil yield remains unchanged for medium and small particle size. At 150 min, the oil yield was 55.64 wt.% from the large particle size. This shows that at the same extraction time and using different waste tyres size, the oil yield increased significantly when the larger waste tyres size were used. This is due to the slow effect of solvent extraction on the large particle size and the more significant change in the heteroatoms removal. According to the proximate analysis results, there is a decrease in their yield percentage in terms of char and gas due to the less amount of fixed carbon in the sample. The average char and gas was around 37 wt.% and 20 wt.% respectively. Figure 4.20 shows the pyrolysis result for waste tyres treated with DCM.

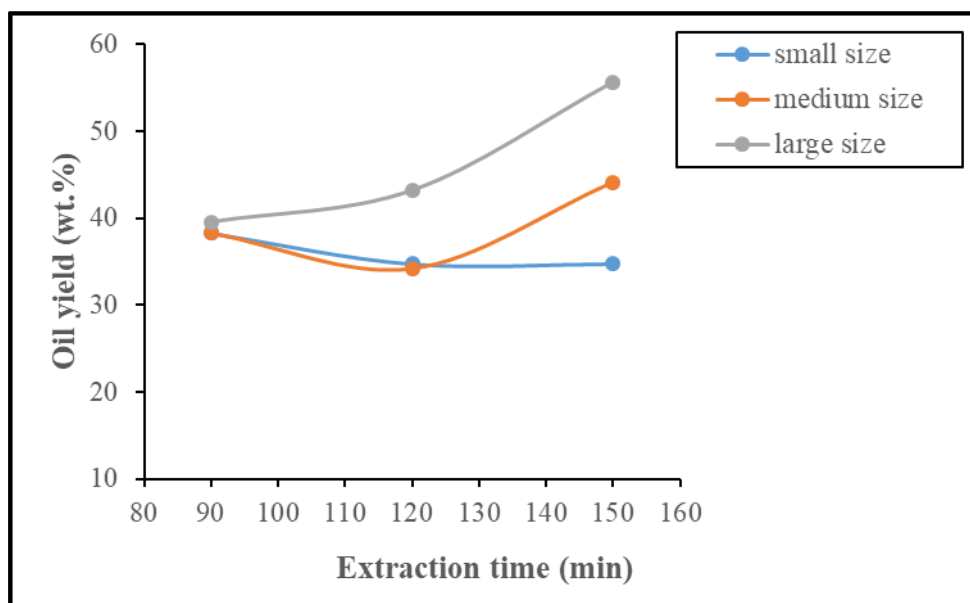


Figure 4.20: Pyrolysis result curves for waste tyres treated with DCM.

Table 4.10 shows the result for waste tyres pyrolysis treated with DEE. Nine tests were conducted at 550°C with different samples, 6.5 l min⁻¹ nitrogen flow rate at a heating rate for 15°C min⁻¹. It can be seen that nine runs were done in the optimum condition, and with the rise in the extraction time, the oil increases, while the char and gas remain unchanged. Table 4.10 shows the pyrolysis result for waste tyres treated with DEE.

Table 4.10: Pyrolysis result for waste tyres treated with DEE at 550°C

N°	Sample name	Weight %		
		Oil	Char	Gas
1	Small size 90	37.41	37.32	25.27
2	Medium size 90	37.97	35.22	26.81
3	Large size 90	32.41	38.18	29.41
4	Small size 120	39.86	35.19	24.95
5	Medium size 120	37.15	37.25	25.60
6	Large size 120	38.74	35.23	26.03
7	Small size 150	39.86	39.05	21.09
8	Medium size 150	40.60	34.32	25.08
9	Large size 150	44.12	34.79	21.09

Figure 4.21 shows the result for pyrolysis oil for waste tyres treated with DEE. As can be seen from the shape, the oil yield increased when the tyres crumb have been treated with a higher

solvent extraction time and small particle size. At 90 min, there is a different behaviour due to the particle size in oil production using small and medium-size instead of considerable measure. The oil yield was 37.97 and 32.41 wt%, respectively. This is due to the relatively larger surface area in the small and medium particle size compared to the large particle size when treated with the solvent extraction. The behaviour changes at 150 min using the large particles, resulting in a significant increase in oil yield due to the large particle's volatile matter. The oil yield was 44.12 wt.%, which is less than those from waste tyres treated by DCM. The result from waste tyres pre-treated shows that DCM is a suitable solvent that can be used in tyres pretreatment because of the polarity and the substantial heteroatom removal. The solvent can break some weak bonds in the waste tyres and facilitate the volatile matter's transformation into pyrolysis oil.

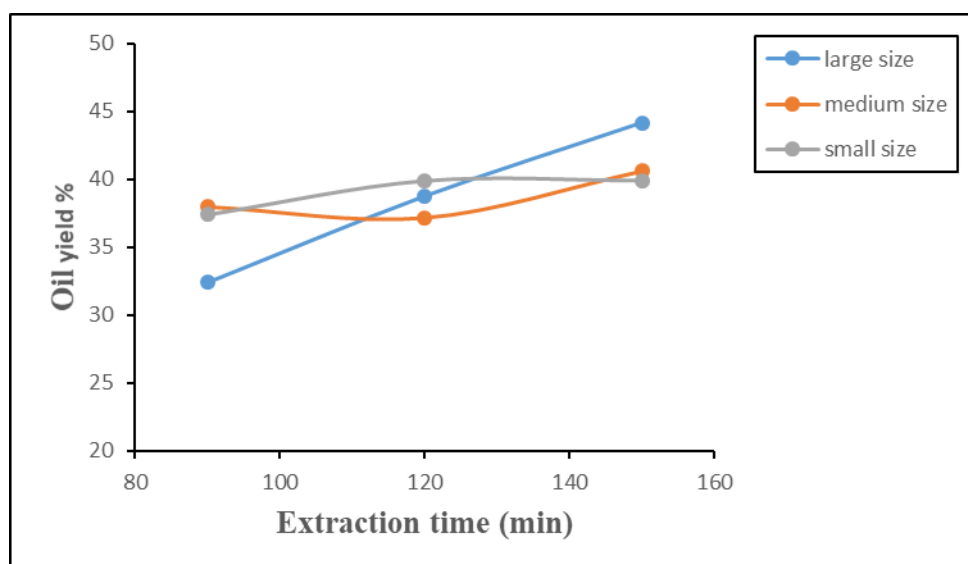


Figure 4.21: Pyrolysis result from waste tyres treated with DEE.

Table 4.11 shows the pyrolysis result for untreated tyres. Three experiments were done at 550°C, with three types of samples and Table 4.11 displays the experimental pyrolysis results for oil, char and gas. It has been observed that the large particle size is still producing more oil than smaller and medium. The higher yield of oil was 47.5 wt.% less than those from waste tyres after being treated with DCM in the same conditions.

Table 4.11: Pyrolysis result for untreated tyres.

N°	Sample name	Weight %		
		Oil	Char	Gas
1	Tyres small size	36.00	42.50	21.50
2	Tyres medium size	44.00	36.00	20.00
3	Tyres large size	47.50	34.00	18.50

4.2.4 GCMS results for pyrolysis oil

As shown in Table 4.12, there is a considerable difference between the oil from solvent extraction and the TDO in terms of composition. Most of the TDO components are derived from NR and SBR during the pyrolysis process, while those from solvent extraction mostly come from the additives processing. Besides, removing the processing additives has already simply the TDO composition because 14 wt.% was readily extracted by solvent extraction when DCM was used.

Table 4.12 : Composition of TDO from waste tyres treated with DCM.

Peak N°	R time (s)	Area %	Name
1	3.67	2.21	Acetic acid, dichloro
2	4.63	1.88	Cyclobutane, (1-methylethylidene)
3	4.80	3.59	Toluene
4	5.94	3.75	o-Xylene
5	6.08	5.67	Benzene, 1,3-dimethyl
6	6.45	1.53	1,3,5,7-Cyclooctatetraene
7	7.71	2.24	Cyclohexanol, 1-methyl, 4,1-methylethyl
8	7.79	1.40	Benzene, 1,2,4-trimethyl
9	7.86	2.79	Benzene, 1-ethyl-3-methyl
10	8.54	2.10	1,5-Heptadiene, 2,3,6-trimethyl
11	9.31	10.11	Cyclohexene, 1-methyl, 4,1-methylethyl
12	9.36	3.92	o-Cymene
13	9.51	41.37	D-Limonene
14	10.85	4.28	Cyclohexene, 1-methyl, 4,1-methylethylidene
15	11.11	2.58	Benzene, 1-methyl, 3,1-methylethenyl
16	15.05	1.71	Benzothiazole
17	17.97	2.09	2,4,4,6,6,8,8-Heptamethyl-2-nonene
18	18.96	1.49	2,4,4,6,6,8,8-Heptamethyl-1-nonene
19	22.92	1.27	Naphtalene, 2,3,6-trimethyl
20	26.06	2.14	Sulfurous acid, cyclohexylmethyl tridecyl ester
21	33.21	1.88	Sulfurous acid, cyclohexylmethyl hexyl ester

Figure 4.22 show the GCMS result for oil from the waste tyres pyrolysis after being treated by DCM. As can be seen from the chromatograph, there is a predominance of DL-limonene, which is one of the market-valuable and the primary chemical component in the TDO. DL-limonene is often using in the solvents, resins and adhesives manufacturing (Pakdel et al., 2001). Xylene toluene and benzene were also detected, they are using in the plastics and polymer industry as feedstock. There is also some of the component such as benzothiazole, that should be removed during the solvent extraction pre-treatment, but only 14 wt.% of them were recovered during the solvent extraction. the most of valuable chemicals such as DL-limonene, from waste tyres devolatilization is ended up in the TDO.

The constituent 4-vinyl-cyclohexene was detected, it is an organic compound obtained by dimerization of 1,3-butadiene by Diels-Alder reaction (Pakdel et al., 2001).

Figure 4.22 shows the chromatogram for the TDO obtained from waste tyres treated with DCM.

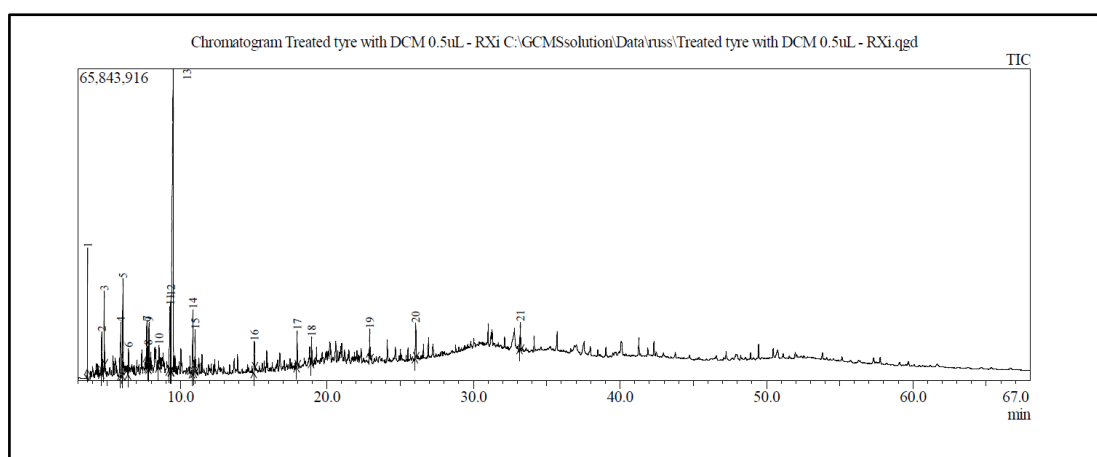


Figure 4.22: Chromatogram for TDO obtained from waste tyres treated with DCM.

Table 4.13 shows the component obtained from waste tyres treated with DEE. Table 4.13 revealed that the composition of the TDO from waste tyres pre-treated with DEE is slightly different compared to those from waste tyres when DCM was used. Even though the main components in TDO are the BTXE, DL-limonene is showing as the primary chemical in the TDO obtained after DEE was used as a solvent for pre-treatment.

Table 4.13: Composition of TDO from waste tyres treated with DEE.

Peak N°	R time (s)	Area %	Name
1	4.61	1.15	Cyclobutane, 1-methylethylidene
2	4.78	1.92	Toluene
3	5.92	2.25	Ethylbenzene
4	6.06	3.94	o-Xylene
5	7.36	1.61	1,3,6-Heptatriene, 2,5,6-trimethyl
6	7.701	2.27	D-limonene
7	7.77	1.52	Benzene, 1,2,4-trimethyl
8	7.84	2.40	Benzene, 1-ethyl-3-methyl
9	9.28	14.04	Benzene, 1-methyl, 3,1-methylethyl
10	9.46	49.07	D-limonene
11	10.64	0.83	Benzene, 1-methyl, 3,1-methylethylidene
12	10.84	4.81	Cyclohexene, 1-methyl, 4,1-methylethylidene
13	10.98	2.54	Benzene, 1-methyl, 4,1 methylethyl
14	17.97	2.04	2,4,4,6,6,8,8-Heptamethyl-2-nonene
15	18.95	1.11	2,4,4,6,6,8,8-Heptamethyl-1-nonene
16	20.17	1.17	Naphtalene, 2,6-dimethyl
17	22.89	1.09	Naphtalene-2,3,6-trimethyl
18	24.11	1.47	Heptamethyl-2-nonene
19	26.05	1.89	Sulfurous acid, cyclohexylmethyl pentadecyle
20	30.94	1.02	Heptadecanenitrile
21	33.15	1.84	Sulfurous acid,cyclonehexylmethyl dodecyl ester

It can be seen from Figure 4.23 that the peak for DL-limonene in the TDO obtained from the waste tyres treated with DEE is higher than those treated with DCM. The phenomenon is due to solvent extraction pre-treatment using DEE, which is less robust than DCM in the heteroatom removal and chemical recovery.

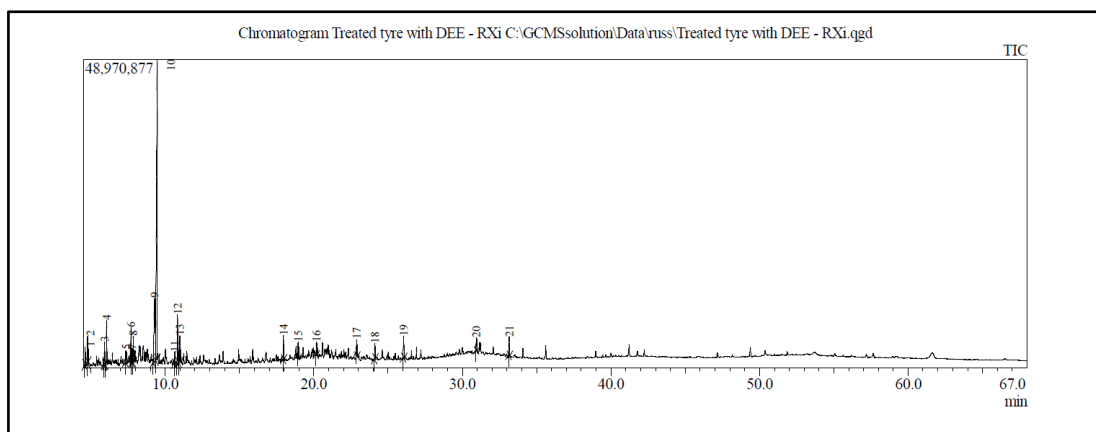


Figure 4.23: Chromatogram for TDO obtained from waste tyres treated with DEE.

Table 4.14 shows the component of TDO from untreated tyres that contain PAHs, BTXE, and the compound from processing additives such as methyl chloride and sulphurous acid, cyclohexylmethyl tridecyl ester. Moreover, DL-limonene is significantly higher in wt.% in the TDO from untreated tyres, which is the market's valuable and primary component.

Table 4.14 : Composition of TDO from untreated tyres.

Peak N°	R time (s)	Area %	Name
1	3.65	8.79	Methylene chloride
2	4.59	1.51	Cyclobutane, 1-methylethylidene
3	4.76	2.71	Toluene
4	5.89	2.80	Ethylbenzene
5	6.03	4.34	o-Xylene
6	6.41	1.21	1,6-Heptadien-3-yne, 5-methyl
7	7.65	2.17	D-limonene
8	7.73	1.51	Benzene, 1,2,4-trimethyl
9	7.81	2.35	Benzene, 1-methyl, 1,4-methylethylidene
10	9.22	11.37	Benzene, 1-methyl-1,3methylethyl
11	9.38	45.16	D-limonene
12	10.77	3.73	Cyclohexene, 1-methyl, 1,4-methylethyl
13	10.91	1.71	Benzene, 1-methyl, 1,4-methylethyl
14	17.87	1.59	2,4,4,6,6,8,8-Heptamethyl-2-nonene
15	22.78	1.10	Naphtalene, 2,3,6-trimethyl
16	24.00	1.18	2,4,4,6,6,8,8-Heptamethyl-1-nonene
17	25.94	1.45	Sulphurous acid, cyclohexylmethyl tridecyl ester
18	26.47	0.89	Heptadecane
19	30.82	1.30	Hexadecanenitrile
20	33.00	1.23	Bis(2-ethylhexyl) methylphosphonate
21	35.46	1.89	Heptadecanenitrile

As can be seen in Figure 4.24, the chromatogram shows the presence of DL-limonene as a significant component. The TDO obtained in this case contains more heteroatom than the previous due to additive processing during the tyres manufacturing, and it is not pre-treated.

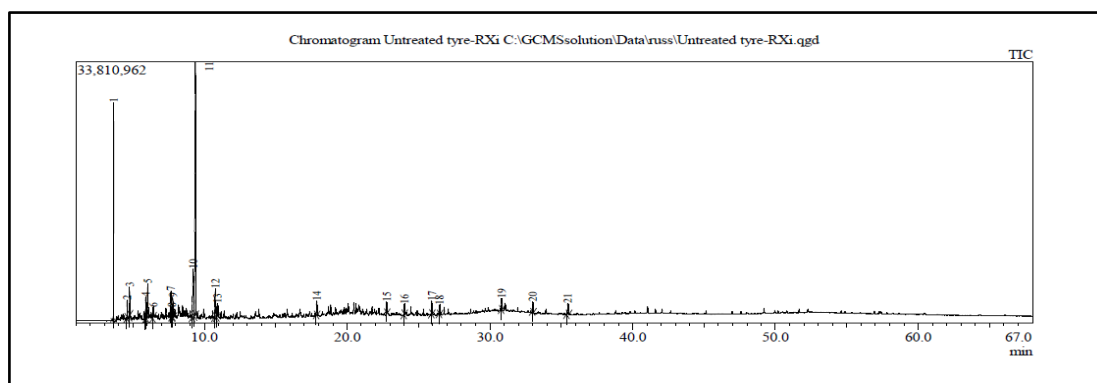


Figure 4.24: GCMS results for TDO obtained from the untreated tyres

4.2.5 FTIR results for pyrolysis oil

The FTIR analysis results for pyrolysis oil are presented in Figure 4.25, Figure 4.26, and Figure 4.27. Respectively, the FTIR for pyrolysis oil from waste tyres treated by DCM, DEE and untreated small size, medium size, and large size. The wavenumber range was 4000-400 cm^{-1} ; the number of the scanner was 40 with a resolution of 4.

Figure 4.25 shows the FTIR result for pyrolysis oil from small particle size waste tyres. It can be seen from the curve shapes of Figure 4.25 that in the wavenumber range between 3800-3500 cm^{-1} , there is strong alcohol O-H functional groups and amide in the waste tyres pre-treated. Between 3000-2800 cm^{-1} , there is medium to solid alkane C-H medium alkene C=C-H medium in all the sample. Between 2350-2280 cm^{-1} , there is weak nitrile functional group CN and C-O bonds. Between 1800-1700 cm^{-1} , a strong presence of the aromatics bond. There is a wide range with many compounds between 1700-1200 cm^{-1} such as carbonyls C=O, aldehyde CHO, ketone RCOR, Ester RCOOR, acid RCOOH, N-H bending amine with a strong bond. Between 880-400 cm^{-1} , there is C=C bending, C-Br stretching halo compounds, C-H bending.

As illustrated in the results, more organic functional compounds are used when the small particle size waste tyre is used in the range of 880-400. This is attributed to the presence of low hydrocarbons in the NR and SBR during the tyres manufacturing.

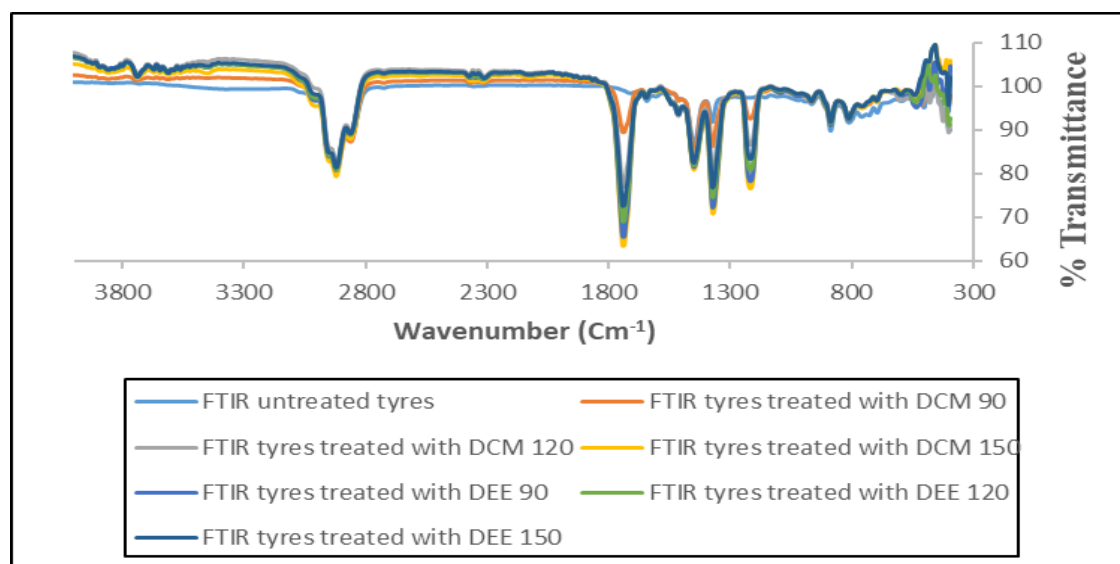


Figure 4.25: FTIR result for pyrolysis oil from waste tyres small size.

Figure 4.26 shows the FTIR result for untreated, DCM and DEE treated medium particle size waste tyre crumb is used. As shown in Figure 4.26, there is a significant difference between the untreated tyre and operated in the range of $3850 - 3500 \text{ cm}^{-1}$. As can be seen, the straight line for untreated tyres shows that the functional groups are absent in that wavenumber range while there is still a strong alcohol active group in the treated tyres. Between $3000 - 2800 \text{ cm}^{-1}$, the alkane C-H functional group is predominant in both samples. Between $1800 - 1080 \text{ cm}^{-1}$, there is a substantial presence of active group such as C-O stretching primary alcohol, S=O stretching sulfoxide, C-O-C-O anhydride, C=O pushing carboxylic acid, aldehyde, amide, oxime, alkene and N-O stretching nitro compound. Between $900 - 400 \text{ cm}^{-1}$, there is a significant presence of C-H bending trisubstituted, disubstituted and monosubstituted. Figure 4.26 shows the FTIR results for pyrolysis oil from waste tyres medium size.

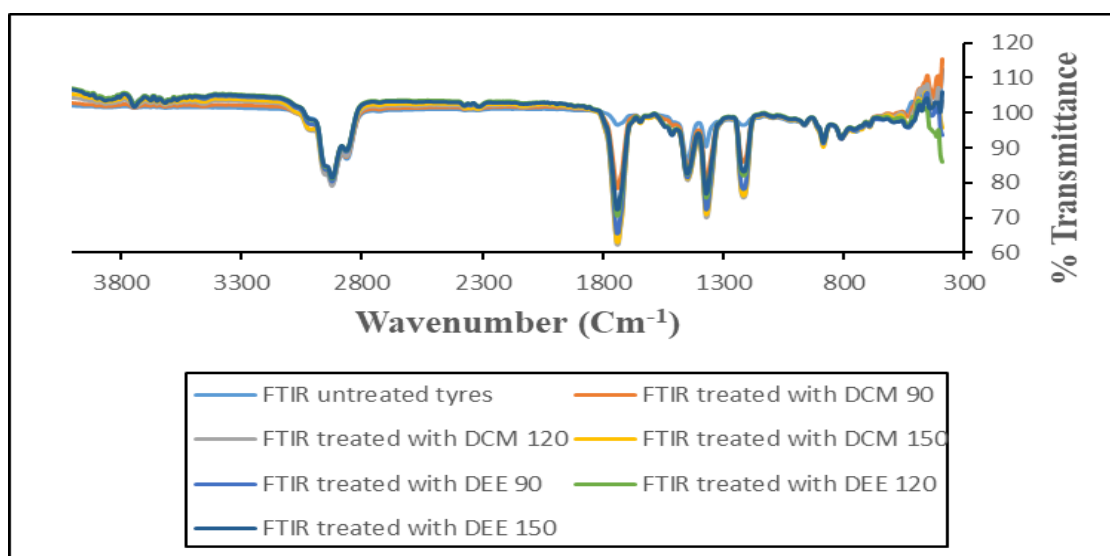


Figure 4.26: FTIR result for pyrolysis oil from waste tyre medium size.

Figure 4.27 shows the FTIR result from untreated DCM and DEE treated medium particle size waste tyres. The results are similar to those from Figure 4.27, showing an increase in the active groups in the range between $1800 - 1150 \text{ cm}^{-1}$. There is a predominance of C-O, C-H bending, alkyl ketone, alkyl amine functional groups.

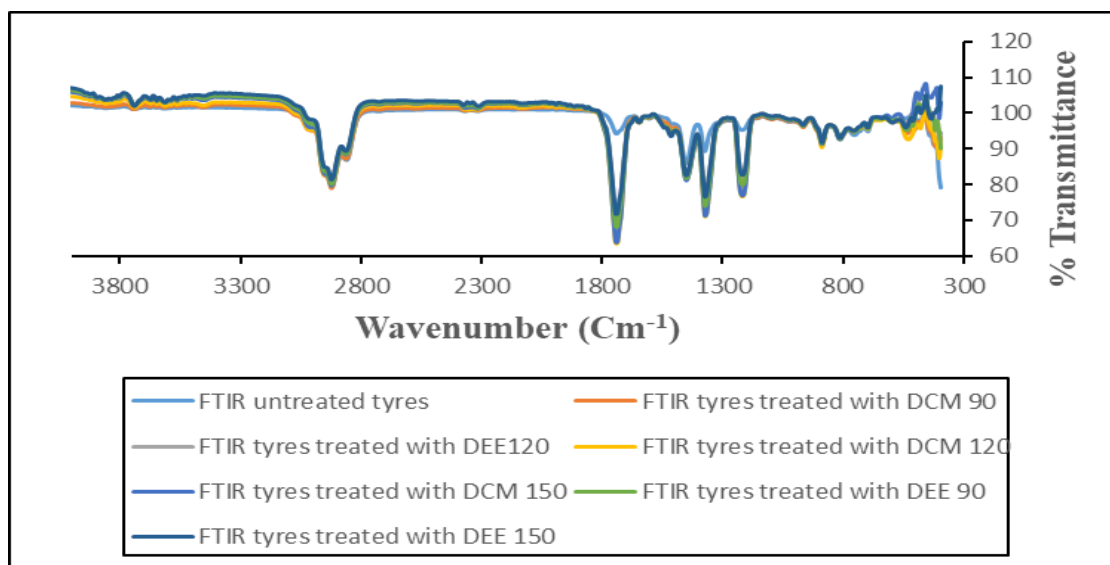


Figure 4.27: FTIR results for pyrolysis oil from waste tyres large size.

4.2.6 Physical properties for pyrolysis oil

The physical properties of the treated and untreated waste tyres are shown in Table 4.15. As can be seen in Table 4.15, as a pre-treatment process, solvent extraction has a minor impact on TDO physical properties such as density, viscosity, and HHV as a pre-treatment process.

Table 4.15: Physical properties for untreated and treated waste tyres.

Types of pyrolysis oil	Density at 25°C (Kg m ⁻³)	Kinematic viscosity at 25°C (mm ² s ⁻¹)	High calorific value (MJ kg ⁻¹)
Oil from untreated waste tyres	0.92	11.03	42.61
Oil from waste tyres treated with DCM	0.90	8.22	41.98
Oil from waste tyres treated with DEE	0.91	9.34	42.17

4.2.7 Pyrolysis char analysis

Two types of analysis are conducted, the proximate analysis shows mainly the amount of fixed carbon in the char and the volatile matter remaining. The ultimate study shows the amount of carbon, oxygen, nitrogen and sulphur in the char.

Figure 4.28 shows the proximate analysis results for char from untreated and treated waste tyres. The curves show a small amount of moisture content and high volatile matter, at 2.24 and 1.47 wt.%, respectively. However, there is 5.71 wt.% of fixed carbon and a considerable amount of ash content, approximately 90.58 %. Usually, the pyro char contains more carbon black, which is very useful in active carbon manufacturing.

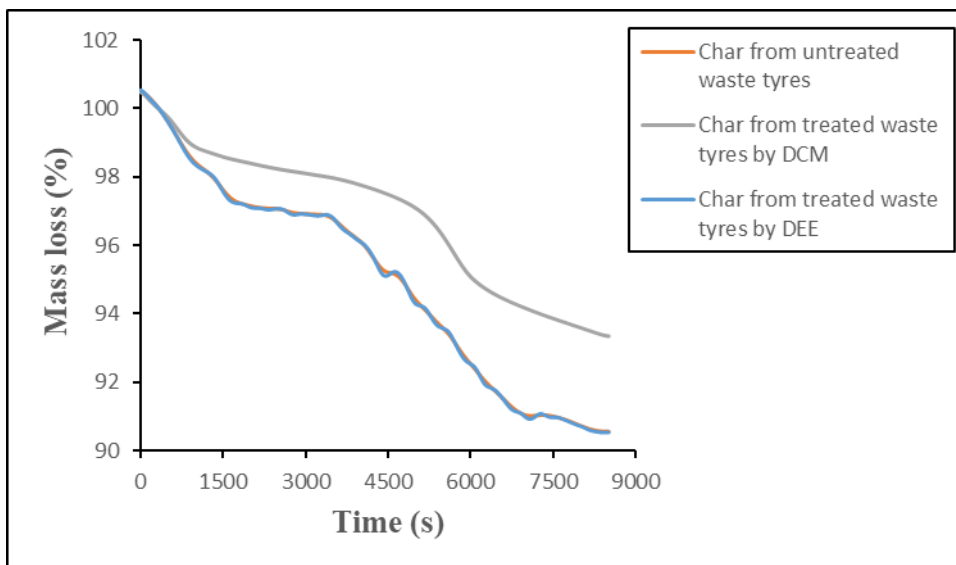


Figure 4.28: Proximate analysis for pyrolysis char.

5 Conclusions and future work

Solvent extraction was used as a pre-treatment method for waste tyres crumb before pyrolysis. DCM and DEE were used as a solvent to extract the additive compounds in the waste tyres crumb and promote the recovery of value compounds through pyrolysis. It was observed that solvent extraction affects the waste tyres crumb by removing some additives, plasticizers and heteroatoms before the pyrolysis process. However, three parameters were varied, i.e., solvent type, extraction time and particle size, to demonstrate the effect of solvent extraction on the waste tyres crumb. The results have shown that DCM is an effective solvent due to its polarity and slowest solvent degradation for the heteroatoms removal and impurities.

The optimum effect of solvent extraction using DCM was found at an extraction time of 150 min with a small particle size (0.5- 1 mm). The yield of oil was 14.15 wt.% with a selectivity of 1.35 due to the influence of the more critical specific areas that were provided by the small particle size in the reaction conditions. The solvent extraction oil shows a predominance of 4-Benzenediamine, N-(1,3-dimethylbutyl)-N. This component is used during the tyres manufacturing process as a rubber accelerator. A predominance of alkane, alkene, aldehyde and halo-compound functional group was found in the FTIR study. DCM is a comparable suitable solvent in the pre-treatment of waste tyres before pyrolysis.

The thermal decomposition of waste tyres using the thermogravimetry analysis showed that the devolatilization of untreated tyres occurs in the temperature range 200-550 °C, while the treated started at 200-500. This thermal behaviour in the treated tyres is due to solvent extraction by removing the impurities such as additives and heteroatoms, which have an influence on the composition of waste tyres crumb. The DTG results showed the temperature range of the preliminary pyrolysis experiments for the untreated and treated waste tyres. The particle size significantly influences the thermal devolatilization of waste tyres, which justify the best result obtained during pyrolysis using the large particle size (4 – 5 mm).

Six preliminary experiments were conducted to find the optimum pyrolysis temperature based on the TGA and DTG results. The initial experiments were carried out at 350, 400, 450, 500, 550 °C, and 600 °C. The optimum result was found at 550 °C, with 51.40 wt.% yield oil, 31.90 wt.% pyro char and 16.70 wt.% permanent gas, while the heating rate at 15 °C min⁻¹, the nitrogen flow rate at 6 l min⁻¹ and the cooling medium (water from the chiller bath) at 2.1/2.3

°C was kept constant. The optimum parameters were used to produce TDO from untreated and treated tyres through pyrolysis.

Twenty-one runs were performed in particular conditions (pyrolysis temperature 550 °C, heating rate 15 °C min⁻¹, nitrogen flow rate 6 l min⁻¹ and water bath temperature 2.1/2.3 °C), nine runs for waste tyres treated with DCM, nine for the treated tyres with DEE and three for untreated tyres. The best results were obtained by feeding the waste tyres crumb treated with DCM for 150 min using a large particle size (4-5 mm). The percentage of oil yield was 55.64 wt.%, while the pyro chars and gas yield percentage were respectively 29.36 wt.% and 15 wt.%. The FTIR analysis using the TDO shows a predominance of carbonyls C=O, aldehyde CHO, ketone RCOR, ester RCOOR, acid RCOOH, N-H bending amine with a strong bond in the wavenumber range between 1700-400. In comparison, the GCMS analysis shows the predominance of DL-limonene and the BTXE compounds.

Finally, the easiest way to deal with waste tyres is to pre-treat them with DCM as a solvent for 150 min and use the particle size between 1-5 mm. in addition, the pyrolysis process is done after the solvent extraction using 550 °C as the pyrolysis temperature, heating rate 15 °C min⁻¹, nitrogen flow rate 6 l min⁻¹ and water bath temperature 2.1/2.3 °C. These conditions are more acceptable for TDO with a substantial decrease in impurities compared to the results from some authors such as Williams et al. (2003), Aguardo et al. (2002) and other authors.

References

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Appendix

A. Selectivity and oil yield

The follow equation serves for the calculation of percentage yield for the tyres derived oil from pyrolysis and solvent extraction:

$$\% Yield = \frac{\text{Mass loss of tyre crumb sample}}{\text{Initial mass of tyre sample}} \times 100 \quad (1)$$

The following equation serves as an illustration for the selectivity calculation:

$$\text{Selectivity} = \frac{\sum \text{Heteroatomic compounds}}{\sum \text{Non - heteroatomic compounds}} \times 100 \quad (2)$$

B. Proximate analysis

B.1 Waste tyre treated by DCM

- ✓ High volatile matter (Moisture content)

The highly volatile matter content may be determined by the following equation:

$$V = \frac{W - R}{W} \times 100 \quad (3)$$

Where:

V = highly volatile matter content, as received basis (%),

W = original specimen mass (mg), and

R = mass measured at Temperature X (mg).

W = 14.75429 mg, R = 14.68968, and V = 0.44 %, T_x = 110°C

- ✓ Medium volatile matter

The medium volatile matter content can be determined using the following equation:

$$O = \frac{R - S}{W} \times 100 \quad (3)$$

Where:

O = medium volatile matter content, as-received basis, %,

R = mass measures at Temperature X, (mg),

S = mass measured at Temperature Y, (mg), and

W = original specimen mass, (mg).

R = 14.68968 mg, S = 5.449437 mg, W = 14.75429 mg, and O = 62.63%, $T_y = 750^\circ\text{C}$

✓ Combustible material content

The combustible material can be determined using the following equation:

$$C = \frac{S - T}{W} \times 100 \quad (4)$$

Where:

C = combustible material content, as-received basis, (%),

S = mass measured at Temperature Y, (mg),

T = mass measured at Temperature Z, (mg) and

W = original specimen mass, (mg).

S = 5.449437 mg, T = 1.084245, W = 14.75429 mg, and C = 29.59 %, $T_z = 900^\circ\text{C}$

✓ Ash content

The ash content can be determined using the following equation:

$$C = \frac{T}{W} \times 100 \quad (4)$$

Where:

A = ash content as-received basis, (%),

T = mass measured at Temperature Z, (mg) and

W = original specimen mass, (mg).

T = 1.084245, W = 14.75429 mg and A = 7.34%

B.2 waste tyres treated by DEE

✓ High volatile matter (Moisture content)

The highly volatile matter content may be determined by the following equation:

$$V = \frac{W - R}{W} \times 100$$

Where:

V₁ = highly volatile matter content, as received basis (%),

W₁ = original specimen mass (mg), and

R₁ = mass measured at Temperature X (mg).

W₁ = 15.61333 mg, R₁ = 15.51554, and V₁ = 0.63 %, T_x = 110°C

✓ Medium volatile matter

The medium volatile matter content can be determined using the following equation:

$$O = \frac{R - S}{W} \times 100$$

Where:

O₁ = medium volatile matter content, as-received basis, %,

R₁ = mass measures at Temperature X, (mg),

S₁ = mass measured at Temperature Y, (mg), and

W₁ = original specimen mass, (mg).

R₁ = 15.51554 mg, S₁ = 5.893408 mg, W₁ = 15.61333 mg, and O₁ = 61.63 %, T_y = 750°C

✓ Combustible material content

The combustible material can be determined using the following equation:

$$C = \frac{S - T}{W} \times 100$$

Where:

C₁ = combustible material content, as-received basis, (%),

S₁ = mass measured at Temperature Y, (mg),

T₁ = mass measured at Temperature Z, (mg) and

W_1 = original specimen mass, (mg).

$S_1 = 5.893408$ mg, $T_1 = 1.113355$, $W_1 = 15.61333$ mg, and $C_1 = 30.62$ %, $T_z = 900^\circ\text{C}$

✓ Ash content

The ash content can be determined using the following equation:

$$A = \frac{T}{W} \times 100$$

Where:

A_1 = ash content as-received basis, (%),

T_1 = mass measured at Temperature Z, (mg) and

W_1 = original specimen mass, (mg).

$T_1 = 1.052824$, $W_1 = 15.61333$ mg and $A_1 = 7.12\%$

B.3 waste tyres untreated

✓ High volatile matter (Moisture content)

The highly volatile matter content may be determined by the following equation:

$$V = \frac{W - R}{W} \times 100$$

Where:

V_2 = highly volatile matter content, as received basis (%),

W_2 = original specimen mass (mg), and

R_2 = mass measured at Temperature X (mg).

$W_2 = 15.25832$ mg, $R_2 = 15.20038$, and $V_2 = 0.38$ %, $T_x = 110^\circ\text{C}$

✓ Medium volatile matter

The medium volatile matter content can be determined using the following equation:

$$O = \frac{R - S}{W} \times 100$$

Where:

O_2 = medium volatile matter content, as-received basis, %,

R_2 = mass measures at Temperature X, (mg),

S_2 = mass measured at Temperature Y, (mg), and

W_2 = original specimen mass, (mg).

$R_2 = 15.20038$ mg, $S_2 = 5.42814$ mg, $W_2 = 15.25832$ mg, and $O_2 = 64.05$ %, $T_y = 750^\circ\text{C}$

✓ Combustible material content

The combustible material can be determined using the following equation:

$$C = \frac{S - T}{W} \times 100$$

Where:

C_2 = combustible material content, as-received basis, (%),

S_2 = mass measured at Temperature Y, (mg),

T_2 = mass measured at Temperature Z, (mg) and

W_2 = original specimen mass, (mg).

$S_2 = 5.42814$ mg, $T_2 = 1.050621$, $W_2 = 15.25832$ mg, and $C_2 = 28.69$ %, $T_z = 900^\circ\text{C}$

✓ Ash content

The ash content can be determined using the following equation:

$$A = \frac{T}{W} \times 100$$

Where:

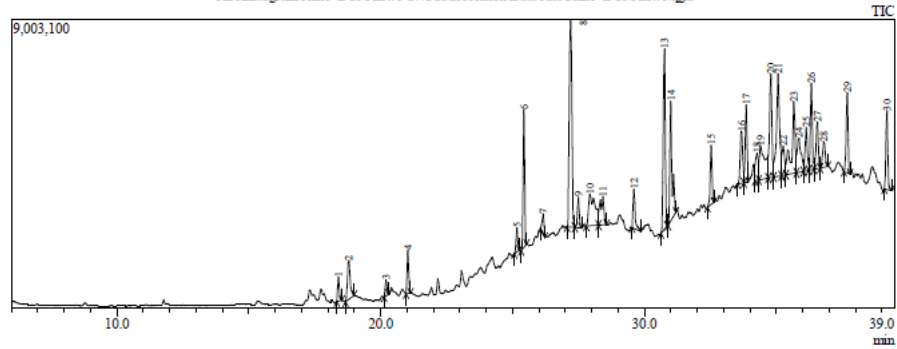
A_2 = ash content as-received basis, (%),

T_2 = mass measured at Temperature Z, (mg) and

W_2 = original specimen mass, (mg).

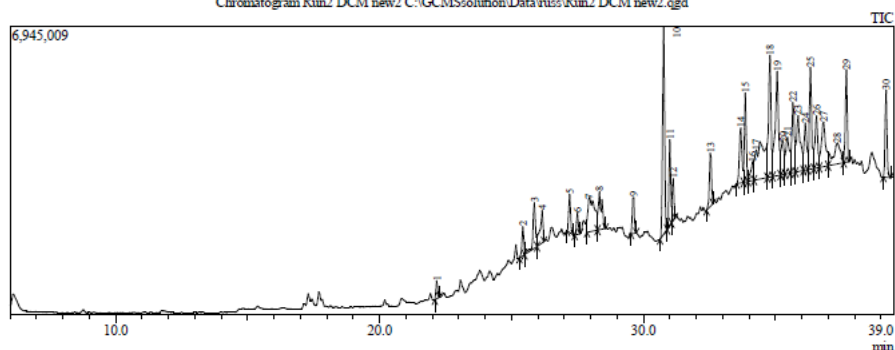
$T_2 = 1.050621$, $W_1 = 15.25832$ mg and $A_1 = 6.88\%$

C. GCMS results



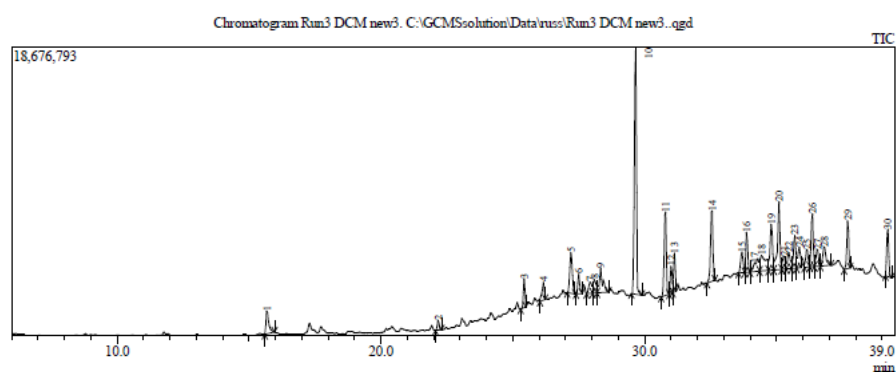
Peak Report TIC

Peak#	R.Time	Area%	Name
1	18.402	0.92	Decanoic acid, methyl ester
2	18.790	2.42	Hexanoic acid, 6-bromo-
3	20.205	0.63	Quinoline, 1,2-dihydro-2,2,4-trimethyl-
4	21.034	1.46	Tridecanoic acid, methyl ester
5	25.168	0.86	Heneicosane
6	25.433	4.79	Hexadecanoic acid, methyl ester
7	26.161	0.74	Pentadecane
8	27.200	12.14	E,E,Z-1,3,12-Nonadecatriene-5,14-diol
9	27.498	1.23	Methyl stearate
10	27.933	4.60	2-Methylhexacosane
11	28.431	2.17	Heptadecyl acetate
12	29.603	1.70	Eicosane
13	30.757	7.84	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
14	30.999	6.05	Hexanedioic acid, bis(2-ethylhexyl) ester
15	32.534	2.44	Nonacosane
16	33.682	2.87	Hexatriacontane
17	33.863	3.07	Heneicosane
18	34.267	1.54	Benz[a]anthracene, 7-methyl-
19	34.400	4.36	4',4''-Biacetamide, 3',3''-dimethyl-
20	34.793	5.23	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
21	35.069	7.03	Hexatriacontane
22	35.265	1.69	1,4-Benzenediamine, N,N-diphenyl-
23	35.671	5.43	N-Benzyl-N-phenyl-p-phenylenediamine
24	35.855	2.80	15-Hydroxydehydroabietic acid, methyl ester
25	36.134	2.09	1,4-benzenediamine, N1,N1-bis(4-methylphen
26	36.332	3.45	Pentacosane
27	36.556	2.32	Tetratetracontane
28	36.810	1.54	gamma-Sitosterol
29	37.692	3.29	Heneicosane
30	39.195	3.29	Tetratetracontane
		100.00	

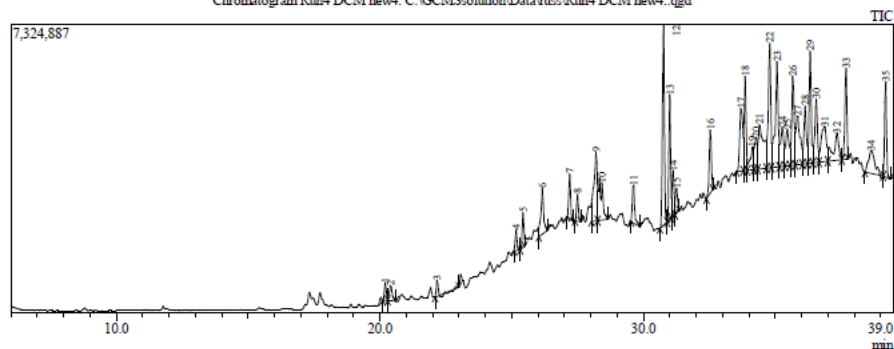


Peak Report TIC

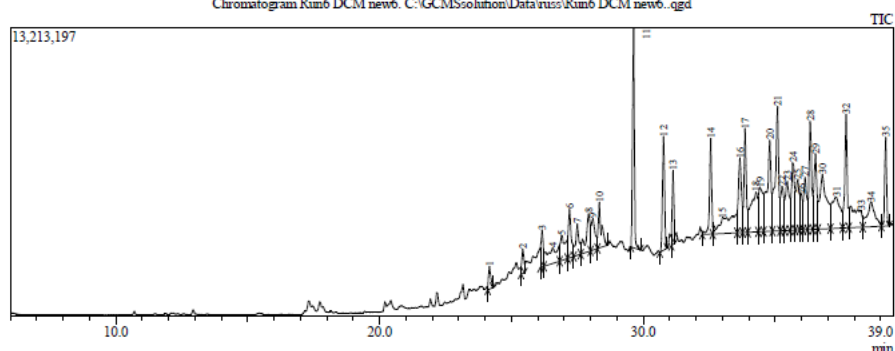
Peak#	R.Time	Area%	Name
1	22.171	0.66	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
2	25.434	1.20	Hexadecanoic acid, methyl ester
3	25.864	2.51	n-Hexadecanoic acid
4	26.163	2.03	Heptacosane
5	27.202	1.48	2-Methyltetracosane
6	27.500	0.81	Methyl stearate
7	27.933	4.85	2-Methylhexacosane
8	28.331	2.46	Octadecane
9	29.617	1.54	Hexacosane
10	30.767	8.56	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
11	31.002	3.19	Hexanedioic acid, bis(2-ethylhexyl) ester
12	31.123	1.55	Octadecane
13	32.546	2.44	Nonacosane
14	33.688	3.13	Hexatriacontane
15	33.867	3.21	Heptacosane
16	34.133	1.48	Adipic acid, cis-hex-3-enyl isobutyl ester
17	34.267	7.20	Benz[a]anthracene, 7-methyl-
18	34.796	6.17	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
19	35.069	7.44	Nonacosane
20	35.300	2.20	1,4-Benzenediamine, N,N-diphenyl-
21	35.459	2.67	Pentatriacontane
22	35.675	4.13	N-Benzyl-N-phenyl-p-phenylenediamine
23	35.863	4.65	15-Hydroxydehydroabietic acid, methyl ester
24	36.133	2.47	1,4-benzenediamine, N1,N1-bis(4-methylphen
25	36.334	4.91	Tetratetracontane
26	36.559	2.88	Nonacosane
27	36.823	3.99	gamma-Sitosterol
28	37.333	3.20	Tetrapentacontane, 1,54-dibromo-
29	37.694	3.55	Heptacosane
30	39.198	3.46	Tetratetracontane
		100.00	



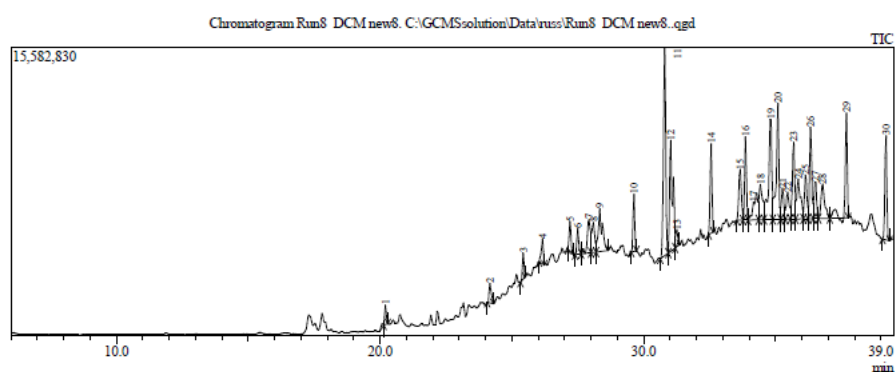
Peak#	R.Time	Area%	Name
1	15.680	2.47	1-Hexanol, 6-chloro-
2	22.172	0.67	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
3	25.434	1.83	Hexadecanoic acid, methyl ester
4	26.163	1.51	Eicosane
5	27.207	3.91	7-Hexadecenal, (Z)-
6	27.502	1.43	Methyl stearate
7	27.933	1.43	Tetrapentacontane, 1,54-dibromo-
8	28.101	1.41	Pyrene
9	28.332	2.93	Heneicosane
10	29.655	19.44	9-Octadecenoic acid, 12-hydroxy-, methyl ester
11	30.785	6.83	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
12	31.000	1.96	Hexanedioic acid, bis(2-ethylhexyl) ester
13	31.133	2.47	Heneicosane
14	32.551	6.22	2-Methylhexacosane
15	33.692	1.98	Tetratetracontane
16	33.867	2.83	Tetracosane
17	34.167	2.31	Octanoic acid, morpholide
18	34.433	3.37	Acetic acid 4-[(4-acetylamino-phenylimino)-m
19	34.807	4.18	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
20	35.096	6.09	Heneicosane
21	35.300	1.35	1,4-Benzenediamine, N,N'-diphenyl-
22	35.468	1.77	2-Methylhexacosane
23	35.695	2.99	N-(2,4-Dinitrophenyl)-m-phenylenediamine
24	35.867	2.01	Succinic acid, 2,2,3,3,4,4,5,5-octafluoropentyl
25	36.154	1.69	1,4-benzenediamine, N1,N1-bis(4-methylphenyl)-
26	36.358	3.98	Heneicosane
27	36.552	1.65	2-Methylhexacosane
28	36.812	2.24	gamma-Sitosterol
29	37.707	3.50	Nonacosane
30	39.221	3.55	Tetratetracontane
		100.00	



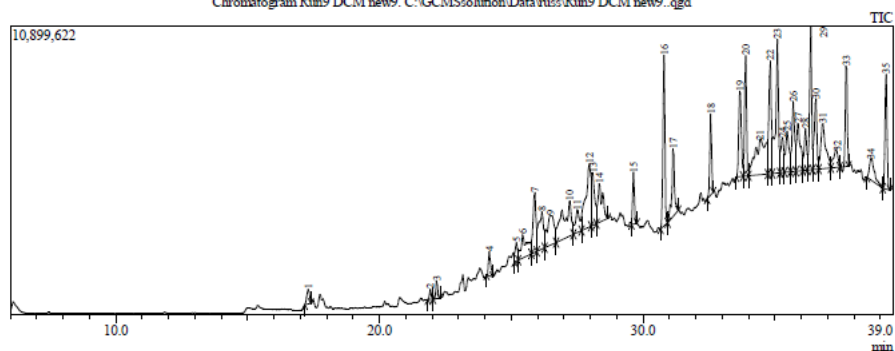
Peak Report TIC			
Peak#	R.Time	Area%	Name
1	20.204	0.64	Quinoline, 1,2-dihydro-2,2,4-trimethyl-
2	20.409	0.83	Cyclohexanamine, N-cyclohexyl-
3	22.167	0.50	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
4	25.168	0.68	Eicosane
5	25.435	1.22	Tridecanoic acid, methyl ester
6	26.167	2.35	Hexacosane
7	27.202	1.48	2-Methyltetracosane
8	27.500	0.93	Methyl stearate
9	28.204	4.38	Hexatriacontane
10	28.433	2.81	1-Docosanol, acetate
11	29.619	1.65	Heptacosane
12	30.762	7.26	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
13	31.001	4.17	Hexanedioic acid, bis(2-ethylhexyl) ester
14	31.122	1.82	Octadecane
15	31.267	0.95	Undec-10-ynoic acid, octadecyl ester
16	32.542	2.62	Tetratetracontane
17	33.710	3.85	Nonacosane
18	33.864	3.02	Heptacosane
19	34.133	1.69	Adipic acid, cis-hex-3-enyl isobutyl ester
20	34.267	1.62	Benz[a]anthracene, 7-methyl-
21	34.400	4.59	4,4'-Biacetamide, 3',3''-dimethyl-
22	34.794	5.72	Indole-3-carboxaldehyde, 1-[2-(4-chlorophenyl)-
23	35.070	6.12	Hexatriacontane
24	35.270	2.43	1,4-Benzenediamine, N,N'-diphenyl-
25	35.461	2.29	2-Methylhexacosane
26	35.675	4.47	N-Benzyl-N'-phenyl-p-phenylenediamine
27	35.851	3.70	15-Hydroxydehydroabietic acid, methyl ester
28	36.136	2.77	1,4-benzenediamine, N1,N1-bis(4-methylphenyl)-
29	36.332	4.34	Heptacosane
30	36.558	3.22	Tetratetracontane
31	36.876	3.51	beta.-Sitosterol
32	37.349	2.80	Pentatriacontane
33	37.689	3.44	Heptacosane
34	38.633	2.67	Hexadecanoic acid, (3-bromoprop-2-ynyl) ester
35	39.193	3.46	Tetratetracontane
100.00			



Peak#	R.Time	Area%	Name	Peak Report TIC
1	24.171	0.72	Hexadecane	
2	25.436	0.73	Hexadecanoic acid, methyl ester	
3	26.165	1.13	Tetracosane	
4	26.567	2.46	1,6-Diisilacyclodeca-3,8-diene, 1,6-dimethyl-1,	
5	26.900	1.86	10,18-Bisnorabieta-8,11,13-triene	
6	27.204	1.93	2-Methylhexacosane	
7	27.502	1.43	Methyl stearate	
8	27.931	2.30	2-Methylhexacosane	
9	28.091	1.79	Pyrene	
10	28.333	1.93	Heneicosane	
11	29.630	5.52	9-Octadecenoic acid, 12-hydroxy-, methyl ester	
12	30.772	3.31	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N	
13	31.131	1.80	Heneicosane	
14	32.562	2.80	Heneicosane	
15	33.000	3.90	Eicosane	
16	33.669	3.18	Hexatriacontane	
17	33.867	3.35	Hexatriacontane	
18	34.267	4.10	Dotriacontane, 2-methyl-	
19	34.433	2.65	Aminoformic acid, N-n-decyl-, pentafluorophenyl-	
20	34.797	5.46	Indole-3-carboxaldehyde, 1-[2-(4-chlorophenyl)-	
21	35.091	6.06	Hexacosane	
22	35.267	2.04	1,4-Benzenediamine, N,N-diphenyl-	
23	35.459	2.58	Pentatriacontane	
24	35.681	3.21	N-Benzyl-N'-phenyl-p-phenylenediamine	
25	35.860	2.32	Silane, diethyldodecyloxytetrahydrofurfuryloxy-	
26	36.000	1.43	2-Thiopheneacetamide, N-decyl-N-methyl-	
27	36.138	2.16	1,4-benzenediamine, N1,N1-bis(4-methylphenyl)-	
28	36.337	3.95	Hexatriacontane	
29	36.532	3.17	Tetratetracontane	
30	36.797	5.23	gamma-Sitosterol	
31	37.333	3.73	Tetrapentacontane, 1,54-dibromo-	
32	37.696	3.80	Tetratetracontane	
33	38.267	2.85	Hexanoic acid, 3,5,5-trimethyl-, pentadec-6-yl	
34	38.648	2.68	benzenesulfonyl fluoride, 4-(hexadecyloxy)-3-	
35	39.197	2.44	Tetratetracontane	
		100.00		

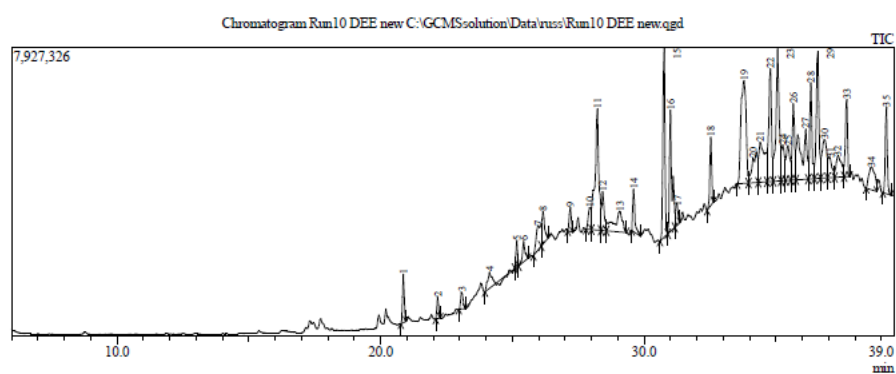


Peak Report TIC			
Peak#	R.Time	Area%	Name
1	20.204	0.75	Quinoline, 1,2-dihydro-2,2,4-trimethyl-
2	24.171	1.00	Eicosane
3	25.434	1.00	Hexadecanoic acid, methyl ester
4	26.163	1.15	Eicosane
5	27.205	1.24	Eicosane
6	27.502	1.15	Methyl stearate
7	27.923	2.52	2-Methylhexacosane
8	28.100	2.02	Pyrene
9	28.332	3.82	Eicosane
10	29.631	2.18	Heneicosane
11	30.798	11.05	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
12	31.024	8.02	Hexanedioic acid, bis(2-ethylhexyl) ester
13	31.267	0.80	Eicosyl acetate
14	32.562	3.60	Heneicosane
15	33.659	3.11	Hexatriacontane
16	33.867	3.34	Hexatriacontane
17	34.167	2.94	Octanoic acid, morpholide
18	34.430	2.67	Aminoformic acid, N-n-decyl-, pentafluorophe
19	34.816	7.50	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
20	35.094	6.89	Heneicosane
21	35.267	1.73	1,4-Benzenediamine, N,N-diphenyl-
22	35.462	1.87	2-Methylhexacosane
23	35.692	4.29	N-Benzyl-N-phenyl-p-phenylenediamine
24	35.866	3.52	15-Hydroxydehydroabietic acid, methyl ester
25	36.133	2.40	1,4-benzenediamine, N1,N1-bis(4-methylphen
26	36.337	4.47	Tetracontane
27	36.516	2.13	Tetratetracontane
28	36.789	3.04	gamma-Sitosterol
29	37.693	5.08	Heneicosane
30	39.193	4.72	Tetratetracontane
		100.00	



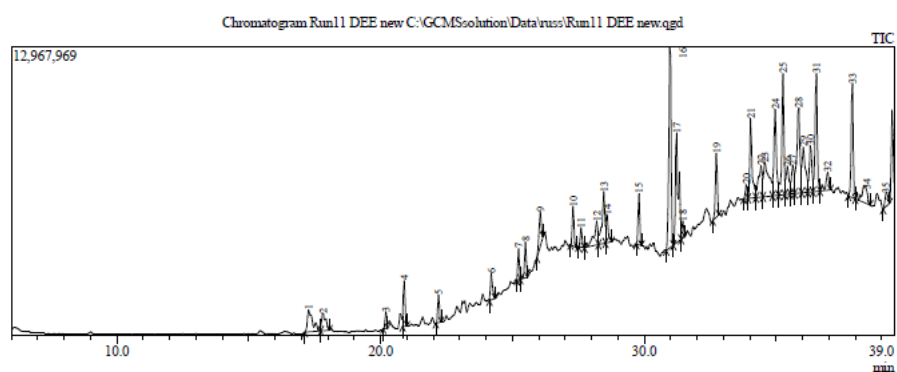
Peak Report TIC

Peak#	R.Time	Area%	Name
1	17.301	0.64	Benzothiazole
2	21.933	0.28	Heptadecane
3	22.174	0.51	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
4	24.171	0.82	Octadecane
5	25.197	0.65	Hexadecane
6	25.433	2.39	Hexadecanoic acid, methyl ester
7	25.888	2.76	n-Hexadecanoic acid
8	26.166	2.96	Eicosane
9	26.479	3.42	2-Mercaptobenzothiazole
10	27.218	5.01	2-Methyltetracosane
11	27.500	1.58	Methyl stearate
12	27.963	5.26	Pentatriacontane
13	28.100	2.53	Pyrene
14	28.345	2.78	Docosane
15	29.638	1.42	Heneicosane
16	30.796	5.43	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
17	31.145	3.00	Heneicosane
18	32.569	2.32	Nonacosane
19	33.681	3.57	Hexatriacontane
20	33.894	3.66	Heneicosane
21	34.433	6.34	N-(4'-Propionylaminobiphenyl-4-yl)-propionar
22	34.825	4.34	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
23	35.099	6.00	Hexatriacontane
24	35.300	1.63	1,4-Benzenediamine, N,N'-diphenyl-
25	35.472	2.26	Pentatriacontane
26	35.703	3.00	N-Benzyl-N'-phenyl-p-phenylenediamine
27	35.883	2.83	15-Hydroxydehydroabietic acid, methyl ester
28	36.164	1.59	1,4-benzenediamine, N1,N1-bis(4-methylphen
29	36.363	4.61	Heneicosane
30	36.554	3.05	Tetratetracontane
31	36.819	3.55	gamma-Sitosterol
32	37.367	1.27	Octatriacontane, 1,38-dibromo-
33	37.715	3.21	Tetratetracontane
34	38.633	1.62	benzenesulfonyl fluoride, 4-(hexadecyloxy)-3-
35	39.223	3.72	Tetratetracontane
		100.00	



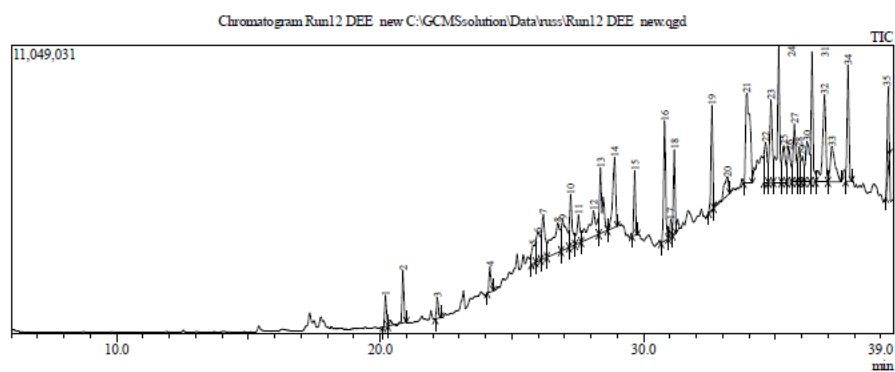
Peak Report TIC

Peak#	R.Time	Area%	Name
1	20.867	1.28	Butylated Hydroxytoluene
2	22.169	0.59	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
3	23.077	0.65	Hexadecane
4	24.133	1.00	Tetracosane
5	25.167	0.70	Nonadecane
6	25.432	0.91	Hexadecanoic acid, methyl ester
7	25.967	1.96	n-Hexadecanoic acid
8	26.166	1.42	Hexadecane
9	27.197	0.78	2-Methyltetracosane
10	27.933	1.12	2-Methylhexacosane
11	28.224	7.59	Hexatriacontane
12	28.433	1.49	1-Docosanol, acetate
13	29.076	2.71	Stigmat-4-en-3-one
14	29.603	1.38	Heptacosane
15	30.757	6.29	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
16	30.998	5.01	Hexanedioic acid, bis(2-ethylhexyl) ester
17	31.267	0.88	Baccharane
18	32.533	2.08	2-Methylhexacosane
19	33.788	8.53	Tetratetracontane
20	34.133	2.70	Adipic acid, heptyl trans-hex-3-enyl ester
21	34.400	3.92	4',4''-Biacetamide, 3',3''-dimethyl-
22	34.789	5.14	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
23	35.069	6.82	Tetratetracontane
24	35.267	1.79	1,4-Benzenediamine, N,N'-diphenyl-
25	35.467	2.01	2-Methylhexacosane
26	35.669	3.27	N-Benzyl-N'-phenyl-p-phenylenediamine
27	36.132	5.18	1,4-benzenediamine, N1,N1-bis(4-methylphen
28	36.331	3.42	Heptacosane
29	36.588	5.49	Tetratetracontane
30	36.846	2.95	Cholesterol
31	37.067	1.28	Cyclohexane, eicosyl-
32	37.333	1.98	Tetrapentacontane, 1,54-dibromo-
33	37.686	2.59	Heptacosane
34	38.630	2.26	Tetrapentacontane, 1,54-dibromo-
35	39.194	2.83	Tetratetracontane
		100.00	



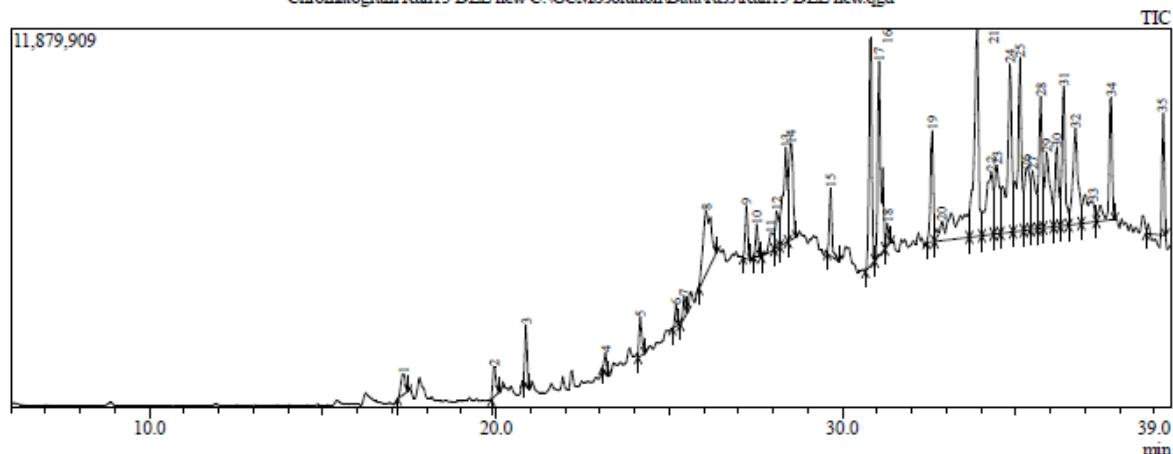
Peak Report TIC

Peak#	R.Time	Area%	Name
1	17.267	2.66	Benzothiazole
2	17.813	1.54	Neodecanoic acid
3	20.205	0.71	Quinoline, 1,2-dihydro-2,2,4-trimethyl-
4	20.895	1.70	Butylated Hydroxytoluene
5	22.202	1.02	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
6	24.203	1.23	Octadecane
7	25.234	1.09	Heptacosane
8	25.498	1.39	Pentadecanoic acid, 14-methyl-, methyl ester
9	26.062	2.00	n-Hexadecanoic acid
10	27.302	1.57	2-Methylhexacosane
11	27.605	0.77	Methyl stearate
12	28.196	2.23	Pyrene
13	28.466	3.26	Heptacosane
14	28.600	1.40	Heptadecyl acetate
15	29.798	1.89	Heptacosane
16	30.980	10.69	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
17	31.223	7.52	Hexanedioic acid, bis(2-ethylhexyl) ester
18	31.464	0.65	Eicosyl acetate
19	32.737	2.78	Nonacosane
20	33.871	0.56	5-Hydroxyisophthalic acid, TBDMS derivative
21	34.038	4.17	Hexatriacontane
22	34.434	2.82	Benz[a]anthracene, 7-methyl-
23	34.567	4.17	4',4''-Biacetanilide, 3',3''-dimethyl-
24	34.967	4.87	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
25	35.263	5.67	Heptacosane
26	35.431	1.93	1,4-Benzenediamine, N,N-diphenyl-
27	35.636	1.82	Heptacosane, 1-chloro-
28	35.853	6.37	3,3'-Dinitrobenzidine
29	36.033	3.29	2H,8H-Benzo[1,2-b:5,4-b']dipyran-10-propan
30	36.310	2.73	1,4-benzenediamine, N1,N1-bis(4-methylphen
31	36.525	5.83	Heptacosane
32	36.959	1.32	N-Decanoylmorpholine
33	37.891	5.24	Heptacosane
34	38.433	2.14	Eicosyl isopropyl ether
35	39.167	0.96	Hexatriacontane
		100.00	



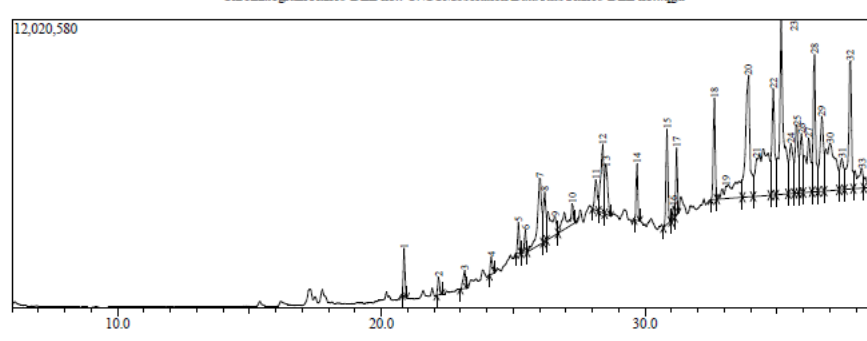
Peak Report TIC

Peak#	R.Time	Area%	Name
1	20.204	1.11	Quinoline, 1,2-dihydro-2,2,4-trimethyl-
2	20.869	1.95	Butylated Hydroxytoluene
3	22.173	0.73	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
4	24.171	0.96	Octadecane
5	25.800	1.24	Cholestane-3,5-diol, (3 beta, 5 alpha)-
6	25.967	2.22	n-Hexadecanoic acid
7	26.194	2.76	Eicosane
8	26.733	4.41	17.alpha.,21.beta.-28,30-Bisnorhopane
9	26.933	2.81	10,18-Bisnorabieta-8,11,13-triene
10	27.233	2.45	Tetracosane
11	27.534	1.54	Methyl stearate
12	28.100	3.83	Pyrene
13	28.365	3.56	Heneicosane
14	28.898	3.88	Tetratetracontane
15	29.664	1.95	Heneicosane
16	30.802	4.50	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
17	31.033	0.76	Hexanedioic acid, bis(2-ethylhexyl) ester
18	31.166	2.62	Heneicosane
19	32.597	3.36	Nonacosane
20	33.185	1.77	Tetratriacontane
21	33.920	7.00	Docosane
22	34.633	2.08	Pentatriacontane
23	34.837	4.02	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
24	35.133	6.14	Hexatriacontane
25	35.333	2.20	1,4-Benzenediamine, N,N-diphenyl-
26	35.333	2.06	2-Methylhexacosane
27	35.731	2.88	N-Benzyl-N-phenyl-p-phenylenediamine
28	35.900	1.58	Succinic acid, 2,2,3,3,4,4,5,5-octafluoropentyl
29	36.033	1.20	2-Thiophenacetamide, N-decyl-N-methyl-
30	36.200	3.07	1,4-benzenediamine, N1,N1-bis(4-methylphen
31	36.397	4.40	Eicosane
32	36.870	5.34	Tetratetracontane
33	37.156	3.17	gamma-Sitosterol
34	37.765	3.84	Tetratriacontane
35	39.291	2.61	Hexatriacontane
		100.00	

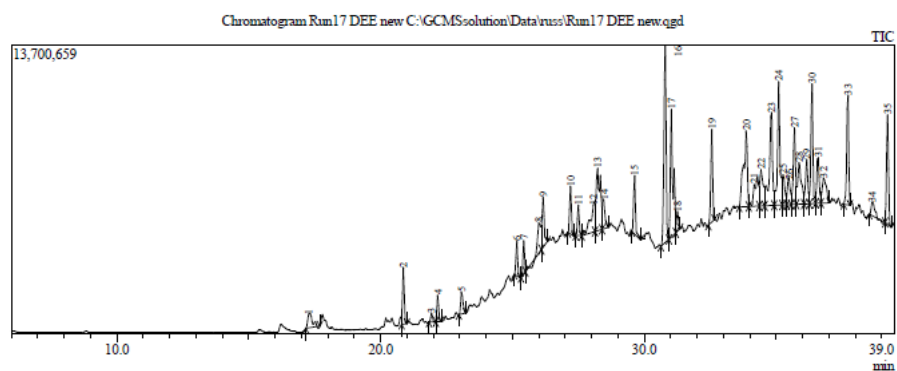


Peak Report TIC

Peak#	R.Time	Area%	Name
1	17.325	0.82	Benzothiazole
2	19.950	0.89	Cyclohexanamine, N-cyclohexyl-
3	20.868	1.09	Burylated Hydroxytoluene
4	23.161	0.39	Sulfurous acid, cyclohexylmethyl heptyl ester
5	24.170	0.93	Octadecane
6	25.199	0.41	Eicosane
7	25.433	0.52	Pentadecanoic acid, 14-methyl-, methyl ester
8	26.069	4.45	n-Hexadecanoic acid
9	27.233	1.16	2-Methyltetracosane
10	27.533	0.64	Methyl stearate
11	27.933	0.88	14-Oxabicyclo[10.3.0]pentadecane, 2-chloro-
12	28.100	1.29	Pyrene
13	28.367	3.67	Docosane, 1-iodo-
14	28.517	3.37	Nonacosane
15	29.661	1.56	Nonadecane
16	30.817	5.90	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
17	31.060	5.63	Hexanedioic acid, bis(2-ethylhexyl) ester
18	31.306	0.49	Tetracosyl acetate
19	32.590	2.72	Hexacosane
20	32.867	4.64	Triphenylene
21	33.889	7.87	Heneicosane
22	34.301	3.83	2,5-Di(trifluoromethyl)benzoic acid, 3-hexade-
23	34.467	2.88	Acetic acid 4-[(4-acetylamino-phenylimino)-m
24	34.842	7.06	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
25	35.129	6.06	2-methyloctacosane
26	35.300	2.91	1,4-Benzenediamine, N,N'-diphenyl-
27	35.496	2.37	Carbonic acid, decyl tetradecyl ester
28	35.726	3.59	N-Benzyl-N'-phenyl-p-phenylenediamine
29	35.907	3.55	15-Hydroxydehydroabietic acid, methyl ester
30	36.189	2.58	1,4-benzenediamine, N1,N1-bis(4-methylphen
31	36.388	3.83	Heneicosane
32	36.729	4.36	Hexatriacontane
33	37.233	2.12	Tetrapentacontane, 1,54-dibromo-
34	37.751	3.63	Heneicosane
35	39.266	1.92	Hexatriacontane
		100.00	

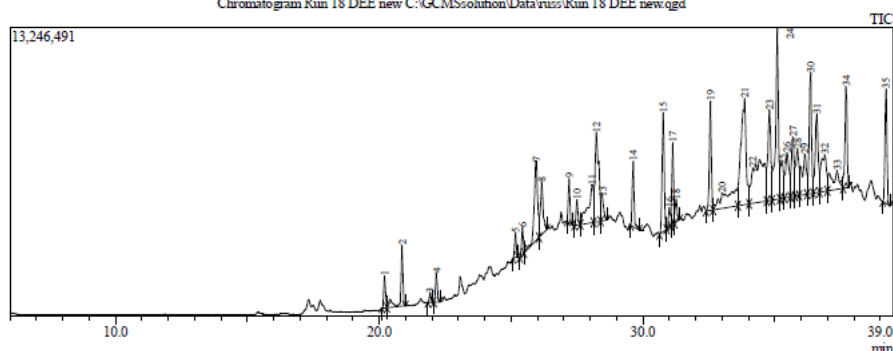


Peak#	R. Time	Area%	Name	Peak Report TIC
1	20.867	1.01	Butylated Hydroxytoluene	
2	22.172	0.46	Phenol, 4-(1,1,3,3-tetramethylbutyl)-	
3	23.158	0.61	Sulfurous acid, cyclohexylmethyl hexadecyl es	
4	24.172	0.54	Eicosane	
5	25.201	0.69	Heptacosane	
6	25.464	0.51	Hexadecanoic acid, methyl ester	
7	26.016	4.20	n-Hexadecanoic acid	
8	26.200	1.57	Eicosane	
9	26.600	2.34	Tetrapentacontane, 1,54-dibromo-	
10	27.243	1.90	Eicosane	
11	28.138	1.15	Carbonic acid, monoamide, N-decyl-, decyl est	
12	28.393	3.10	Docosane	
13	28.533	1.76	11,15-Dimethylpentatriacontane	
14	29.696	1.32	Heptacosane	
15	30.834	2.60	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N	
16	31.067	0.36	Hexanedioic acid, bis(2-ethylhexyl) ester	
17	31.200	1.48	Heptacosane	
18	32.629	2.61	2-methyloctacosane	
19	33.067	3.43	Heptacosane	
20	33.921	7.22	Tetratetracontane	
21	34.233	7.96	N-Decanoylmorpholine	
22	34.864	4.11	1,2,5-Oxadiazole-3-carboxamide, 4-amino-N-[
23	35.166	9.60	2-methyloctacosane	
24	35.535	2.96	Eicosane	
25	35.767	2.78	N-Benzyl-N'-phenyl-p-phenylenediamine	
26	35.932	2.47	Succinic acid, 2,2,3,3,4,4,5,5-octafluoropentyl	
27	36.211	3.96	1,4-benzenediamine, NI,NI-bis(4-methylphen	
28	36.423	4.90	Heptacosane	
29	36.709	3.76	Tetratetracontane	
30	37.023	6.35	3.beta.-Hydroxy-5-cholen-24-oic acid	
31	37.467	1.64	26,26-Dimethyl-5,24(28)-ergostadien-3.beta.-c	
32	37.785	5.33	Heptacosane	
33	38.233	1.82	2-Methylhexacosane	
34	38.726	1.91	2-Methyltetracosane	
35	39.297	1.58	Hexatriacontane	
		100.00		



Peak Report TIC

Peak#	R.Time	Area%	Name
1	17.267	1.27	Benztiazole
2	20.866	1.87	Butylated Hydroxytoluene
3	21.933	0.32	Hexadecane
4	22.169	0.90	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
5	23.076	1.03	Heptacosane
6	25.166	1.11	Heptacosane
7	25.432	1.16	Hexadecanoic acid, methyl ester
8	26.000	2.23	n-Hexadecanoic acid
9	26.165	2.14	Heptacosane
10	27.202	1.66	2-Methylhexacosane
11	27.501	1.10	Methyl stearate
12	28.067	2.83	Pyrene
13	28.226	5.32	Tetratetracontane
14	28.467	1.42	Tetratetracontane
15	29.630	2.14	Heptacosane
16	30.792	8.72	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
17	31.028	6.89	Hexanedioic acid, bis(2-ethylhexyl) ester
18	31.265	0.78	1-Docosanol, acetate
19	32.563	3.40	Heptacosane
20	33.872	5.78	Tetratetracontane
21	34.167	2.74	Octanoic acid, morpholide
22	34.433	2.40	Acetic acid 4-[(4-acetylamino-phenylimino)-m
23	34.819	6.13	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
24	35.100	6.36	Hexatriacontane
25	35.267	1.40	1,4-Benzenediamine, N,N-diphenyl-
26	35.500	1.49	Tetratetracontane
27	35.697	3.49	N-Benzyl-N-phenyl-p-phenylenediamine
28	35.878	3.22	15-Hydroxydehydroabietic acid, methyl ester
29	36.161	2.17	1,4-benzenediamine, N1,N1-bis(4-methylphenyl)-
30	36.361	4.67	Heptacosane
31	36.600	2.33	Tetratetracontane
32	36.808	2.06	N-Decanoylmorpholine
33	37.722	4.52	hexacosane
34	38.633	0.79	2-Methylhexacosane
35	39.229	4.17	Tetratetracontane
		100.00	



Peak Report TIC

Peak#	R.Time	Area%	Name
1	20.203	0.94	Quinoline, 1,2-dihydro-2,2,4-trimethyl-
2	20.867	2.15	Butylated Hydroxytoluene
3	21.933	0.24	Pentadecane
4	22.169	0.77	Phenol, 4-(1,1,3,3-tetramethylbutyl)-
5	25.167	0.62	Eicosane
6	25.434	0.78	Pentadecanoic acid, 14-methyl-, methyl ester
7	25.950	4.59	n-Hexadecanoic acid
8	26.167	2.20	Heptacosane
9	27.201	1.05	Heptacosane
10	27.502	0.72	Methyl stearate
11	28.067	3.25	Glutaric acid, dodec-2-en-1-yl 4-bromo-2-methyl
12	28.239	5.16	Hexatriacontane
13	28.467	0.97	1-Acetoxynonadecane
14	29.631	1.81	Heptacosane
15	30.770	3.84	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N
16	31.000	0.64	Hexanedioic acid, bis(2-ethylhexyl) ester
17	31.132	2.18	Heptacosane
18	31.266	0.71	Undec-10-ynoic acid, octadecyl ester
19	32.563	3.26	Heptacosane
20	33.000	3.88	2-Methylhexacosane
21	33.859	8.43	Tetratetracontane
22	34.167	8.03	N-Decanoylmorpholine
23	34.801	3.99	Indole-3-carboxaldehyde, 1-[2-(4-chloropheno
24	35.097	7.34	Tetratetracontane
25	35.300	1.83	1,4-Benzenediamine, N,N-diphenyl-
26	35.474	2.61	Pentatriacontane
27	35.700	2.57	N-Benzyl-N-phenyl-p-phenylenediamine
28	35.864	2.18	Succinic acid, 2,2,3,3,4,4,5,5-octafluoropentyl
29	36.144	2.90	1,4-benzenediamine, N1,N1-bis(4-methylphenyl)-
30	36.357	4.46	Heptacosane
31	36.594	3.65	Tetratetracontane
32	36.901	3.00	Cholesterol
33	37.367	2.42	Stigmasta-5,24(28)-dien-3-ol, (3.beta.,24Z)-
34	37.709	3.29	Tetratetracontane
35	39.223	3.52	Tetratetracontane
		100.00	

D. Pyrolysis results

Untreated tyre				Small size (0.5-1 mm)			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
1	A	230.40	244.80	14.40	36.00	42.50	21.50
	B	220.00	220.00	0.00			
	C	288.20	288.20	0.00			
Condenser		1230.90	1231.30	0.40			
Reactor		3842.6	3859.6	17.00			

Untreated tyre				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
2	A	230.40	220.00	9.70	44.00	36.00	20.00
	B	220.00	224.20	4.30			
	C	288.20	290.60	2.40			
Condenser		1230.90	1232.10	1.20			
Reactor		3842.6	3857.30	14.40			

Untreated tyre				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
3	A	230.40	242.00	11.60	47.50	34.00	18.50
	B	220.00	224.40	4.40			
	C	288.20	290.10	1.90			
Condenser		1230.90	1232.00	1.10			
Reactor		3842.60	3856.20	13.60			

Treated tyre with DCM 90'				Small size 0.5-1mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
4	A	230.40	239.40	9.10	38.25	40.62	21.13
	B	220.00	223.30	3.30			
	C	288.20	290.00	1.80			
Condenser		1230.90	1232.30	1.10			
Reactor		3842.6	3858.85	16.25			

treated tyre with DCM 90'				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
5	A	230.40	239.02	8.62	38.31	39.51	21.78
	B	220.00	223.80	3.80			
	C	288.20	290.20	2.00			
Condenser		1230.90	1231.80	0.90			
Reactor		3842.6	3858.40	15.80			

treated tyre with DCM 90'				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
6	A	230.40	239.32	8.92	39.55	39.02	21.43
	B	220.00	223.00	3.00			
	C	288.20	290.30	2.10			
Condenser		1230.90	1232.70	1.80			
Reactor		3842.60	3858.21	15.61			

Treated tyre with DCM 120'				Small size 0.5-1mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
7	A	230.40	239.10	8.70	34.75	36.50	28.75
	B	220.00	222.00	2.00			
	C	288.20	290.50	2.30			
Condenser		1230.90	1231.80	0.90			
Reactor		3842.6	3857.20	14.60			

treated tyre with DCM 120'				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
8	A	230.40	237.80	7.40	34.25	39.00	26.75
	B	220.00	223.60	3.60			
	C	288.20	290.00	1.80			
Condenser		1230.90	1231.70	0.90			
Reactor		3842.6	3858.20	15.60			

treated tyre with DCM 120'				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
9	A	230.40	240.28	9.88	43.19	33.68	23.13
	B	220.00	223.40	3.40			
	C	288.20	289.70	1.50			
Condenser		1230.90	1233.40	2.50			
Reactor		3842.60	3856.07	13.47			

Treated tyre with DCM 150'				Small size 0.5-1mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
10	A	230.40	237.31	6.91	34.78	40.17	25.05
	B	220.00	223.50	3.50			
	C	288.20	290.50	2.30			
Condenser		1230.90	1232.10	1.20			
Reactor		3842.6	3858.67	16.07			

treated tyre with DCM 150'				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
11	A	230.40	243.75	13.35	44.12	39.69	16.22
	B	220.00	220.10	0.10			
	C	288.20	290.20	2.00			
Condenser		1230.90	1233.10	2.20			
Reactor		3842.6	3858.48	15.88			

treated tyre with DCM 150'				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
12	A	230.40	242.73	12.33	55.64	29.36	15.00
	B	220.00	224.56	4.56			
	C	288.20	291.13	2.83			
Condenser		1230.90	1233.43	2.53			
Reactor		3842.60	3852.34	11.74			

Treated tyre with DEE 90'				Small size 0.5-1mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
13	A	230.40	239.30	8.90	37.41	37.32	25.27
	B	220.00	222.80	2.80			
	C	288.20	289.88	1.68			
Condenser		1230.90	1232.48	1.58			
Reactor		3842.60	3857.53	14.93			

treated tyre with DEE 90'				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
14	A	230.40	239.50	9.10	37.97	35.22	26.81
	B	220.00	222.79	2.79			
	C	288.20	290.60	2.40			
Condenser		1230.90	1231.80	0.90			
Reactor		3842.60	3856.69	14.09			

treated tyre with DEE 90'				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
15	A	230.40	236.90	6.50	32.41	38.18	29.41
	B	220.00	223.10	3.10			
	C	288.20	290.76	2.56			
Condenser		1230.90	1231.70	0.80			
Reactor		3842.60	3857.87	15.27			

Treated tyre with DEE 120'				Small size 0.5-1mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
16	A	230.40	242.74	12.34	39.86	35.19	24.95
	B	220.00	221.40	1.40			
	C	288.20	288.90	0.70			
Condenser		1230.90	1232.40	1.50			
Reactor		3842.60	3856.68	14.08			

treated tyre with DEE 120'				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
17	A	230.40	239.00	8.60	37.15	37.25	25.60
	B	220.00	223.86	3.86			
	C	288.20	289.90	1.70			
Condenser		1230.90	1231.60	0.70			
Reactor		3842.60	3857.50	14.90			

treated tyre with DEE 120'				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
18	A	230.40	238.60	8.20	38.74	35.23	26.03
	B	220.00	224.80	4.80			
	C	288.20	289.90	1.70			
Condenser		1230.90	1231.70	0.80			
Reactor		3842.60	3856.79	14.09			

treated tyre with DEE 150'				Small size 0.5-1mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
19	A	230.40	240.34	9.94	39.86	39.05	21.09
	B	220.00	222.30	2.30			
	C	288.20	290.80	2.60			
Condenser		1230.90	1232.00	1.10			
Reactor		3842.60	3858.22	15.62			

treated tyre with DEE 150'				Medium size 2-3 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
20	A	230.40	238.30	9.84	40.60	34.32	25.08
	B	220.00	222.50	2.50			
	C	288.20	291.10	2.90			
Condenser		1230.90	1231.90	1.00			
Reactor		3842.60	3856.33	13.73			

treated tyre with DEE 150'				Large size 4-5 mm			
Run N°	Beaker	Initial mass (g)	Final mass (g)	Total mass (g)	Oil (%)	Char (%)	Gas (%)
21	A	230.40	240.92	10.52	44.12	34.79	21.09
	B	220.00	224.32	4.32			
	C	288.20	290.40	2.20			
Condenser		1230.90	1231.50	0.60			
Reactor		3842.60	3856.52	13.92			