

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING

EXTRACTION AND CHARACTERIZATION OF
FUEL OIL FROM WASTE TYER

A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Process Engineering Stream

By Genet Melese

MARCH 2018
ADDIS ABABA, ETHIOPIA

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List of acronym

GCV	Gross calorific value
TPO	Tyre yrolytic oil
FTIR	Fourier transforms infrared spectroscopy
GC	Gas chromatography
MS	Mass spectroscopy
DOE	Design of experiment
RSM	Response surface methods
NGO	Nongovernmental organization
TRIA	Tyre retreading industry Addis Ababa
BAT	Best available technology
BAP	Best available practice

Abstract

The aim of this study was to argue the economic and environmental benefits of waste tyre recycling in Ethiopia using pyrolysis and indicate the importance of the by-products during the pyrolysis process such as waste steel and solid char. The study sketches the uses of waste tyres as an alternative source of energy and use for various applications based on chemical analysis. The GC-MS result indicates that the maximum composition of extracted oil was dl-Limonene, Cyclohexene, 1-methyl-4-(1-methylethenyl) obtained in peak retention time (15.302) and high percentage area of (11%). Limonene is an environmentally acceptable solvent for industrial use and cleaning agent of electrical circuit boards by replacing ozone-depleting chlorofluorocarbons and as a dispersing agent in cleaning products. In this study, the maximum average fuel oil yield (52.11%) was obtained at a time of 75 minutes and a temperature of 550 °C, and the minimum average oil yield (42.05%) was obtained at a temperature of 500 °C and a time of 45 minutes. From the two process variables, the optimum operating condition was 75 (minutes) and 550 (°C). The extracted fuel oil at these optimum conditions has a low flash point (36 °C) compared to other literature results (>50 °C).

1. Introduction

1.1 Background

The energy crisis and environmental degradation are the main problems mankind is facing today. These problems owe their origin to a growing population, rapid industrialization and huge quantities of solid waste, which are generated daily. To alleviate part of the energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for the possible recovery of resources from non-conventional sources, like municipal and/or industrial wastes, refused plastics, scrap tires...etc. The disposal of these solid wastes from human activity is a growing environmental problem for modern society, especially in developing countries. The scrap tire is one of the very common and most important hazardous solid wastes all over the world. In recent years, the quantity of solid wastes has increased significantly in both industrialized and developing countries, raising the question of the sustainability of disposal management [1].

Globally, about 1.5 billion waste tyres are generated annually. In addition to the annual continuous flow of waste tyres, billions of tyres are already stocked in piles. When tyres are disposed off, they have lost only a small percentage of their original mass, indicating that used tyres are essentially the same in physical and chemical properties to that of new tyres. Hence, scrap tyres present both an environmental challenge and a resource opportunity [2].

The use of renewable sources and waste recycling is increasing because of factors such as global warming, the increase of energy demand and availability of waste materials. Therefore, it is necessary to study how to obtain energy benefit with a minimum of environmental impact [3].

Globally, the effort for solving waste tyre problems through market-based value-adding waste tyre management options is as old as tyre itself. These include reusing de-vulcanization; mechanical and thermal (including pyrolysis) processing Disposal options such as land filling and stockpiling are also practiced. Developed countries have been paying great attention to the effective utilization of discarded tyres to achieve the goals of protecting environment, recycling resources and preserving energy. For many reasons, recycling of waste rubber has received much attention in recent years all over the world, due to the present rate of economic growth in utilization of the fossil fuels like, crude oil, natural gas or coal without saving for the future [4].

The automobile industry is the largest consumer of rubber, about 65% being used for tyres alone [5]. The average tyre last for about 50,000 km before it is likely to require replacement. Then it has to be replaced and disposed off, making used tyres one of the very familiar solid wastes in the world [6].

The environmental challenges come from the property of the tyres themselves. Tyres are designed to be abrasive, load carrying and indestructible made to high quality standards. These distinctive properties that ensure safe travel and long service life make scrap tyre disposal a difficult task. Rubber, the major component of tyre, is non-biodegradable material. In addition to being unpleasant, tyre piles are breeding grounds for mosquitoes and rats, and they are susceptible to fire hazards. Uncontrolled open-air burning of tyres releases potentially hazardous chemicals that affect the ground, surface water and the air [7].

In Ethiopia, the amount of waste tyres generation is expected to grow with the increase with the vehicle number in the country and the development of infrastructure throughout the country. Increase in energy demand, stringent emission norms and depletion of oil resources led to find alternative fuels for internal combustion engines.

Ethiopia imports its entire petroleum fuel requirement by spending over 80% of the foreign earning annually. Even the demand for petroleum fuel is increasing rapidly due to a growing economy and expanding infrastructure.

Hence, it is very critical to look for alternative energy sources in order to contribute for solving economic, environmental and social problems. To solve this energy crisis and environmental degradation, our country putting much effort on the potentials of utilizing appropriate technologies to recover energy and useful by-products from domestic and industrial solid wastes.

1.2 Problem statement

The situation of waste tyres either as a resource opportunity or as an environmental problem is not studied in Ethiopia well. Some of the current applications of scrap tyres include: making of rubber-based items, construction applications (e.g., retaining walls), burning as fuel, and cutting for the nylon cord, shoe sol, for animal feeding material and other uses. However, a considerable amount of used tyres are piled up in the shops of tyre repairers and traders, It is observed that the current practices of utilizing used tyres in Ethiopia do not result in higher value-added products and are not environment-friendly. The current applications do not take full advantage of the potential value-added recovery for energy and materials from scrap tyres. Due to these our country needs environmentally safe and feasible recycling technologies.

Hence, given the availability of used tyres, appropriate technology and demand for the oil as fuel, carbon char (to replace coal or firewood) and steel in Ethiopia, pyrolysis offers the opportunity to recover value-added products and at the same time solve sustainably the potential waste tyre environmental and health impact.

The environmental and health impacts due to improper management of solid waste in Ethiopia become a series issue now days. One of the municipal solid wastes is waste tires resulting from the increase in vehicle ownership and traffic volume throughout the

country. These waste tires represent a major environmental problem due to their volume and properties.

This polymer solid waste is non-biodegradable because of their complex mixture of very different materials, which include several rubbers, carbon black, steel cord and other organic and inorganic components. The Stagnant water that collects inside tires is suitable ideal breeding grounds for disease carrying mosquitoes and other vermin.

1.3 Objective

1.3.1 General objectives

The general objective of this study is extraction of fuel oil from waste tyres using thermal pyrolysis.

1.3.2 Specific objectives

The specific objectives are:

- Characterize the raw material using proximate analysis to measure moisture and ash content.
- To purify extracted fuel oil by using hydrosulferic acid and removing of moisture.
- To specify the optimum operating time and temperature in order to maximize yield of fuel oil.
- To characterize the extracted fuel oil using chemical and physical analysis.
- Characterize the solid char or measure ash and moisture.

1.4 Significance of the study

Ethiopia annually imports thousands of tons of fuel oil, coal and steel raw materials which consume a significant percent of its export earnings. Moreover, huge amounts of firewood are consumed every year which is a cause to deforestation reduce the green technology. Thus, this study provides an insight into a potentially viable means of recovering value-added products from waste tyres in order to substitute these products.

It also addresses sustainably the potential environmental and health problems due to waste tyres. Hence, it will be concerned with waste management and environmental protection.

Moreover, the project, when implemented, is expected to contribute nationally to the transfer of knowledge and technology, and development of a new industry, and creation of new jobs in the chain of waste tyre collection, transportation, processing and product marketing. The implementation of effective waste management practices has been identified as essential for economic development in low-income countries like Ethiopia in order to improve the environmental health.

2. Literature review

2.1 History of fuel

Fuel is combustible substance which on combustion produces a large amount of heat which can be used for various domestic and industrial purposes. The fuel commonly contains carbon as the main constituent and some common fuel are wood charcoal, kerosene, diesel and producer gas [8].

2.2 Classification of fuels based on origins

Fuels can be classified into natural and derived, and it is summarized as a flow chart below.

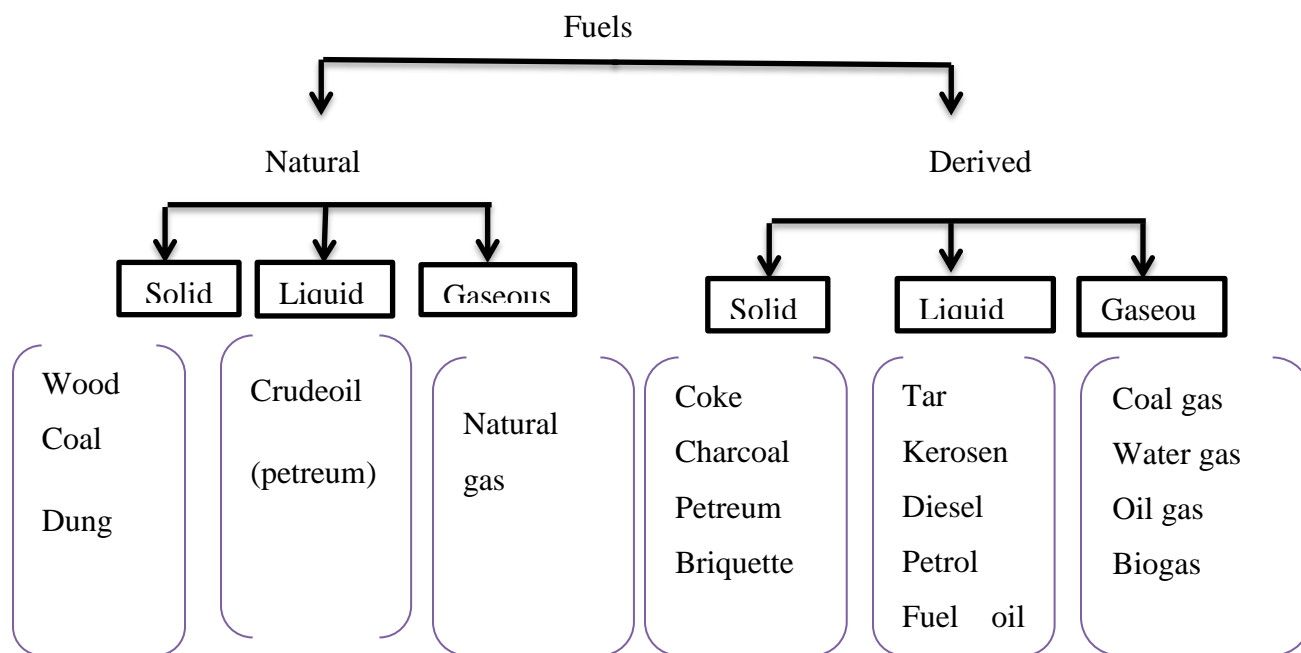


Figure 2.1 Classification of fuel

2.2.1 Liquid fuels

It is produced from the natural or derived sources of fuel. Petroleum or crude oil is deep brown oil consisting of mainly hydrocarbons, paraffinenes, naphtanese and aromatics in varying proportions. Sulfur, hydrogen and oxygen are present in the form of derivatives of hydrocarbon in the oil. The average ultimate analysis of liquid fuels is shown below in the table [8].

Table 2.1average ultimate values of fuel oil

Constituent	Average values in (%)
Carbon	83-87
Hydrogen	11-14
Sulpher	0.5-3
Nitrogen	0.3
Oxygen	2-3

Sources [8]

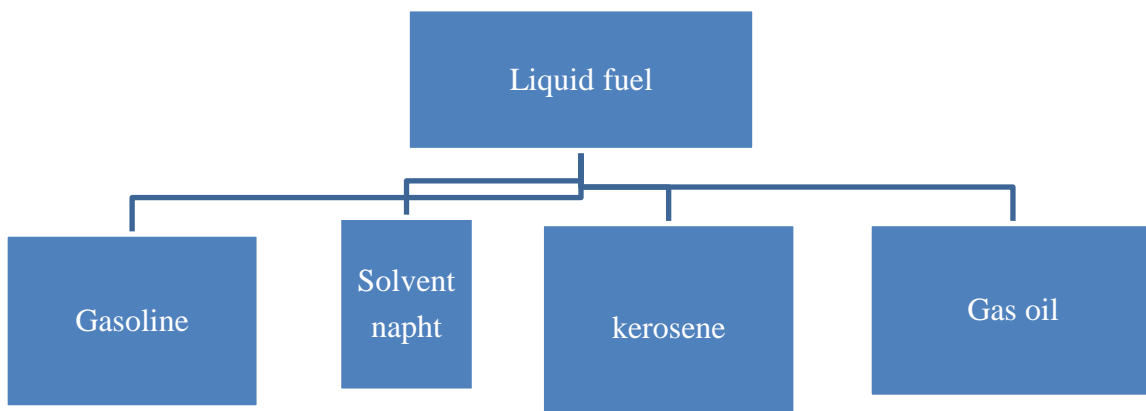


Figure 1.2Classification of liquid fuel

2.2.1.1 Kerosene

It is a complex mixture of hydrocarbons, usually containing 10 to 16 carbon atoms per molecule with the average being 12. The average chemical composition by percent is: 35 percent alkanes (paraffins), 60 percent cyclic alkanes (naphthenes), 15 percent aromatics. A light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue. Flash point: (100-165) °F or (38-74°C). Auto-ignition temperature: 444°F (229°C). Density range: 0.80 to 0.875 [8].

2.2.1.2 Gasoline

The straight run gasoline is obtained either from distillation of crude petroleum or by synthesis. It contains some undesirable unsaturated straight chain hydrocarbons and sulphur compounds. It has boiling point range of 40-120°C (10). The, unsaturated hydrocarbons get oxidized and polymerized, thereby causing gum and sludge formation on storing, on the other hand, sulphur compounds lead to corrosion of internal combustion engine and at the same time they adversely affect tetraethyl lead, which is generally added to gasoline for better ignition properties. It is used in air-crafts. It is also used as motor fuel, in dry-cleaning and as a solvent. Some of the characteristics of an ideal gasoline are cheap, readily available, easily vaporize, knock resistant and have a high calorific value [8].

2.2.1.3 Solvent Naphtha

It is obtained as a side stream between 200 °C-250 °C. This contains some gasoline, which is passed back to the main fractionating column. Naphtha contains 6-10 carbon atoms.

2.2.1.4 Gas oil

It is obtained between 300 °C-350 °C. This is passed through a cooler and then extracted with liquid SO₂ to remove sulfur. It is used as diesel engine fuel with calorific values of 11000 Kcal/kg.

2.3 Basic raw materials of tyre

2.3.1 Natural rubber

The chemical formula of natural rubber is a polymer of isoprene (2-methyl-1,3butadiene). Natural rubber is produced from the sap of rubber tree (*Heveabrasiliensis*) which grows primarily in South East Asian countries; there are a number of other trees that also produce rubber such as the *Ficus elastica*, which is a native of the Congo, and *Guayule*, a desert scrub from Mexico and Arizona. *Hevea* is a native of the Amazon basin. It can withstand temperature up to the range of 10-60 °C, has tensile strength 200 kg/cm² and it has high elasticity ranging from 300 to 1000 % [9].

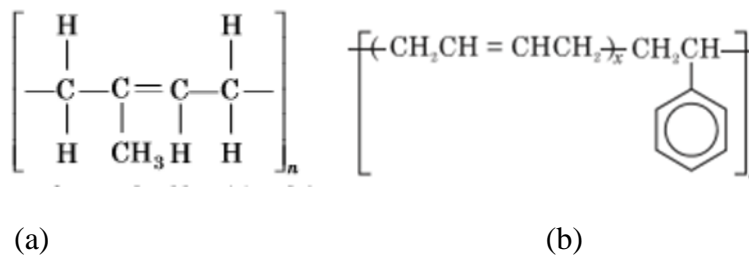


Figure 2.3 (a) Structure of natural rubber [8], (b) Synthetic rubber structures [9]

2.3.2 Synthetic rubber

Synthetic rubber is artificial rubber, made from raw materials such as butadiene, styrene, isoprene, chloroprene, isobutylene, acrylonitrile, ethylene and propylene. More than half of the world's synthetic rubber is styrene-butadiene rubber (SBR) made from styrene and butadiene monomers which are abundant in petroleum production [9].

2.3.3 Reclaimed rubber

Reclaimed rubber is defined as de-vulcanized rubber that has regained its viscosity as well as the characteristics of the original compound. This reclaimed rubber is made by the treatment of ground vulcanized scrap of rubber tyre, tube and miscellaneous waste rubber articles, through the application of heat and chemical agents. The waste rubber article is cut and powdered in a cracker. The unwanted ferrous materials are separated by electromagnetic separator and then charged to an autoclave and digested with caustic soda solution at 200 °c under pressure for 8-15 hours. The fibers get hydrolyzed or de-vulcanization is takes place. Sulfur is removed as sodium sulfide and it is washed, deride and finally rain forced with carbon black [9].

2.3.4 Fillers

Carbon black is the most commonly used reinforcement filler in rubber. It is usually manufactured by the incomplete combustion of heavy hydrocarbons, which has a considerable carbon footprint. Current global production of carbon black is estimated to be 8.1 million tons per year of which 70% is used in the tyre rubber industry, 20% in other rubber applications while the rest is used for other purposes such as a pigment for printing inks, coatings and plastics [10].

2.3.5 Composition of tyre

The composition of tyres consists of four main ingredients: rubber, carbon black, metal and textiles. The remaining materials are additives, which facilitate compounding, and vulcanization. Tyre composition can be summarized in the table below.

Table 2.2 Typical composition of tyre [10]

Material	Wight (%)
Rubber (natural/synthetic)	43
Filler (carbon, silica)	27
Reinforcing materials	16
• Metals	11
• Textile	5
Chemical additives	14
• Vulcanizing agent	3
• Other additives	3
• Aromatics	8

2.3.5 Proximate and ultimate analysis of tyre

The proximate analysis was done by ASTM D3173-75. And the ultimate analysis was done by using Elemental CHNS analyzer. Calorific value of the raw material was found by ASTM D5868-10a. The samples such as tyres were identified with the following characteristics using proximate and ultimate analysis [1].

Table 2.3 proximate analysis of of tyre

Proximate analysis	Percentage (% w/w)
Fixed Carbon	35.5
Volatile	61.3
Ash	4.4
Moisture	0.8

Table 2.4 ultimate analysis of tyre

Ultimate analysis	Percentage(%w/w)
Nitrogen	0.4
Carbon	85.2
Hydrogen	7.3
Sulpher	2.3
Ash	4.4
Oxygen	0.4

2.4 Solid waste

The solid wastes are of different types; because they are generated by different people of various economic statuses, through their various activities involving a variety of products and commodities. The quantum of solid wastes generated is also burgeoning as people's activities have increased very much in this materialistic world and the most common problems associated with improper management of solid waste include diseases transmission, fire hazards, odor nuisance, atmospheric and water pollution, aesthetic nuisance and economic losses [13],[36].

Table 2.5 Composition of global MSW (16)

MSW	Composition (%)
Organic	46
Paper	17
Plastic	10
Glass	5
Others	18

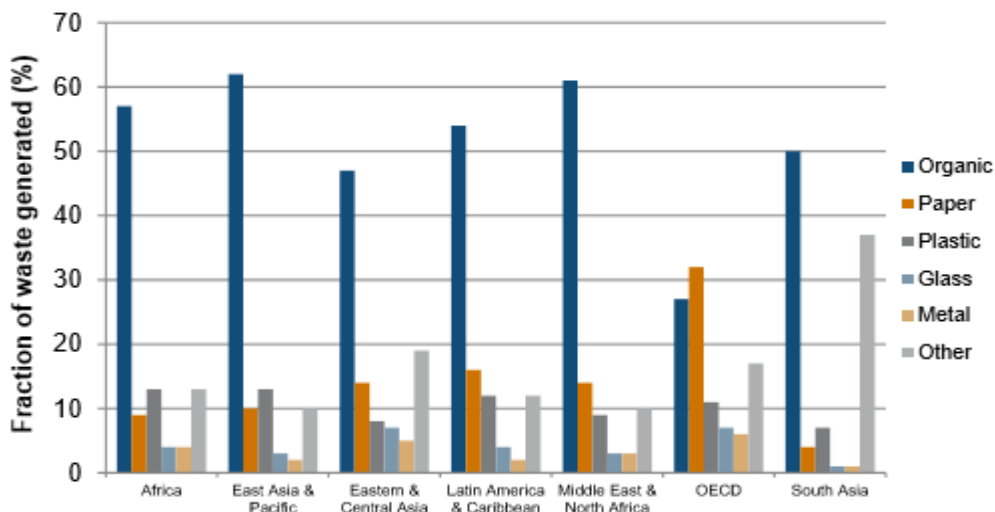


Figure 2.4 Composition of MSW [16]

2.4.1 Waste tyre

The Part-Worn Tyre (or Used Tyre): is a rejected or unwanted tyre, which can be reused as a second-hand purchase or re-usable after reprocessing (retreading and reroofing). It can be reused as its original purpose when a residual tread depth remains. Different minimum legal remaining tread depths are set in different countries.

The End-of-Life Tyre (or Waste Tyre): is a non-reusable tyre in its originally intended purpose and it cannot retread. This tyre may enter a waste management system based on product /material recycling, energy recovery or goes to landfill.

Scrap tyre: is a non-usable tyre in its originally intended purpose due to different internal problem like utility or human error.

2.4.2 Waste tyre in the world

Waste tyres also referred to as used tyres can be defined as tyres that have expired as a result of exceeding their production life span or are no longer safe for usage due to defects, such as degradation of its physical composition/structure from use and cannot be retreaded.

It is one of the most challenging hazardous solid wastes facing modern society, particularly in developing countries. Waste tires pose a health hazard since tire piles are excellent breeding grounds for mosquitoes. Because of the shape and impermeability of tires, they may hold water for long periods providing sites for mosquito larvae development. Waste tires also pose a serious fire hazard since waste tires and waste tire stockpiles are difficult to ignite. However, once ignited tires burn very hot and are very difficult to extinguish. This is due to the 75% void space present in a whole waste tire, which makes it difficult to quench the tires with water or to eliminate the oxygen supply [12].

In addition, the doughnut-shaped tire casings allow air drafts to stoke the fire. There are major aspects of tyre problems such as tyres stockpiles provide breeding ground for mosquitoes and vermin, this in turn, causing serious disease and affecting human health. Fire hazards in large stockpiles could consequently cause uncontrollable burning and air pollution where it will be emitting large amounts of thick black smoke and noxious gases including carcinogens. In fact, due to the high cost of legal disposal for tyres, illegal dumping will be increased [13].

The disposal of tyres is also becoming more expensive, while this trend is likely to continue as landfill space becomes scarcer. Waste tyres are bulky and difficult to dispose because of their large size and hollow structure. Tyres generally do not decay nearly as quickly as other waste in the landfill. This is due to the process of vulcanization, a method of treating rubber with extreme heat and adding sulfur to make it extremely durable; because of this, other material around the tyre will decompose and cause the tyre to rise to the surface of the landfill. Subsequently, many landfills around the world stopped accepting waste tyres due to the aforementioned problem of size among others where the land becomes filled quickly.



Source [13]

Figure 2.5 Land fill waste tyre in the world

2.4.3 Waste tyre in Ethiopia

According to the increment of production and number of vehicle the number of scrap tyre also increase in horizon addis trye. The number of scrap tyre in this Company was 4% of its total production according to 2013/14 data due to different internal causes. The number of automobile also increases alarmingly in Ethiopia due to the expansion of infrastructure and population growth. Because of these reason the number of waste tyre in Ethiopia become a major solid waste problem now a days [14].



Source around kaliti mini tyre service

Figure 2.6 Waste tyre in Ethiopia

2.5 Health and Environmental concerns of waste tyres

Waste tyres are considered a problem because they are difficult to get rid of safely through normal means such as leaving them in a landfill to decay or incinerating them. A tyre by itself is generally fairly large, but a great deal of that is open space. Their nature does not allow compression or folding in order to reduce the space occupied during disposal at landfills and they also do not degrade easily because of the chemical and physical feature. This often causes the following problem.

This section presents some of the claimed health concern that are caused as a result of exposure to waste tyre products/services and potential environmental issues as result of illegal activities. Waste tyre illegal disposal and landfilling of waste tyres because such practices are viewed as unsustainable and risk to the environment and human health [15].

2.5.1 Environmental concern

Currently in many developing nations, the disposal of waste tyres have been uncontrolled landfilling, illegally dumping and illegal burning due to poor or lack of regulation and policies While, in many developed nations disposal of waste tyres are regulated and controlled. For instance, in the European Union, most member countries have banned [35].

Air pollution: Illegal and uncontrolled burning of waste tyres produces thick toxic smoke that is bad for the ozone layer due to greenhouse gaseous (carbon monoxide) and the living creatures such as humans, insects, animals, vegetation etc. Waste tyre is highly flammable and the fire is hard to control due to that tyres contain rubber, oil, resin and other chemical.



Source [15]

Figure 2.7 Firing of waste tyre fir

Water drainage pollution: Waste tyres are illegally dumped in the drainage system which can result into blockage causing floods and water contamination. Due to the bulky, and durability nature of the tyres because of rubber, steel wires and fiber cotton, tyres create more risks when dumped in drainage systems in term of causing floods during the rain seasons. Due to that tyres don't decompose easily and they can contribute to trapping other waste material causing drainage system to be blocked and creating water stagnation



Source [15]

Figure 2.8 Dumping of waste tyre in water

Soil pollution: Illegally and uncontrolled burning of tyres can easily contaminate the soil causing loss of vegetation, ecosystem and resulting into soil erosion due to lack of vegetation in the area. Due to some chemicals, oil and carbon black exuded from the burnt tyres results into loss of vegetation and soil contamination [15].



Source [15]

Figure2.9 Soil contamination due to waste tyre

2.5.2 Health concern

Claims on the health effects from exposures and contact with waste tyres by the people making products and using products made from waste tyres has been reported. However, Brown argues that the actual levels of risks to human health due to waste tyre rubber exposures are not well known and are unfounded and have been some claims such as allergic reaction and respiratory irritations. Besides, illegal burning of waste tyres have been linked to human health issues. While illegally damped waste tyres due to holding stagnant water has been linked to the potential breeding space for mosquitoes that causes malaria [15]

Allergic reaction: Some entrepreneur's up cycling waste tyres in Lusaka, Zambia have reported having skin and eye itching. Some entrepreneur's up cycling waste tyres in Lusaka, Zambia have reported having skin and eye itching. They claimed to have experienced skin and eye itching.

The plausible causes could be linked to lack of proper personal protective equipment such as overalls, hand gloves and protective goggles. As a results, some people when are in contact with rubber particles they can develop eyes irritations and skin itching.



Source [15]

Figure 2.10 Allergic causes due to waste tyre

Respiratory irritations: Coughing, headaches and running nose as a result of rubber dust particles and toxic smoke produced when burning rubber during up cycling of waste tyres. It was noted that some of people that were up cycling waste tyres used risk methods such as burning rubber without proper breathing mask. This is likely a plausible cause of respiratory irritations [15].



Source [15]

Figure 2.12 Irritation causes due to improper waste tyre recycling

Mosquito carrying diseases: Research has shown that mosquitos can breed in discarded or stockpiled tyres that contain water. Tyres have a hollow space that can hold stagnant water for a long time making it suitable place for mosquito breeding [15].



Source [15]

Figure 2.12 Waste tyre causes for mosquito breeding

The above health and environmental implications associated with poor management of waste tyres requires sustainable solutions particularly in the developing countries. Consequently, the question of what should happen to a tyre after it has reached its end of life is increasingly being asked by various concern stakeholders such as environmentalist, the governments, researchers and by non-governmental organization (NGO) both in developing and developed nations [15].

However, entrepreneurs, recycling companies, NGO and various stakeholders have started to rethink the way waste tyres can create environmental, economic and social benefits by turning waste tyres into various products and services, and by adopting sustainable regulations and policies. What is more, today, there are existing best available models best available technologies (BAT) and best available practice (BAP) for managing and turning waste tyres into variable products to create worth and employment both in developed and developing nations [15]

2.6 Recycling mechanism

2.6.1 Recycling mechanism in the world

Recycling of rubber is worldwide of growing importance due to increasing of raw material costs, diminishing resources and growing awareness of environmental issues and sustainability. The labeling of tires, which ranks them in terms of fuel efficiency, noise and safety, is an expression of this growing awareness. In addition, many countries pay more and more attention to extended utilization of used rubber in order to achieve the goals of protecting the environment and saving resources. Those technics are discussed as follows.

Land fill: Waste tyres are bulky and difficult to dispose because of their large size and hollow structure. Tyres generally do not decay nearly as quickly as other waste in the landfill. This is due to the process of vulcanization, a method of treating rubber with extreme heat and adding sulfur to make it extremely durable; because of this, other material around the tyre will decompose and cause the tyre to rise to the surface of the landfill. Subsequently, many landfills around the world stopped accepting waste tyres due to the aforementioned problem of size among others where the land becomes filled quickly. Tires occupy a large space and remain intact for decades and leaching of rubber additives and uncontrolled burning pose an environmental and public health risk [10].



Source [10]

Figure 2.13 Land fill waste tyre

Re-Treading: Retread also referred to as “remold” involves buffing away of the remaining tread in a spent tyre and replacing it with a new tread rubber strip by vulcanization. It is carried out only on used tyres casing that have been inspected and repaired. Although it is economically advantageous, product quality confidence is a major challenge of the process.

In the European countries, more than 10% of the used tires were re-treaded and returned to service .Re-treading offers the most resource-efficient strategy for tire recovery, saving both material and energy. It comprises removing the old tread from a worn-out tire and replacing it by a new one. The benefit of re-treading is that it extends the tire life span. It saves 80% of the raw materials and energy and reduces the quantity of waste to be disposed [16].

The energy consumption for production of a new tire is 15 times higher than for re-treading and the price of retreaded tires is 30 to 50% lower than the price of a new tire. Nevertheless, they deliver the same mileage as new tires. Truck tires are often retreaded up to three times before finally being discarded, and this business is growing [18].



Source [16]

Figure 2.14 Re grooving and retreading

Energy recovery: Tires are made of elastomeric materials in the form of C_xH_y . It possesses a high carbon content making it a suitable material for energy recovery. Direct burning of used tires is one method of recovering energy.

Tires can be used as fuel either as a whole or in a shredded form, depending on the type of combustion furnace. Burning of tire material requires a sophisticated high-temperature combustion facility to keep emissions within environmental limits, and in the case of whole tire handling, special equipment for feeding them into the combustion chamber is necessary.

Application in rubber products: In the reclaiming or de-vulcanization process, used tire rubber is initially ground, then reclaimed or de-vulcanized, and re-used in a virgin compound from which new rubber products are made. Reclaimed rubber can be used in high value applications such as tires, automotive molded parts, soles and heels, etc. Using rubber reclaim can be even more profitable for the rubber industry, when production waste is recycled and reused within the factory where it is generated.

This might result in additional revenues from eliminating waste disposal fees and transportation costs. However, reclaimed rubber has in general poorer mechanical properties than comparable virgin rubber due to the uncontrolled polymer scission which occurs during the reclaiming process.

Pyrolysis: Pyrolysis is one of the unique methods of recycling the organic waste. It is a thermo-chemical process which involves heating organic waste material at higher temperatures in the oxygen free atmosphere to break them down to simpler organic compounds. Carbon, solid char, oil and gas are produced on the pyrolysis of organic solid wastes. For example, pyrolysis can convert wood to charcoal and a low-Btu gas.

There is a renewed interest to pyrolysis as a method for recycling and reuse of waste tyres because it is an environmentally friendly process yielding useful products. The latter include pyrolysis oil (40 - 60 %), solid carbon residue (30 – 40 %), steel and gaseous products. Each of those products can find various industrial applications. For instance,

the pyrolysis oil, which is a complex mixture of organic components, can be used as a plasticizer in rubber industry, as diesel oil or as a carbon black source. The application of the pyrolysis products in the former two cases is hampered by the high carbohydrates concentrations [17].

The gaseous products contain H_2 , H_2S , CO , CO_2 , CH_4 , C_2H_4 , C_3H_6 , etc. It can be used as the energy source required for the pyrolysis proceeding. The solid product of waste tyres pyrolysis (called also pyrolysis carbon black) includes carbon black (80 - 90 %) and inorganic substances (10 - 20 %) which are always present in the rubber compounds used to manufacture car tyres. It is hypothesized that the pyrolysis carbon black can entirely or partially replace the conventional carbon black in rubber industry following a subsequent mechanical or chemical treatment. That product may be quite effective in manufacturing less demanding rubber items such as floorings for various usages, isolation stall mats, hit resistant coatings, etc.

Pyrolysis usually occurs at temperature between $400^{\circ}C$ and $800^{\circ}C$. In case of pyrolysis, lower temperature produces more oil products and higher temperature produces more gases. This process has a number of advantages. Only few of the scrap tyre utilization options are commercially established, and others are still either at the pilot or bench scale and most are investment intensive and are not without environmental concerns [18].

In addition, the demand for materials and energy surpasses them. Hence, pyrolysis is emerging as a more efficient way to utilize the resources in scrap tyres compared to the other options. From pyrolysis of scrap tyres, four products are obtained: oil, carbon char, fuel gas and steel wire. Typical product yield ranges are oil: 40-45%, carbon char: 30-35%, gas: 10-15% and steel 10-15% of waste tyres pyrolyzed at a temperature range of $430-600^{\circ}C$ [19].

The derived oil from tyre pyrolysis may be used directly as fuels or added to petroleum refinery feed stocks, and also helpful for the refined chemicals. The derived gases are also useful as fuel and the solid char may be used either as activated carbon and carbon

black. Pyrolysis basically involves the thermal decomposition of the tyre rubber at high temperatures in an inert atmosphere.

Thermal pyrolysis: Thermal pyrolysis is the decomposition of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at high temperatures and it results in the formation of a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and a non-condensable high calorific value gas. The production yield was depending on the temperature and time range of the processes [9].

Catalytic pyrolysis: Catalyst is generally used to improve the product yield and to speed up the reaction with minimum temperature. Objective of the study was to increase the yield of oil product. Therefore, some catalysts were used to increase the oil yield with minimum temperature range.

The derived oils from tyre pyrolysis without catalyst have been revealed to be highly aromatic, which are partial to be used as an alternate oil fuel. Since the derived oils contain concentrations of valuable chemicals such as benzene, toluene, xylenes, etc., so they can be extracted from the derived oils and used as chemical feed stocks in the chemical industry. So catalysts are used to produce more single ring aromatic compounds during tyre pyrolysis [39].

The waste tyre has been pyrolyzed by using zeolite catalyst and studied the influence of the pyrolysis temperature, catalytic temperature, catalyst/ tyre ratio and heating rate on the yield of the products. From the derived oil was found to be influenced by pyrolysis temperature, catalysis temperature and catalyst/tyre ratio, and was around 60 wt% in the derived oil.

Evaluation of waste tyre rubber using catalytic pyrolysis is very important from economic and environmental point of view as the gas and oil can be utilized and since as catalytic pyrolysis using solid bases as catalysts requires lower temperature. Pyrolysis for producing carbon black and oil Pyrolysis involves the thermal decomposition of a

substance into low molecular weight products under an inert atmosphere. The derived oils contain high concentrations of potentially valuable chemicals such as benzene, toluene and xylene [9].

2.6.2 Recycling of waste tyres in Ethiopia

In Ethiopia, waste tyre recycling is an old and informal sector business. The main applications include reusing, open burning and retreading. The technique of sandal shoe making introduced by an Italian is said to have started in Asmara in 1928 [20].



Source from Debre-Brehan reuse applications for animal feeding

Figure 2.15 Waste tyre for animal feeding material

The waste tyre are converted into shoes known as Barabaso and also cut to long ‘ropes’ that are commonly used for horse-drawn carriages in rural areas of Ethiopia. Reuse applications (shoes, straps, stool and chair seats, ceiling dividers, animal feeding troughs, carrier straps (mechagna), etc.) are providing various items that are substitute to products produced in factories which are beyond reach to customers. Nylon cords pulled out of bias tyres are used for making musical instruments and sewing shoes, bags, etc. The activity provides employment and income to many citizens [38].



Source, [38]

Figure 2.16 Barabaso Shoes and Shoes Sole.

However, according to recyclers, the demand for the products is decreasing nowadays mainly due to modernization and the change in the living condition of the people, particularly the urban dwellers. Radial tyres are more difficult to cut and are not usable for reuse as bias tyres. Hence, radial tyres are burned to obtain the steel wires or for energy sources such as asphalt melting and Stone mining, or are used for septic tank retaining wall construction or are lying idle in various places.

The steel wires are sold to scrap dealers for recycling, for making egg containers, fence, etc. The pieces leftover from recycled tyres and smaller tyres of both types are sold to road contractors to be used as fuel to melt asphalt. Retreading of tyres extends the life of tyres. But it will have little effect on the amount of scrap tyres generated as the retreated tyres will later join the scrap tyre pool. Ethiopian Roads Authority, Tyre Retreading Industry Addis Ababa PLC (TRIA), and Ethiopian Tire and Rubber Economy Plant plc. are engaged in tyre retreading.

However, not disregarding the possible health and environmental impacts, the current applications are not effective and do not consume the bulk of scrap tyres, and other value-

adding uses can still be studied and practiced. It had studied the use of scrap tyres as a partial replacement for coarse aggregates in concrete [20].

Laws and regulations are expected to be issued by the Government as environmental problems become severe and experiences are taken from other countries that aid value-adding uses. Articles on prohibition of importation of used tyres are included in the Solid Waste Management Proclamation No. 513/2007. In addition, the new Ministry is working on a draft regulation to comply with the basil convention.

2.7 The main pyrolysis products

Use of pyrolysis as a method for recycling waste tire depends on the market for pyrolysis products. For this reason, characterization of pyrolysis products and possibilities of their application in other processes is very important. At present time, the main application for solid char is its use as active carbon, as reinforcement in rubber industry and as smokeless fuel. The liquid product is used as a fuel, or a source of chemicals, and the gas fraction as a fuel in the pyrolysis process.

2.7.1 Pyrolysis liquid product

Their chemical structure with aromatic and aliphatic constituents plays an important role in determining the composition of the oils derived from was tyre. The liquid phase is the most important product of tire pyrolysis process. There are several papers in the literature devoted to the study of the characteristics of pyrolysis liquid products. Gas chromatography/Mass spectroscopy (GC/MS) is the most often method used not only for analyzing pyrolysis liquid product, but also for analyzing the gas yield and products of char combustion. Tire derived liquids are a complex mixture of C₆-C₂₄ organic compounds, containing a lot of aromatics (53.4–74.8%), some nitrogenized (2.47–3.5%) and some oxygenated compounds (2.29–4.85%). Their GCV (42 MJ kg⁻¹) is even higher than that specified for commercial heating oil's, but the sulphur content (1–1.4%) is close to or slightly over the limit value.

Significant quantities of valuable light hydrocarbons such as benzene, toluene, xylene, limonene, etc. were obtained. The concentration of these compounds increases with temperature up to 500°C and then decreases. There is also an important portion of polycyclic aromatics, such as naphthalene, phenanthrene, fluorine, biphenyl, etc.; their concentration as well as that of total aromatics increase significantly with temperature [21].



Source [21]

Figure 2.17 Liquid product

2.7.2 Solid residue

The solid residue contains carbon black and the mineral matter initially present in the tire. Several studies have reported the production of char and active carbon from waste tires. These active carbons have been used to adsorb phenols, basic dyes and metals, phenols, butane and natural gas. Active carbon from solid product of pyrolysis process is produced by activation with an activating gas at 800-1000°C.

Carbon characteristics (especially specific area) are greatly influenced by the degree of the activation also by nature of activating agent (steam or CO₂) and process temperature. Based on the current technology and literature results tire char activation below 700°C looks impractical.

The particle size of the tire rubber was found to have influence on the porosity of the resultant carbon generated from steam activation (29). Elemental analysis carried out by shows that pyrolysis char contains 71 wt. % of C, 13.3% wt. of O, 5.4 wt. % of Fe, 2.8 wt.% of S, 2.3 wt.% of Zn, 1.3 wt.% of Ca, and 0.3 wt.% of Al [21].



Source [22]

Figure 2.18 Residual product

2.7.3 Pyrolysis gases

The yield of the gas fraction obtained in different experimental systems shows important variations. For example: Berries et al., obtained the gas yield 2.4-4.4 wt. %, but Chang wt. % using an autoclave in a nitrogen atmosphere at temperatures between 400 and 700°C, found that the pyrolysis gases consisted of CO, CO₂, H₂S and hydrocarbons such as CH₄, C₂H₄, C₃H₆ and C₄H₈, and their unsaturated 16 derivatives. Berries ET. Al. analyzing pyrolysis gases by gas chromatography, found that the main gases produced by the pyrolysis process are H₂, CO, CO₂ and hydrocarbons: CH₄, C₂H₄, C₃H₆ and C₄H₈. Pyrolysis mainly composed of H₂, CO, CO₂ and a few hydrocarbon gases [21].

2.7.4 Scrap steel

Waste tyre pyrolysis can also generate scrap steel wire due to the fact that steel wires can be used as reinforcement agent for tyre. There are little studies for the scrap steel produced by waste tyre pyrolysis. It is believed that the scrap steel would be similar to its original quality if the pyrolysis temperature is kept below 600°C. Whereas, increasing the pyrolysis temperature would cause damage to the steel due to carbonization or other

possible chemical reactions from scrap tyre 10-15% weight is scrap steel. The quality is also influenced by the pyrolytic process conditions. For a batch process, the separation of steel and carbon black from pyrolytic oil is fairly simple. This is complex for continuous pyrolysis [23].



Sours [23]

Figure 2.19 Scrap steel

Table 2.6 Approximate values of pyrolysis product

Product	Approximate yield (%)
Fuel gas	10-12
Fuel oil	40-45
Carbon black	30-35
Steel wire	10-15
Inorganic metal	>15



Source (30)

Figure 2.20 Products % after recycling by pyrolysis

2.8 Factor affecting the product yield

The yield and composition of each pyrolytic product (char, liquid and gas) is affected by the conditions of the pyrolysis process. The product yields and products' qualities of the pyrolysis process depend on a number of parameters, including pyrolysis temperature, pyrolysis pressure, residence time of the pyrolysis products, heating rate, types of waste tyre, tyre shred size, reactor size and catalyst used.

The pyrolysis process yields a gaseous fraction of mainly non-condensable gases, a solid fraction mainly composed of carbon, metal and others inert material as well as an oily fraction mainly composed of organic substances condensable at ambient temperature and pressure. The composition of the pyrolysis products is influenced by the process operating conditions such as, feed size, operating temperature and pressure, residence time, heating rate and as well as the presence of catalytic medium [1].

2.8.1 Feed Size

Smaller feed size particles provide more reaction surface giving high heating rate and rapid decomposition of rubber. The oil product vapors comparatively get enough time for secondary reactions in the reactor and this consequently increases gas yield and reduces liquid and char yields [23].

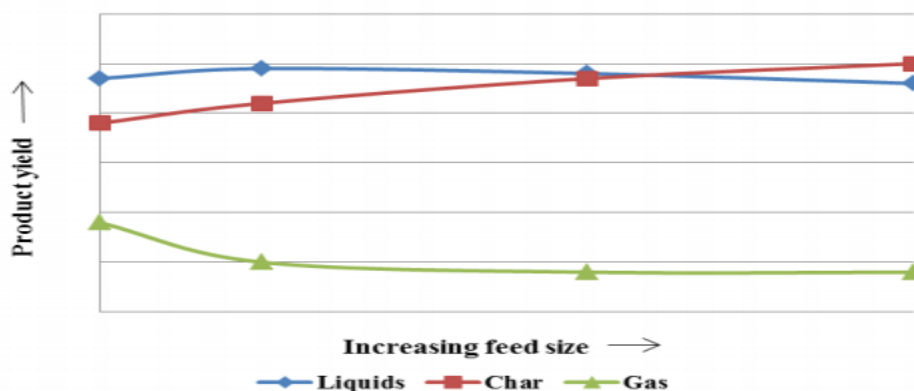


Figure 2.21 Effect of feed size on oil yield

2.8.2 Reactor temperature

Rubber tire starts to decompose at 375°C. The amount of liquid product increase with temperature until 475°C. The temperature found at 500°C is the optimum point for pyrolytic oil products and decrease above 500°C. The amount of gas yield decrease to the detriment of liquid, but hardly varies the characteristics of the products. In addition, there is no change in the solid yield [1].

The increase in gas yield with a corresponding reduction in liquid yield observed with increase in temperature is due to vapor decomposing into permanent gases, and secondary re-polymerization as well as carbonization reactions of oil hydrocarbons into char. It is also a result of char loss and thermal cracking. Thus, gas yields dominate at higher temperatures [23].

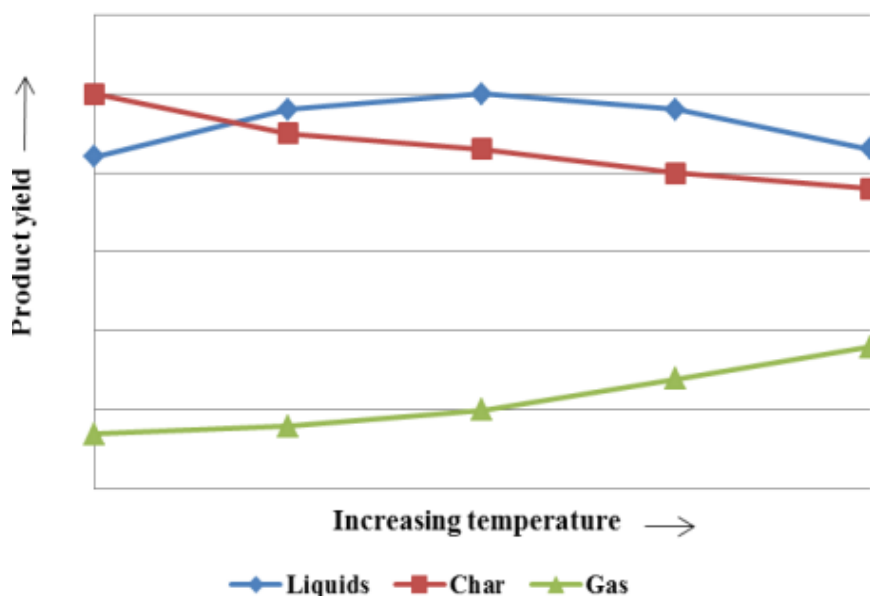


Figure 2.22 Effect of temperature on oil yield

2.8.3 Residence time

Residence time is an important variable in the pyrolysis process; its optimization is a key factor in order to scale up an industrial system. Lower residence times involve lower reactor volumes to process a certain load of tyre and, therefore, lower cost of the system [1].

An increase in vapor residence time decreases liquid and char yields while the gas yield increases slightly. This is due to the decomposition of some oil vapor into secondary permanent gases. Primary vapors are first produced from tyre pyrolysis at optimum temperature, the primary oil vapors then degrade into secondary gases. For instance: oil vapors \rightarrow heavy hydrocarbons + light hydrocarbons leading to less oils and more gaseous products. In addition, longer contact time of the volatiles and char leads to secondary pyrolysis reaction [23].

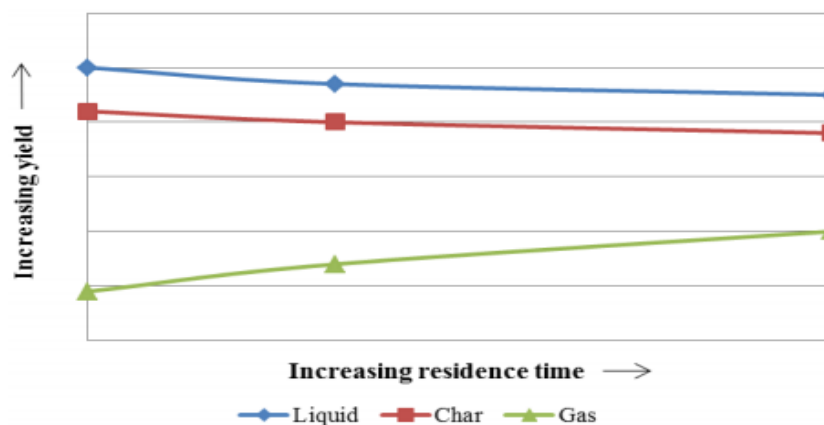


Figure 2.23 Effect of residence time on oil yield

2.8.4 Inert gas flow residence time

The effect of residence time of the vapor in the reactor on gas, char and liquid yields for optimum reactor temperature and for optimum feed size. Then the gas and char yields decrease while the liquid yield increases slightly. But with increase the residence time, it also help to the decomposition of some oil vapor into secondary permanent gases, which leads to less oil and more gases products. In addition, long contact time between the volatiles and the char leads to another parallel secondary pyrolysis reaction and hence reduces in volatiles' yields.

The increase of the gas residence time would favor the cracking of the primary pyrolysis products and would promote a change in the gas: liquid ratio. Nevertheless, it has been considered that higher percentage of nitrogen in the final gas would suppose an excessive dilution of gas fraction and therefore these gases may not have enough calorific value to satisfy the process requirement [1]

2.9 Properties of pyrolytic oil

Pyrolysis of tyre products is obtained oil similar in properties to a light fuel oil, with similar calorific value, sulphur, and nitrogen contents. The oils contained significant concentration of polycyclic aromatic hydrocarbons. Physicochemical properties of

tyrepyrolysis oil such as heating value, viscosity, flash point, pour point etc. compared to diesel oil [24]. 2.9.1 Physical property

Viscosity: It is a very important property of fuel-oil, which determines the flow quality or fluidity of the liquid. It has a big role on the design and manufacturing of engines where a liquid fuel is used. As the viscosity of a liquid increases, it creates some disturbances in pumping and atomization. Many techniques or processes such as addition of polar solvents like methanol or acetone can be applied to reduce the viscosity but at the same time, it effects on some other properties also. The viscosity of the pyrolytic oil varies in a wide range as it is produced from various raw materials, at different operating conditions using different parameters. It is obvious that the viscosity of the pyrolysis oil varies with the type of raw materials [25].

Table 2.7 Tyre pyrolytic oil (TPO) Dynamic viscosity at different temper

Temperature °C	Viscosity(mm/s)
30	2.04
40	1.89
50	1.48
60/70	1.23

Density: The density of the tyre pyrolysis oils was a little higher than that of diesel. The higher density of the pyrolysis oils may be attributed to the presence of aromatic contents in more concentration than that present in diesel. It may also be due to the presence of Sulphur compounds in the oils. The same contributes to the viscosity of the pyrolysis oils. The source of the Sulphur is from the vulcanized rubber tyres used in the process. The values obtained from the various tests conducted in evaluating the properties show that the values of the corresponding properties of the blends were in range to that of diesel.

The similarity in the values indicates that the TPO can be used as an alternative for diesel as a fuel or can be made into a blend with diesel. The density of the fuel-oil affects the energy value of the oil or fuel. The two fuels having same heating value may have different energy quantity due to the variation of density. As the density increases, the energy content also increases [25].

Flash point: The flash point of fuel oil is measured to indicate the maximum temperature at which it can be stored and handled without serious fire hazard. If the flash point is too low it causes the fuel to be subject to flashing and possible continued ignition and explosion. In spite of its importance from a safety standpoint, the flash point of the fuel is of no significance to its performance in an engine. The auto ignition temperature is not generally affected by variations in the flash point, nor is other properties such as fuel injection and combustion performance. The flash point of pyrolysis liquids has been determined according to ASTM D 93 using a Pensky-Martens closed-cup tester [26].

Tabl 2.8 Properties of tyre pyrolytic oil [26]

Property parameter	Result
Total ash	0.01
Gross calorific value	1920 Kcal/Kg
Viscosity at 40 °C	3.23cst
Specific gravity	0.92 gm/cc
Moisture	0.75 %
Carbon	87.2 %

Hydrogen	12.5 %
Nitrogen	0.12 %
Sulphur	0.08 %
Oxygen	0.1 %
Flashpoint	<32

2.9.2 Comparison with diesel oil

The main parameters required by the fuel as per the firm is Gross Calorific Value, Viscosity, Specific gravity, Moisture, Ash, Flash point & Sulphur. From the comparison it's clear that it has the parameters better than the presently using furnace oil and high speed diesel oil. It has high gross calorific value [27].

Table 2.9 Comparison of TPO and diesel oil [28]

Property	TPO	Diesel oil
Heating value (MJ/Kg)	43.22	45
Carbon (%)	84.67	87
Hydrogen (%)	10.44	13
Oxygen (%)	4.17	-
Sulfur (%)	<1	-
Density @ 30°C (g/cm ³)	0.924	0.799
Viscosity@ 40°C(cP)	2.69	1-4.11
Flash point °C	68	70

Tabl2.10 Comparison with kerosene

Property	Kerosene	TPO
Hydrogen (%)	13.48	12.3
Oxygen (%)	0.00	3.68
Sulfur (%)	0.09	0.04
Specific .G(%) at	0.72	0.74
Calorific value(MJ/Kg)	42	40.62
Average Mol. weight	106.51	108.78

2.9.3 Chemical properties of tyre pyrolytic oil

The Fourier Transform Infrared Spectroscopy (FTIR) offers a quantitative and qualitative analysis for organic and inorganic samples. The spectra produce a profile of the sample a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. It identifies chemical bonds in a molecule by producing an infrared absorption spectrum.

The FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding formation. The FTIR test was carried out with Perkin Elmer Spectrum one equipment which has a scan range of 450-4000 cm^{-1} with a resolution of 1.0 cm^{-1} . The FTIR analysis of TPO reveals that, the functional group present are almost aromatics and hydrocarbons. The compounds of light tyre pyrolysis oil are alkanes, alkenes, aromatic compounds, but in case of diesel the compounds are alkanes, alkenes, alcohol, nitrate, chloride and bromide [29].

Table 2.11 FTIR Analysis of TPO [29]

Tyre pyrolysis oil					
Wave number (cm ⁻¹)	Bonds	Class of compound	Frequency Range(cm ⁻¹)	Bonds	Class of Compounds
2921.33	C-H, stretch	Alkanes	3095-3005	C=C stretching	Alkenes
2812.72	C-H, Stretch	Alkanes	300-2800	C-H Stretching	Alkanes
1605.47	C=H,C=N stretch	Alkenes,amide	1680-1620	C=C stretching	Alkenes
1461.19	O-H, Bending	Alcohol	1600-1525	C-C stretching	Aromatic compound
1376.55	Nitrate	Nitrait	1520-1220	C-H Bending	alkenes
722.05	C-Cl	Chloride	1035-830	C-C stretching	alkenes

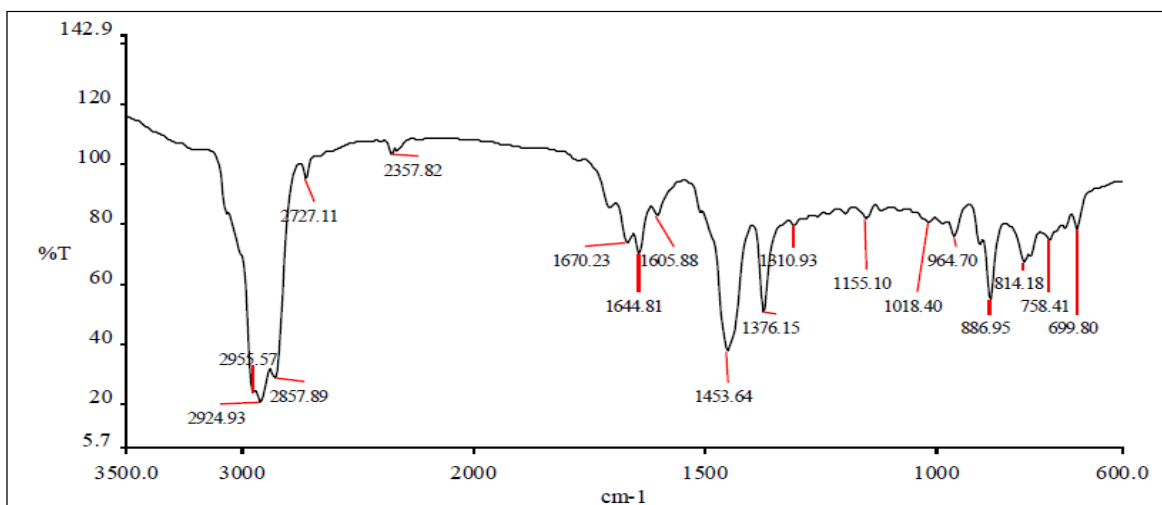


Figure 2.24 FT-IR Spectra

GC-MS Analysis oil: The Gas chromatography (GC) and mass spectrometry (MS) make an effective combination for chemical analysis. Gas chromatography (GC) is used to separate mixtures into individual components using a temperature-controlled capillary column. Smaller molecules with lower boiling points are travel down the column more quickly than larger molecules with higher boiling point. The mass spectrometry (MS) is used to identify the various components from their mass spectra. Each compound has a unique or near unique mass spectrum that can be compared with mass spectral databases and thus identified. Through use of standards, quantification is also possible [30].

Tabl 2.12 Compounds detected in TPO by GC-MS analysis

R. time	Area (%)	Name of compound	Molecular formula
3.290	4.85	P-xylene Benzene,1,3-di methyl	C_8H_{10} Or $C_6H_4(CH_3)_2$ $C_{10}H_{14}$
4.859	6.24	Benzene	C_9H_{12}
5.236	2.17	Benzonitrile	C_6H_5CN
5.962	15.24	Benzene 1,2,3,4tetramethyl,o-cymene	$C_{20}H_{26}O$ $CH_3C_6H_4CH(CH_3)_2$
6.035	5.19	D-limonene	$C_{10}H_{16}$
10.45	2.19	1H-indene2,3di hydro 1,1,5trimethyl	C_9H_8
12.207	3.77	Nyphtaline 2,7dimethyl	$C_{10}H_8$ $C_{10}H_6(CH_3)_2$
3.065	0.98	1-Ethyl- methylchlorohexane	C_9H_{18}
3.359	1.06	Propylcyclohexane	$C_6H_{11}CH_2$ CH_2CH_3
3.782	1.04	M-ethylmethyl benzene	C_9H_{12}
4.274	3.51	Decane	$C_{10}H_{22}$

5.822	2.14	N-undecane	$C_{11}H_{24}$
7.356	2.71	Dodecane	$CH_3(CH_2)_{10}CH_3$
15.959	3.38	n-Hexadecane	$CH_3(CH_2)_{14}CH_3$

2.10 Uses of pyrolytic oil

Industrial and commercial: The liquids obtained are dark brown colored products, resembling petroleum fractions.

The main oil product produced by pyrolysis technology is the fuel oil that is widely used for industrial and commercial purposes. Pyrolysis of scrap tyres produces oil that can be used as liquid fuels for industrial furnaces, foundries and boilers in power plants due to their higher calorific value, low ash, residual carbon and sulphur content. Pyrolysis oil is an effective substitute for diesel, heavy fuel oil, light fuel oil or natural gas in industrial, commercial and residential boilers. Furnaces and boilers are devices commonly used for heat and power generation.

They are usually less efficient than engines and turbines but they can operate with a great variety of fuels ranging from natural gas and petroleum distillates to sawdust and coal/water slurries and oil seems. For a fuel to be suitable for boiler application, it should have consistent characteristics, provide an acceptable emission level and be economically feasible. Use as automobile fuel: High viscosity, delayed ignition time, lower heating value, corrosion and solid content hinder the utilization of pyrolysis oil in combustion devices. Work has been done on the improvement of pyrolysis oil for use in modern combustion. Pyrolytic oils require preliminary treatments such as decanting, centrifugation, filtration, desulphurization, and hydro treating before use as fuels [31].

The use of tyre pyrolysis oil as a substitution to diesel fuel is an opportunity in minimizing the utilization of the fossil fuels to save natural resources and to limit greenhouse gas emission.

3. Materials and Methods

3.1 Materials

The raw materials used for the pyrolysis process waste tyre was collected from Horizon Addis Tyre S.C Addis Ababa, Ethiopia. The equipment that used during the experimental analysis was: plastic bags (different size) grinder, dish, electronic balance (ADAM PW 124), batch reactor, baker (different size) cooler, vessel, cylinders (different volume), Pycnometer, Hydrometer Viscometer and muffle furnace.

3.3 Raw material Preparation and Characterization

3.3.1 Moisture Content

The moisture content of the sample was determined using ASTM standard. An empty crucible and its cover was heated at 110°C for about 15 minutes and cooled. The tyre sample in the crucible was placed in the oven at 110°C for an hour and subsequently cooled in a desiccator. The moisture content was calculated using the mass balance relation.

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} * 100 \dots \dots \dots (3.1)$$

Where: W_1 = Sample used in g

W_2 = Sample after heating in g



Figure 3.1 Sample ready to ash and moisture content measurement

3.3.2 Ash content and volatile organic compound

The ash content of the waste tyre was comes from nonblack component of tyre compositions which are calcium carbonate, clay, precipitated silica [18]. The ash content of the sample was determined using ASTM method. An empty Crucible and its cover are preheated in a muffle furnace at 700°C for about 30 minutes and cooled. The dried waste tyre in crucible was put in the muffle furnace and heated gradually to a temperature of 500°C within the first hour and increased to about 700°C. It was maintained at 700°C for another 2 hours and then cooled and the ash content was calculated as follows.

$$\text{Ash content (\%)} = \frac{w_1 - w_2}{w_3} * 100 \dots\dots\dots (3.2)$$

Where: W_1 = weight of crucible and ash residue in (g)

W_2 = weight of crucible in (g)

W_3 = weight of sample used for analysis in (g)

3.3 Experimental procedure pyrolysis

In this study, waste tyre was cut into a number of pieces and the bead, steel wires and fabrics were removed. Thick rubber of the tyre was alone made into small chips. The tyre chips (feed stock) were washed dried and were can be easily fed into the pyrolyser. The initial quantity of scrap tyre pieces was weighed before charging into reactor. The top lid was tightly secured to the pyrolyser after charging the sample. Cooling water was circulated in the volatiles condenser by means of a pump. During the heating process, temperature was served at regular time intervals. This was continued till the pyrolyser temperature reached. The heating was stopped at this condition. The system was allowed to cool up to room temperature naturally. Then the top lid of the pyrolyser was opened; solid residue remaining in the pyrolyser was taken out and weighed. The stopper at the bottom of the gas-liquid separator was also opened and pyrolytic oil was drained into a

measuring cylinder. The pyrolyser was cleaned and weighed to make ready for the subsequent test.

The same procedure was followed for all runs. The process was carried out at a temperature of 500, 550 and 600 °C. The residence time of the feed stock in the reactor was 45, 60 and 75 minutes. 60 g of feed stock was used for one batch.

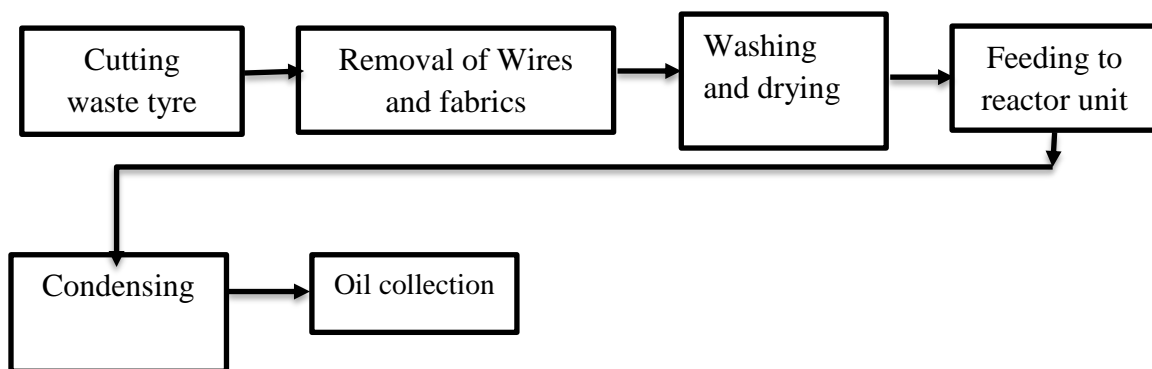


Figure 3.2 Process flow sheet of pyrolysis

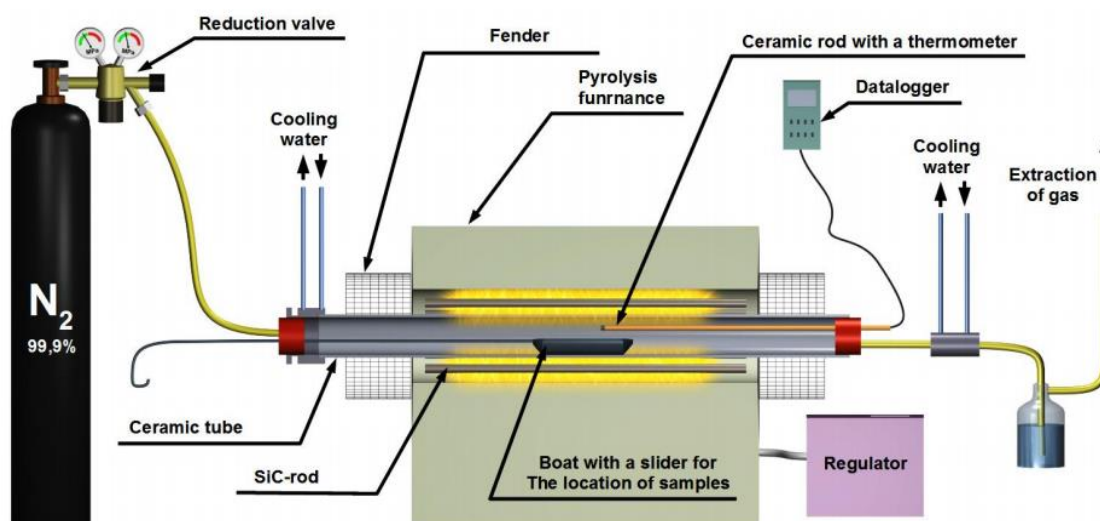


Figure 3.3 Scheme of laboratory pyrolytic unit operation diagram

3.4 Determination oil yield

The percentage fuel oil yield was calculated by using following relation

$$\text{Percentage of fuel oil yield (W/W)} = \frac{\text{mass of oil}}{\text{mas of sample}} * 100 \dots \dots \dots (3.3)$$

3.5 Fuel oil Treatment

3.5.1 Moisture removal

Initially the liquid product was heated with cylindrical vessel using Stainless steel moisture dishes. The dishes were then placed in an oven with the lids off at 105 °C and dried to a constant weight. The lids were replaced and the dishes were transferred into a desiccator for 1h and ready to desulfurization process.



Figure 3.4 Sample ready for desulfurization

3.4.2 Sulfur removal

The raw pyrolytic oil was subjected to 8% by weigh of hydro-sulfuric acid (H_2SO_4), stirred well by an electrical stirrer during 4 h and left to settle for 40 h. Temperature of the mixture was maintained at 50 °C during stirring process. The mixture was found in two layers 40 h later. The top layer was the clear viscous oil, and the bottom layer was the non-viscous acidic sludge.

The clear viscous oil was taken for the Calcium Oxide (CaO) treatment. (100 g activated bentonite for every 1000 ml of acid treated pyrolytic oil and mixed by an electrical stirrer for about 4 h. Temperature of the mixture was maintained at 70 °C during stirring process. The contents were kept for 24 h for the settling of the sludge. Whole contents were then filtered by filter-paper to obtain healed pyrolytic oil.

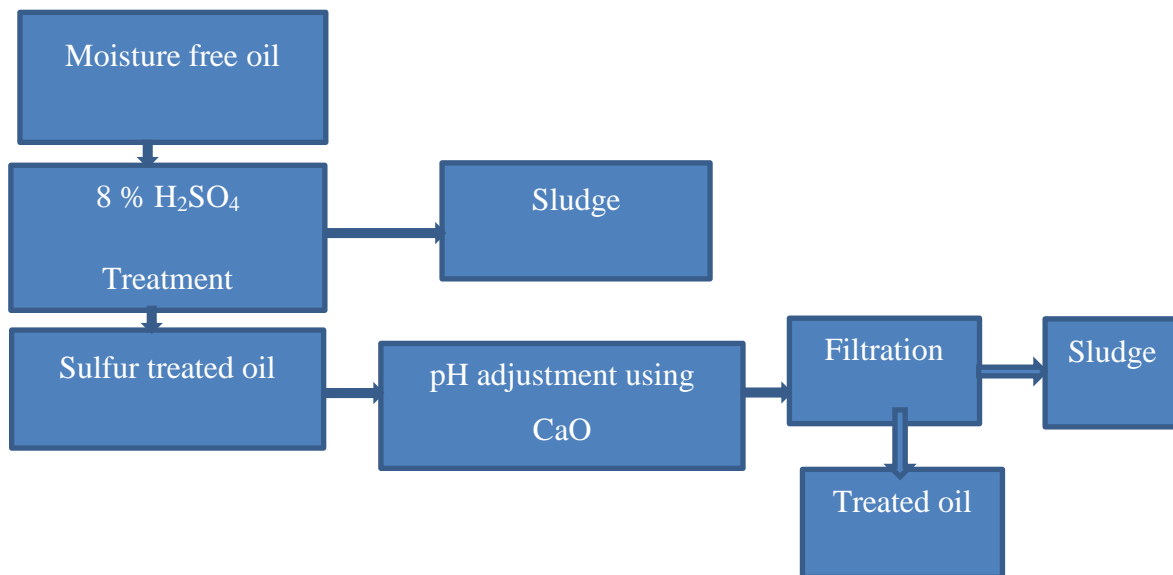


Figure 3.5 Desulfurization flow charts

Table 3.1 Percentage of oil after desulfurization

Oil ready to treatment	Sludge	Treated oil
860ml	240ml	620ml



Figure 3.6 Sample after sulfur removal

3.5 Characterization of pyrolytic oil

3.5.1 Physical characteristics

3.5.1.1 Specific gravity (Density) determination

The specific gravity of the oil was determined by using Specific gravity bottle (pycnometer). The 15ml pycnometer was cleaned and dried first and then weighed (W_0), then after the bottle was filled with oil, stopper inserted and reweighed to give (W_1).

The oil was substituted with water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (Sp.gr)

$$Sp. \text{ gravity} = \frac{(W_1 - W_0)}{(W_2 - W_0)} \dots\dots\dots (3.4)$$

Where:

- W_0 - weight (g) of empty bottle
- W_1 - weight (g) of bottle + sample (oil)
- W_2 - weight (g) of bottle + water

3.5.1.2 Determination of kinematic viscosity

A 15 ml of fuel oil was poured into a test tube and a viscometer was used to measure the viscosity at a temperature of 40°C. A dynamic viscosity of the fuel oil was measured directly using viscometer which was available in laboratory of school of Chemical and Bio Engineering. Then the kinematic viscometer was calculated as follows.

$$\text{Kinematic viscosity} = \frac{\text{Dynamic viscosity of the sample}}{\text{Density of the sample}} \dots\dots\dots (3.5)$$

3.5.1.3 Moisture content of fuel oil

Stainless steel moisture dish ware weighed and desired amount of each sample was added. The dish ware placed in an oven with the lids of 100 °c and deride to a constant weight. The lids ware repelled and the dish ware transferred in to a desiccator for one hour. The dish ware re weighed and the percentage was determined.

$$\% \text{ Moisture content} = \frac{W1 - W2}{W1 - W3} * 100 \dots \dots \dots (3.6)$$

Where w_1 , weight of dish plus sample

w_2 , weight of dish

w_3 sample after moisture removing.

3.5.1.4 Flash point

The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of the stirring and then measures the temperature at this interval using thermometer.

3.5.1.5 Pour point

The pour point was determined according ASTM method. Place a sample of fuel oil in a refrigerator and inspect the sample within five minute intervals and take the temperature when the oil surface dose not sap.

3.5.2 Chemical characteristics.

3.5.2.1 Gas chromatography-mass spectrometry (GC-MS)

The identification and analysis of the extracted fuel oil components were carried out by gas chromatography mass spectrometry (GC-MS).

The operating conditions (refer to table below) were applied to identify the components in the fuel oil extracted by thermal pyrolyzation method for this study.

Table 3.2 Gas chromatography-mass spectrometry method for chemical analysis of the extracted fuel oil samples

Method	
Type	(Agilent Technologies, Palo Alto, CA, USA)
Column	Anon-polar capillary column with dimensions: 60 m × 0.18 mm i.d. × 0.10 µm df Rxi-5 Sil-MS was used.
Carrier Gas	Helium 99.999% purity
Linear Velocity/ cm/s)	27.9
Detector Type	Mass spectroscopy
Injection Volume/µl	1
Injection Type	Split ratio of 1:20.
Detector Temp./°C	250
Injector Temp./°C	280
Oven Temp.	40-280 @ 10C.min ⁻¹
Comparison of.	Retention Indices

3.5.2.2 Fourier transforms infrared spectroscopy (FT-IR)

Fourier Transform infrared (FT-IR) spectroscopy is a dynamical instrumentation technique that is useful for examination of various forms of matter. When a sample is analyzed using infrared radiation, the FT-IR spectra provide information about the vibrational and rotational energies of a molecule. The infrared radiation is absorbed at specific frequencies characteristic of the molecular species, whereby the FT-IR spectrum is a true signature of the molecule.

Knowing the radiation intensity as a function of the infrared frequency, one can specify the types of chemical functional groups. Its distinct advantage of spectral data acquisition is that it has the ability to look at all the wavelengths of a spectral region simultaneously, rather than one wavelength at a time. The IR spectra of the fuel oil were recorded in transmittance (%) and the wave number region for the analysis were (4000 - 600 cm^{-1}).

3.6 Design of Experiment (DOE)

Data analysis for this study was carried out by DESIGN EXPERT software (General factorial design expert) to evaluate the effects of the process variables; pyrolysis temperature (500°C, 550°C and 600°C), pyrolysis time (45min, 60min and 75 min) full factorial experimental design with 27s experiments were done. This design of the experiment helps us to Optimize of Process Parameters Using Response Surface Methodology (RSM).

Significance of the result was set from analysis of variance (ANOVA). This design of experiment helps us to differentiate the significance of the main and the interaction factors.

3.7 Characterization of Solid char

3.7.1 Moisture content Measurement

The moisture content of the prepared char was determined using ASTM. Crucible and its cover were first dried in an oven and allowed to cool. Prepared char sample was put in the crucible and the mass recorded. The crucible was opened and the crucible with its content was placed in the oven for 3 hours at a temperature of 150°C. The crucible was then covered with the lid again and cooled in a desiccator to ambient temperature and the mass of the dried sample was taken again. Finally the moisture content was calculated using mass balance relation.

$$\text{Moisture (\%)} = \frac{W_1 - W_2}{W_1 - W_4} * 100 \dots\dots\dots (3.7)$$

Where: W_1 sample + crucible in gram

W_2 crucible in gram

W_4 sample after moisture removed



Figure 3.7 Sample ready for ash measurement

3.7.2 Ash Content

Ash tests were conducted according to ASTM method. The chars were first dried in the oven at a temperature of 125°C for 1 hour and allowed to cool to room temperature. The dried samples (W_1) were then placed in a porcelain crucible, and heated at 550°C for 16 hours and measure get (W_2). The change in weight was recorded and calculates using mass balance and the experiment was done in Horizon Addis Tyre Company.

$$\text{Ash content (\%)} = \frac{W_2 - W_1}{W_2} * 100 \dots\dots\dots (3.8)$$

4. Results and Discussion

4.1 Fuel oil extraction

The results of fuel oil yield from waste tyre obtained by using thermal pyrolyzation extraction at different extraction temperature and time. The percentage of extracted yield was calculated by using equation 3.1 and the result is summarized in table below.

Table 4.1 Yields obtained by pyrolysis

Temperature (°C)	Time(min.)	test-1 (g)	test -2 (g)	test -3 (g)	Average (g)	Yield (%)
500	45	25	25.8	24.9	25.23	42.05
	60	27	28	27.8	27.6	46
	75	30	31	29.4	30.13	50.22
550	45	25.4	25.6	25.7	25.57	42.61
	60	28.4	28.2	28.7	28.43	47.39
	75	30.2	31.06	32.1	31.27	52.11
600	45	30.1	30.4	30.7	30.4	50.6
	60	27.5	27.2	28	27.57	45.94
	75	25.3	25.7	24.9	25.3	42.17

The maximum oil yield (52.11%) was obtained at pyrolysis time of (75 minute) and temperature of (550°C), and the minimum average yield obtained was (42.05%) at time of (45 minute) and temperature of (500°C).

4.2 Determination of Moisture and ash Content tyre sample

The collected waste tyre of different samples were prepared to determine the moisture content at 100°C and the moisture content of the sample was obtained in table 4.2 at 6 hrs using equation (3.3) and ash content in Horizon Addis Tyre Compan.

Table 4.2 Ash and moisture content of tyre sample

No	Properties	Average (%)	Other literature value (%)
1	Moisture content	1.23	1
2	ash Content	7.65	7

4.4 Physical Characterization of extracted oil at optimum operating conditions.

Table 4.3 Physical property of the extracted fuel oil

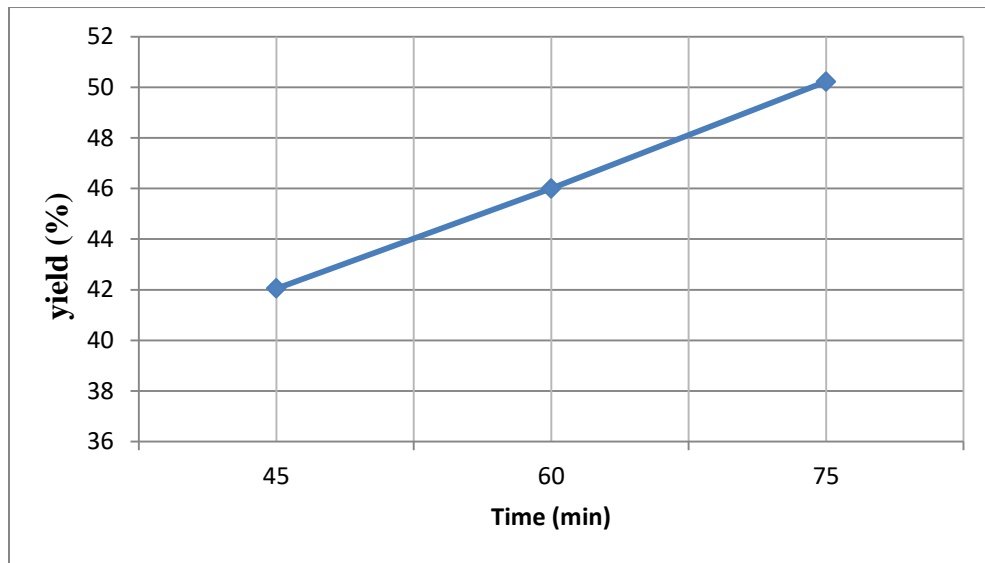
Property parameter	Result	Other literature value
Gross calorific value (MJ/Kg)	41.9	43.8
Viscosity at 40 °C (centi poise)	3.5	3.2
Specific gravity (g/cc)	0.98	0.935
Moisture (%)	6	11
Flash point (°C)	36	40
Pour point (°C)	-3.6	-2

4.4.1 Effects of Experimental Variables on pyrolysis producte

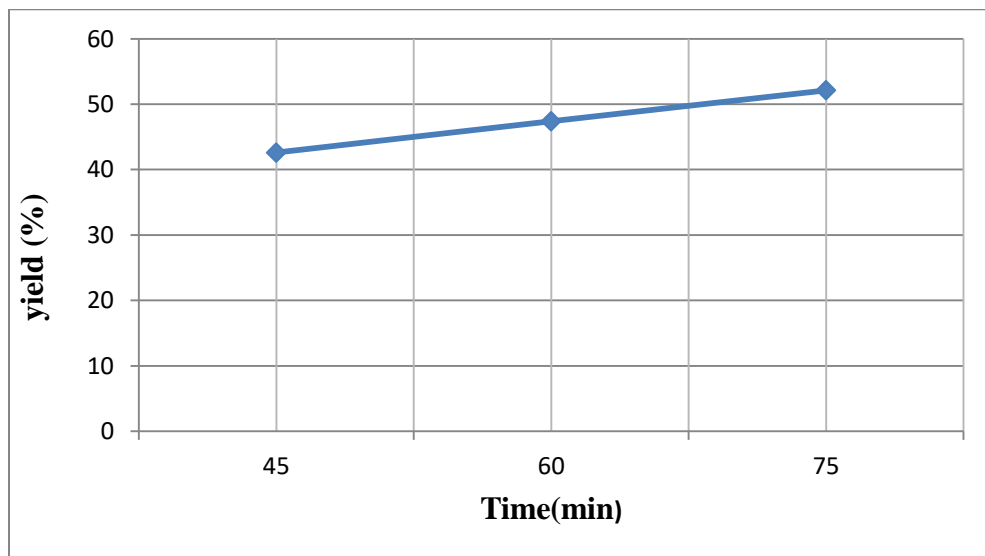
Extraction of fuel oil can be affected by many parameters starting from sample preparation to the pyrolysis steps has a complex connection with independent variables

4.4.1.1 Effect of time on the extracted oil yield

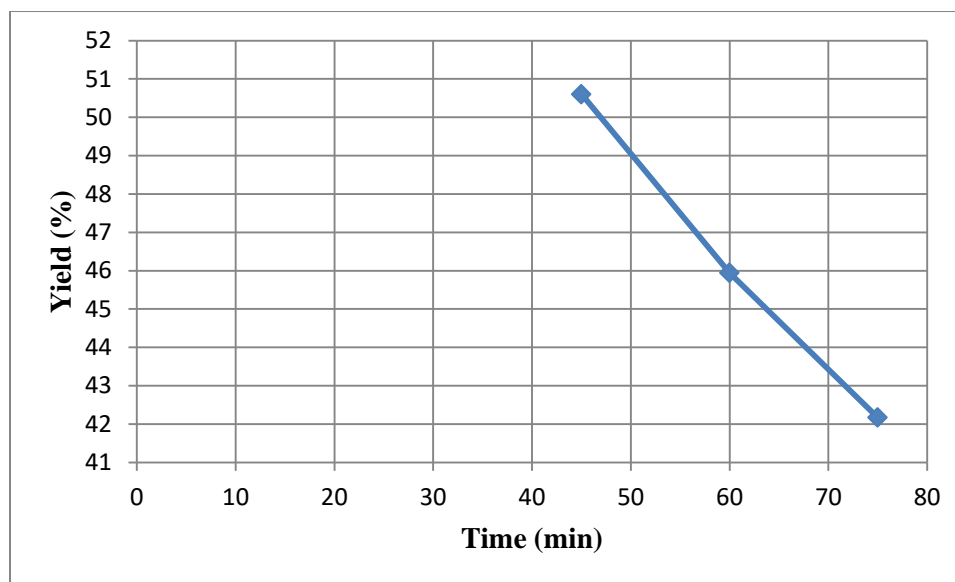
It is an important process condition in the pyrolysis of waste tyre; its optimization is an important factor in order to extract the maximum oil yield and it needs to reduce the reactor volume.



(a)



(b)



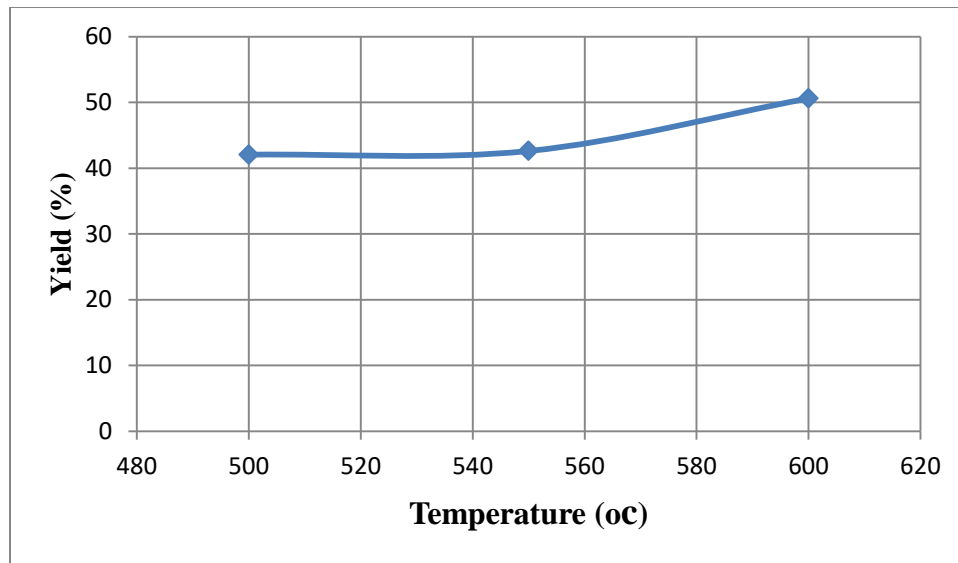
(c)

Figure 4.1 Effect of time on the extracted oil yield

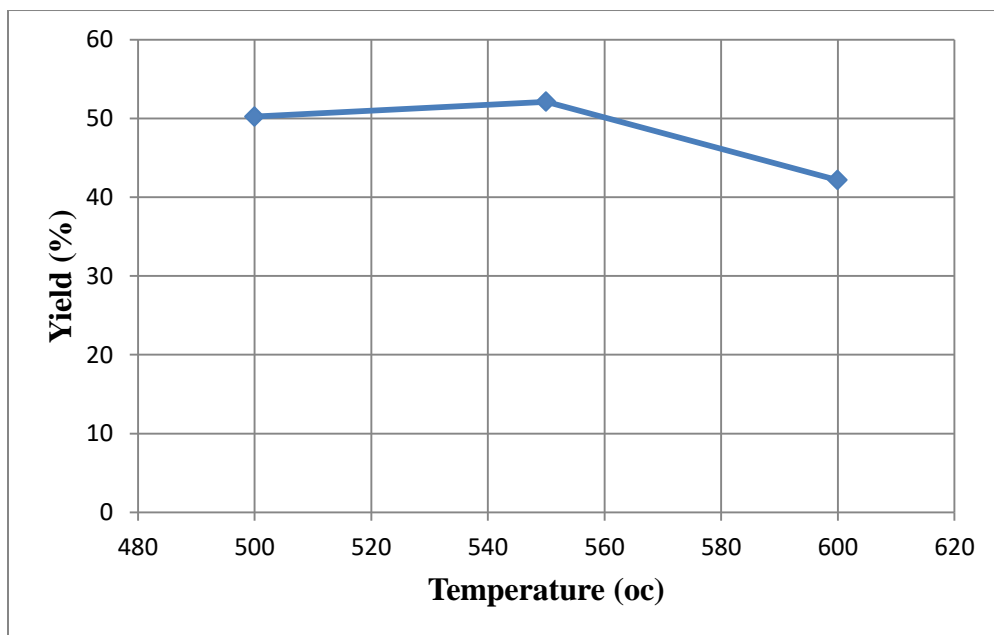
Graph (a), (b) and (c) are the effect of pyrolysing time on fuel oil yield at temperature of 500, 550 and 600 °C respectively and the graph indicates that oil yield increase with time until (75 minute) and decrease gradually with time. The maximum oil yield (52.11%) was obtained at time of 75 °C and temperature of 550 °C in graph (b) and the minimum oil yield (42.055) was obtained at time of 45 minute and temperature of 500 °C in graph (a).

4.4.1.2 Effect of temperature on the fuel oil yield

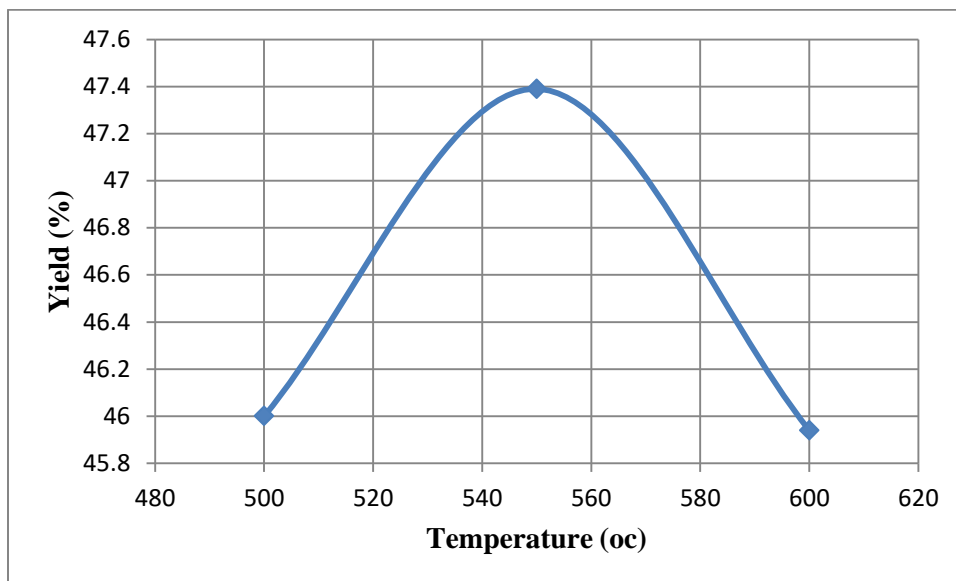
Temperature is the second important process variable in this study and the physico-chemical property and composition of the extracted fuel oil also depend on the operating conditions especially (temperature).



(a)



(b)



(c)

Figure 4.2 Effect of temperature on the fuel oil yield

Graph (a), (b,) and (c) indicates the effect of temperature on oil yield at time of 45,60 and 75 respectively and oil yield increase until the temperature of 550 °C and then decrease gradually with it. It reports that the maximum average yield (52.11%) was occurred at time of 75 minute and temperature of 550 °C in graph(c) and the minimum average oil yield (42.05%) was obtained at temperature of 500°C and time of 45 minute in graph (a).

4.5 Analysis of general factorial experiments

4.5.1 Interaction effect between time and temperature

In this present study, the methods employed in the extraction of fuel oil from waste tyre time and temperature has major significant effects on the final yield of fuel oil.

As we observed from figure below that obtained from design expert software (general variable) the outputs of interaction effect between temperature and time have a significant interaction for oil yield because the line in the graph is not parallel.

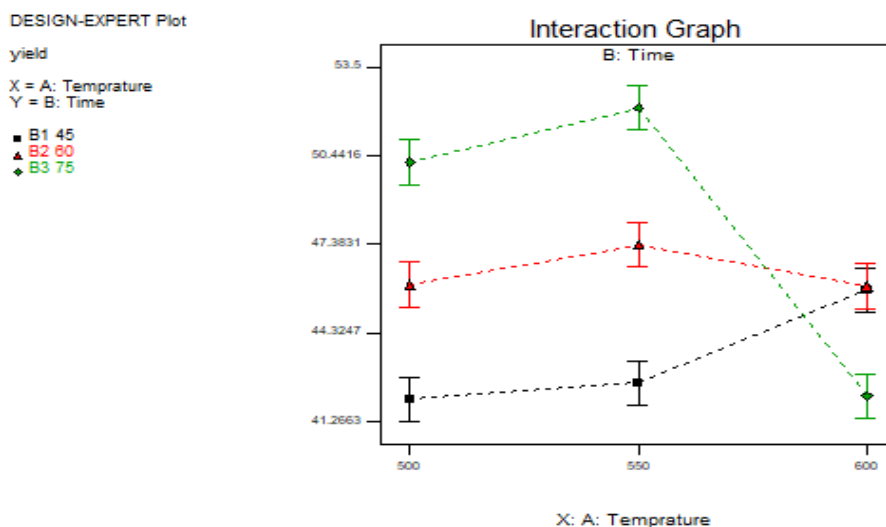


Figure 4.3 Interaction graph between temperature and time

4.6 Optimization of process conditions

From the result shown above (table and figure) the highest fuel oil yield 52.11% of waste tyre) was obtained at 550°C pyrolysis temperature, 75 minute time.

Regression model equation

The ANOVA method is the classical method for estimating variance components in designed experiments. It is more accurate than the X-bar and R- chart methods. The following table shows that analysis of variance obtained from design expert software (general factorial) which tell us the major role of different factors on pyrolysis oil yield.

Table 4.4 Analysis of variance (ANOVA) for the cubic model

ANOVA for Selected Factorial						
Analysis of variance table [Partial sum of squares]						
	Sum of	Degree of	Mean	F		
Source	Squares	DF	Square	Value	Prob > F	
Model	297.34	8	37.17	46.47	< 0.0001	significant
A	33.42	2	16.71	20.89	< 0.0001	
B	101.01	2	50.5	63.14	< 0.0001	
AB	162.91	4	40.73	50.92	< 0.0001	
Pure Error	14.4	18	0.8			
Cor Total	311.74	26				

F- Value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. It is calculated by Model Mean Square divided by Residual Mean Square. Here the Model F-value of 46.47 implies the model is significant. There is only a 0.01% chance that a. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 4.5 Model adequacy measures

Std. Dev.	0.83	R-Squared	0.949
Mean	51.58	Adj R-Squared	0.9132
C.V.	1.6	Pred R-Squared	0.8399
PRESS	21.45	Adeq Precision	14.685

The "Pred R-Squared" of 0.8961 is in reasonable agreement with the "Adj R-Squared" of 0.9333. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is

desirable. ratio of 19.496 indicates an adequate signal. This model can be used to navigate the designspace.

Table 4.6 Regression coefficients and the corresponding 95% CI High and Low

Term	Coefficient Estimate	Degree of freedom	Standard Error	95% CI Low	95% CI High
Intercept	46.02	1	0.17	45.66	46.38
A[1]	0.061	1	0.24	-0.45	0.57
A[2]	1.33	1	0.24	0.82	1.84
B[1]	-2.55	1	0.24	-3.06	-2.04
B[2]	0.41	1	0.24	-0.1	0.92
A[1]B[1]	-1.5	1	0.34	-2.23	-0.78
A[2]B[1]	-2.22	1	0.34	-2.94	-1.49
A[1]B[2]	-0.5	1	0.34	-1.22	0.22
A[2]B[2]	-0.39	1	0.34	-1.12	0.33

Final Equation in Terms of Coded Factors:

$$\text{yield} = +46.02 + 0.061 * A[1] + 1.33 * A[2] - 2.5 * B[1] + 0.41 * B[2] - 1.50 * A[1]B[1] - 2.22 * A[2]B[1] - 0.50 * A[1]B[2] - 0.39 * A[2]B[2]$$

Diagnostics case Statistics: The following figure indicates that, the relationship between the actual value of the experiment and the value predicted by the model equation developed by the Design Expert Software.

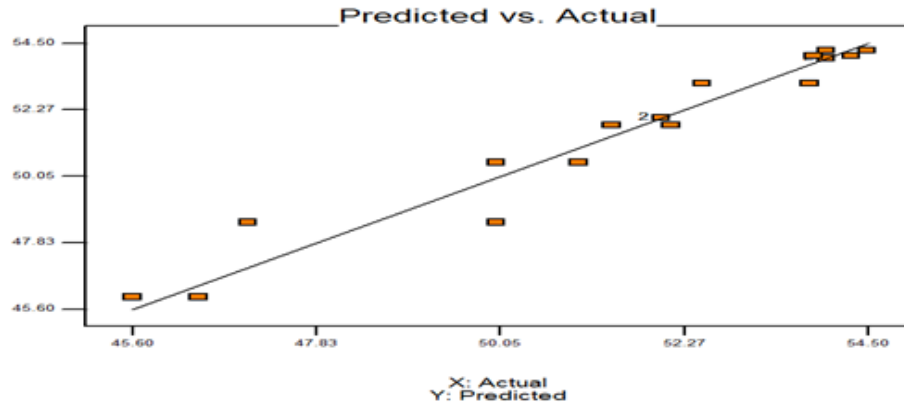


Figure 4.4 Predicted versus actual graph

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

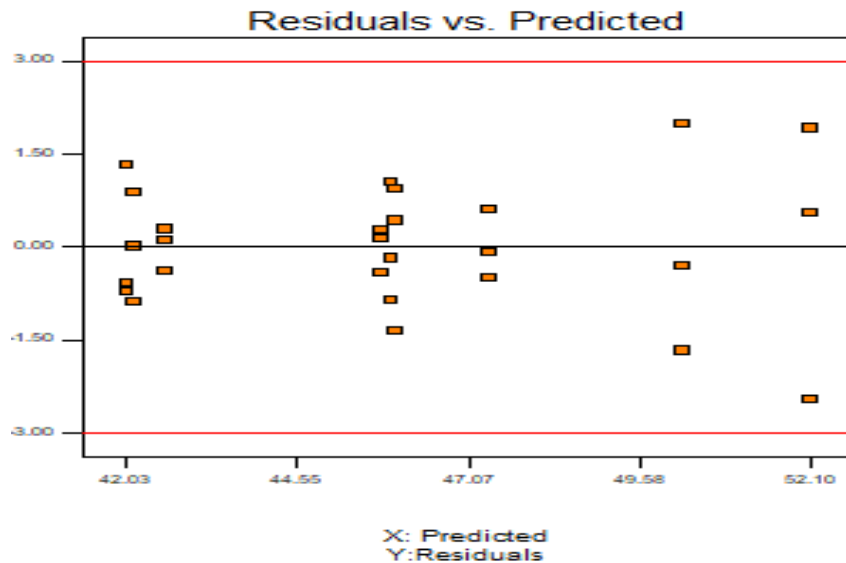


Figure 4.5 Residual versus predicted graph

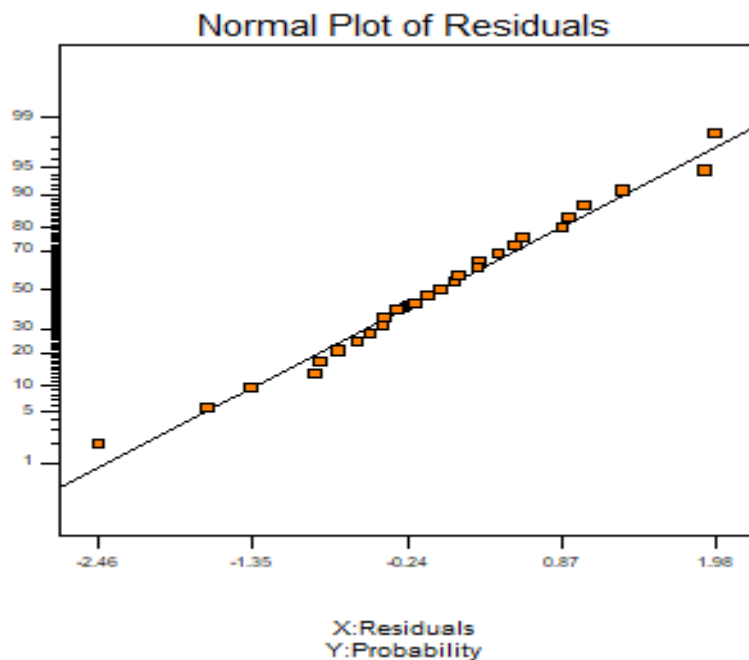


Figure 4.5 Normal plots of residuals

The following figure shows the relation between the actual value of the experiment and the value predicted by the model equation developed by the Design Expert software.

4.8 Chemical Characteristics of extracted fuel oil at optimum operating condition

4.8.1 GC-MS analysis

The GC-MS library available in the laboratory at the Lather Industry Development Institute is the W9N11.L Mass Hunter GC-MS (1) 5977 MS firm ware version revealed that, the fuel oil contained maximum percentage of area was obtained (dl-Limonene Cyclohexene,1-methyl-4-(1-methylethenyl). The table 4.7 below reported that, most of the oil contains dl-Limonene Cyclohexene and different hydrocarbon derivatives that eluted at different retention times depending on the boiling point of the component.

The chromatogram obtained a high concentration of oil indicated by presence of one large peak which eluted at 15.302 minute with peak areas of percentage 11%. (Refer to figure 4.7 below). Mass spectrographs of the identified constituents are given in table below also.

Table 4.7 Chemical composition of extracted fuel oil.

Structural assignment	Library match Quality (%)	Retention time	Area (%)
Benzene, 1,4-dimethyl- Xylene p-Xylol 1,4-Xylene	94	9.952	10.44
Cyclohexene,1-methyl-4-(1-methyle thenyl)-, (S)- p-Mentha-1,8-diene, (S)	90	13.265	10
Benzene,1,2,4-trimethyl1,2,4 Trimethyl benzene	83	14.310	9.2
o-Cymene Benzene, 1-methyl-2- methylethyl)- o-Cymol	94	15.173	10.44
dl-Limonene Cyclohexene, 1-meth yl-4-(1-methylethenyl)	99	15.302	11
Benzene,1,3-diethyl-iethylbenzene 1,3-Diethylbenzen	87	15.811	9.67
Benzene, 2-ethyl-1,3-dimethyl- m-Xylene, 2-ethyl-	81	16.510	9
Benzene, 1-ethyl-2,3-dimethyl- o-Xylene, 3-ethyl-	83	17.447	9.2
Junipene	96	23.801	10.67
4,6,8-trimethylazulene4,6,8-tri methyl azulene	93	24.867	10.33

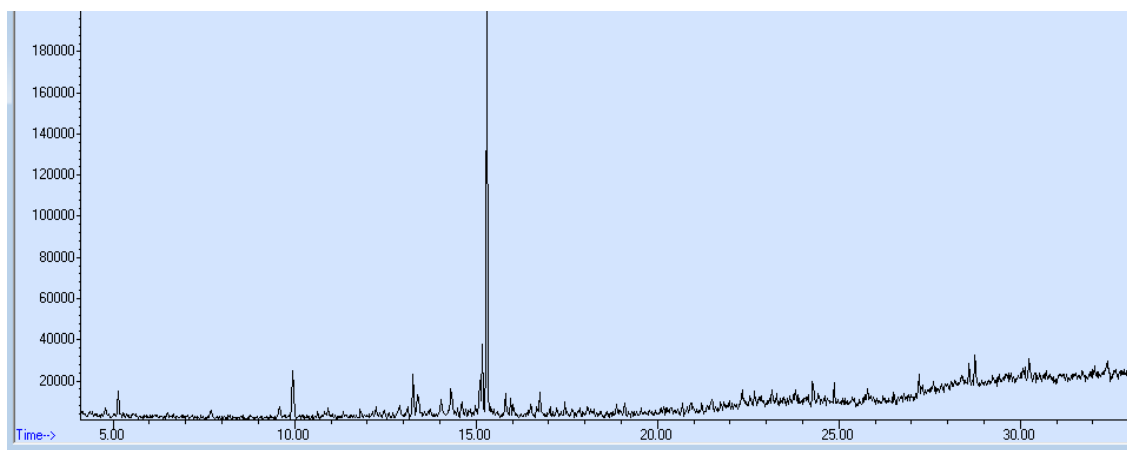


Figure 4.6 GC-MS graph

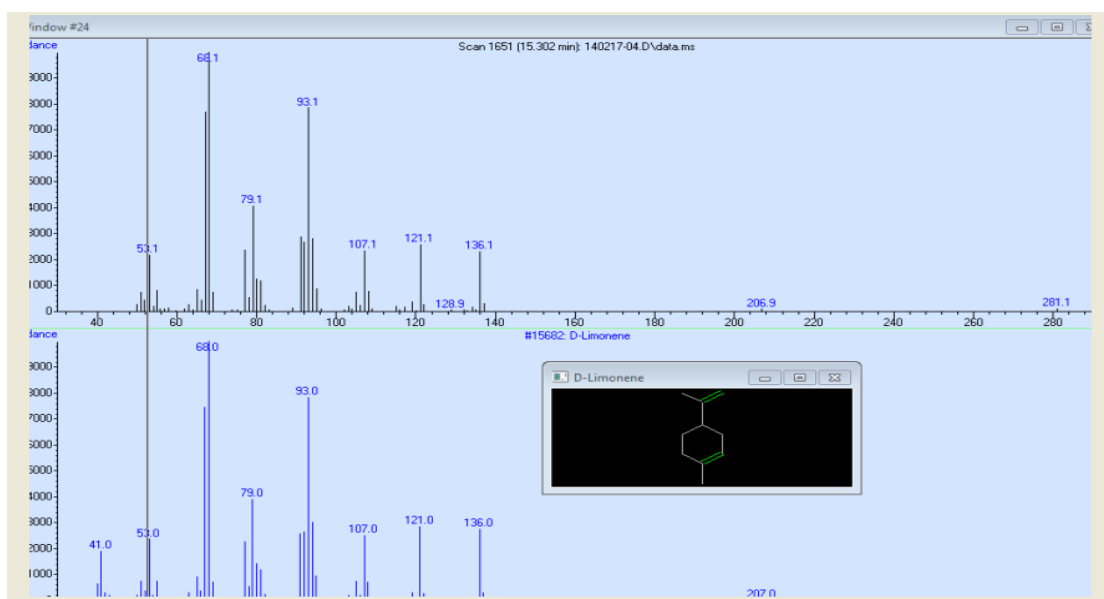


Figure 4.7 GC-MS result profile at high percent of area and quality

From above GC-MS analysis ten volatiles components were identified in the fuel oil obtained by using gas chromatography mass spectrometry which has qualified the minimum quality of (80). Among these components, dl-Limonene Cyclohexene, 1-methyl-4-(1-methylethenyl) was obtained in peak retention time (15.302) and high percentage area of (11%).

4.7.2 Determination of the functional groups in extracted oil using FT-IR

The FTIR analysis of pyrolytic oil merriments that, the functional group present in oil was almost aromatic hydrocarbons. The tyre pyrolysis oil compounds are alkanes, alkenes and aromatic compounds. The experiment was done in lather industry development institute Addis Aaba, Ethiopia. The result of the functional group was summarized in table 4.8 below.

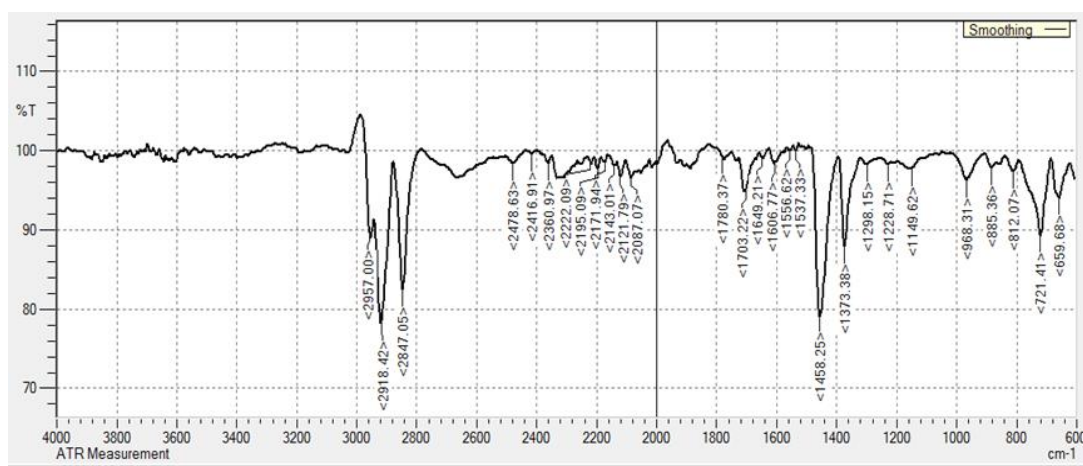


Figure 4.8 FTIR spectrum of extracted fuel oil

Table 4.8 FTIR Characterization of extracted fuel oil

Wave number (cm ⁻¹)	Bonds	Class of compound	Frequency Ran (cm ⁻¹)
2918.42	C-H Stretch	Alkanes	3000-2800
2847.05	C-H Stretch	Alkanes	3000-2800
1606.77	C=H,C=N,Stretch	Alkenes Amide	1640-1600
1458.25	O-H Bending	Alcohol	1600-1400
1373.38	Nitrate	Nitrate	1400-1360
721	C-Cl	Chloride	800-720

The above table and graph of FTIR result indicates the functional group was listed based on the given wave number and frequency and most of the functional group was alkanes and alkenes.

5 Conclusion and Recommendation

5.1. Conclusion

These studies were anticipated to the influence of process conditions and give intentions recycle was tyres using pyrolysis is profit oriented and have better environmental value.

In this study the pyrolysis oil (TPO) from waste tyre has slightly similar physicochemical properties with commercial diesel. The maximum fuel oil yield (52.11%) was obtained at optimum operating conditions of time (75 minute) and temperature (550 °C).

The GC-MS result was dl-Limonene Cyclohexene, 1-meth yl-4-(1-methylethenyl) was obtained in peak retention time (15.302) and high percentage area of (11%).

The GC-MS characterization showed that oil products contain approximately the same chemical compounds of aliphatic (saturated, unsaturated and cyclic) and aromatic compounds. But they differ in concentration which should be study quantitatively from the literature.

The char (solid) part have similar ash and moisture content with activated carbon and which indicates that solid product after pyrolysis will used for different propose after doing different physicochemical analysis. The physical properties (ash and moisture) waste tyre sample and solid residual was done in Horizon Addis Tyre Company.

5.2 Recommendations

Due to high consumption the fuel demand in Ethiopia, the development of alternative fuel technologies has drawn more attraction to deliver the replacement of imported fuel. Many alternative fuels have been developed like alcohols biodiesels and biogas. Pyrolytic fuel oil is one of the alternative technologies which can produce oil, gas and char from waste tyres.

In this study the pyrolysis oil obtained from the waste tyres is getting renewed interest for waste steel recycling from the waste tyre part. Properties of waste tyre oil is compared with the diesel fuel and observed that the properties are quite similar to diesel fuel.

The oil contains much amount of sulfur before desulfurization and this indicates that the produced oil should be treated well before application in order to reduce the gaseous waste (SO_x).

Waste tyre are converted into shoes known as Barabaso and also cut to long ‘ropes’ that are commonly used for horse-drawn carriages in rural areas of Ethiopia. Reuse applications (shoes, straps, stool and chair seats, ceiling dividers, animal feeding troughs, carrier straps (mechagna)...etc. But this technology uses only the cracas part of the tyre from bias type. The part without carcass was loss and also contaminates the environment gradually due to this reason pyrolysis is the best technology to recycle the whole part of tyre.

Ethiopia is a rapidly developing and populated city home to a large number of vehicles, which produce large quantity of waste tyre. It needs valuable space and affectation an environmental risk due to potential leaching of toxins and contamination of soil, water and air. The aim of this study was recycling of tyres using pyrolysis in order to develop sustainable waste tyre management system.

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Appendix

Appendix A. Gas Chromatography mass-spectrometry result

Table A1 GC-MS analysis results for the fuel oil obtained by pyrolysis at 550 °C and 75 minute.

Library Search Report

Data Path : D:\2018\120218petro\
 Data File : 140217-04.D
 Acq On : 14 Feb 2018 15:27
 Operator : manager
 Sample : #13027
 Misc :
 ALS Vial : 2 Sample Multiplier: 1

Search Libraries: C:\Database\W9N11.L Minimum Quality: 80

Unknown Spectrum: Apex
 Integration Events: RTE Integrator - rteint.p

Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	5.139	2.18	C:\Database\W9N11.L			
			Toluene \$\$ Benzene, methyl	7200	000108-88-3	70
			acide \$\$ Methylbenzene \$\$ Methylbenzol			
			Benzene, methyl- (CAS) \$\$ Toluene	7210	000108-88-3	58
			\$\$ CP 25 \$\$ Methylbenzene \$\$ Toluene			
			Benzene, methyl- (CAS) \$\$ Toluene	7204	000108-88-3	58
			\$\$ CP 25 \$\$ Methylbenzene \$\$ Toluene			
2	9.579	1.58	C:\Database\W9N11.L			
			Benzene, 1,3-dimethyl- (CAS) \$\$ m-Xylene	14334	000108-38-3	58
			\$\$ m-Xylol \$\$ 1,3-Xylene \$\$ 2,4-Xylene			
			o-Xylene \$\$ Benzene, 1,2-dimethyl-	14312	000095-47-6	58
			\$\$ o-Dimethylbenzene \$\$ o-Methyltoluene			
			Benzene, 1,2-dimethyl- (CAS) \$\$ o-Xylene	14319	000095-47-6	53
			\$\$ o-Xylol \$\$ 3,4-Xylene \$\$			

- 3 9.952 6.17 C:\Database\W9N11.L
 Benzene, 1,4-dimethyl- (CAS) \$\$ p- 14357 000106-42-3 94
 Xylene \$\$ p-Xylol \$\$ 1,4-Xylene
 Benzene, 1,3-dimethyl- (CAS) \$\$ m- 14340 000108-38-3 94
 Xylene \$\$ m-Xylol \$\$ 1,3-Xylene \$\$
 2,4-Xylene
 o-Xylene \$\$ Benzene, 1,2-dimethyl- 14313 000095-47-6 93
 \$\$ o-Dimethylbenzene \$\$ o-Methylt
 oluene
- 4 12.471 0.90 C:\Database\W9N11.L
 Bicyclo[4.1.0]heptane, 7-(1-methyl 45157 053282-47-6 46
 ethylidene)-
 Camphene (CAS) \$\$ Bicyclo[2.2.1]he 45024 000079-92-5 43
 ptane, 2,2-dimethyl-3-methylene- ((CAS)
 Camphene (CAS) \$\$ Bicyclo[2.2.1]he 45015 000079-92-5 43
 ptane, 2,2-dimethyl-3-methylene- ((CAS)
- 5 12.885 1.74 C:\Database\W9N11.L
 3-C(9),4-C(9)-epoxytricyclo[4.2.2, 67282 117221-81-5 50
 0(1,5)]decane
 2H-2,4a-Ethanopentaleno[1,2-b]oxir 67402 117221-81-5 47
 ene, hexahydro-, (1a.alpha.,1b.alp
 ha.,2.beta.,
 anti-10-Methyl-endo-tricyclo[5.2.1 67768 998067-76-8 47
 .0(2.6)]decane
- 6 13.265 4.36 C:\Database\W9N11.L
 Cyclohexene, 1-methyl-4-(1-methyle 44899 005989-54-8 90
 thenyl)-, (S)- \$\$ p-Mentha-1,8-die
 ne, (S)-(-)-
 1,5-Cyclooctadiene, 1,5-dimethyl- 44973 003760-14-3 86
 \$\$ 1,5-Dimethyl-1,5-cyclooctadiene
 Cyclohexene, 4-ethenyl-1,4-dimethy 44940 001743-61-9 76

7	14.039	2.37	C:\Database\W9N11.L	1-Ethylidene-2,2-dimethyl-3-methyl enecyclopentane	45396	998045-39-6	43
				.BETA.-OCIMENE-X \$\$ 1,3,6-Octatrie ne, 3,7-dimethyl- (CAS) \$\$.BETA.- OCIMENE-Y	44662	013877-91-3	43
				1,3-Cyclopentadiene, 1,2,3,4,5-pen tamethyl-	44750	004045-44-7	42
8	14.310	2.83	C:\Database\W9N11.L	Benzene, 1,2,4-trimethyl- (CAS) \$\$ 1,2,4-Trimethylbenzene	25874	000095-63-6	83
				Benzene, 1,2,4-trimethyl- \$\$.psi. -Cumene \$\$ aS-Trimethylbenzene \$\$ Pseudocumene	25871	000095-63-6	83
				Benzene, 1,2,4-trimethyl- (CAS) \$\$ 1,2,4-Trimethylbenzene	25862	000095-63-6	81
9	14.609	1.84	C:\Database\W9N11.L	2,6,10-Dodecatrien-1-ol, 3,7,11-tr imethyl-, acetate, (E,E)-	365025	004128-17-0	59
				2,6,10-Dodecatrien-1-ol, 3,7,11-tr imethyl- \$\$ Farnesol \$\$ Farnesyl a lcohol	244456	004602-84-0	59
				FARNESYL ACETATE 2	365086	998365-08-6	59
10	15.112	2.33	C:\Database\W9N11.L	Cyclohexene, 1-methyl-4-(1-methyle thyl)- \$\$ p-Menth-1-ene \$\$ Carvome nthene	48138	005502-88-5	64
				Cyclohexene, 1-methyl-4-(1-methyle thyl)- \$\$ p-Menth-1-ene \$\$ Carvome nthene	48137	005502-88-5	58
				Cyclohexene, 1-methyl-4-(1-methyle thyl)-, (R)- \$\$ p-Menth-1-ene, (R) -(+)-	48129	001195-31-9	58

11	15.173	4.14	C:\Database\W9N11.L			
			o-Cymene	\$\$	Benzene, 1-methyl-2-(1-methylethyl)-	41692 000527-84-4 94
				\$\$	o-Cymol	
			Benzene, 1-methyl-2-(1-methylethyl)- (CAS)	\$\$	1-Methyl-2-isopropylbenzene	41695 000527-84-4 94
			Benzene, 1-methyl-3-(1-methylethyl)-	\$\$	m-Cymene	41709 000535-77-3 94
				\$\$.beta.-Cymene	
				\$\$	m-Cymol	
12	15.302	31.16	C:\Database\W9N11.L			
			dl-Limonene	\$\$	Cyclohexene, 1-methyl-4-(1-methylethenyl)- (CAS)	44855 000138-86-3 99
			D-Limonene	\$\$	Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (R)-	44902 005989-27-5 99
			dl-Limonene	\$\$	Cyclohexene, 1-methyl-4-(1-methylethenyl)- (CAS)	44868 000138-86-3 98
13	15.811	1.20	C:\Database\W9N11.L			
			Benzene, 1,3-diethyl- (CAS)	\$\$	m-Diethylbenzene	41753 000141-93-5 87
			Benzene, 1,2-diethyl- (CAS)	\$\$	1,2-Diethylbenzene	41746 000135-01-3 87
			Benzene, 1,2-diethyl-	\$\$	o-Diethylbenzene	41741 000135-01-3 87
			Benzene, 1,2-diethyl-	\$\$	o-Diethylbenzene	
14	15.953	1.38	C:\Database\W9N11.L			
			Benzene, 1,2-diethyl-	\$\$	o-Diethylbenzene	41742 000135-01-3 76
			Benzene, 1,2-diethyl- (CAS)	\$\$	1,2-Diethylbenzene	41745 000135-01-3 64
			Benzene, 1,2-diethyl- (CAS)	\$\$	1,2-Diethylbenzene	41746 000135-01-3 58
			Benzene, 1,2-diethyl-	\$\$	o-Diethylbenzene	
15	16.510	1.02	C:\Database\W9N11.L			
			Benzene, 2-ethyl-1,3-dimethyl-	\$\$		41792 002870-04-4 81

16	16.761	1.56	C:\Database\W9N11.L				
			1-(1-methylvinyl)-4-methyl-benzene	39695	998039-69-5	70	
			2,4-Dimethylstyrene	39741	002234-20-0	64	
			ethenyl-2,4-dimethyl-				
			Benzene, 2-ethenyl-1,3-dimethyl-	39610	002039-90-9	64	
			\$ Styrene, 2,6-dimethyl-				
17	17.447	0.95	C:\Database\W9N11.L				
			Benzene, 1-ethyl-2,3-dimethyl-	41771	000933-98-2	83	
			o-Xylene, 3-ethyl-				
			1,3,8-p-Menthatriene	41843	018368-95-1	83	
			,3,8-triene				
			Benzene, 1,2,3,5-tetramethyl-	41823	000527-53-7	76	
			(CAS) \$ \$ 1,2,3,5-Tetramethylbenzene				
			\$ \$ Isodurene				
18	17.650	0.90	C:\Database\W9N11.L				
			Acetamide, N-(2-cyclopropylphenyl)	412946	998412-94-6	43	
			-2-(3-methylphenoxy)-				
			6,6'-bi-Oxabicyclo[3.1.0]hexyliden	94674	998094-67-4	43	
			Pentacyclo[9.1.0.0(2,4).0(5,7).0(8	84733	998084-73-3	43	
			,10)]dodec-1-ene				
19	18.071	0.88	C:\Database\W9N11.L				
			N-ethoxycarbonyl-5-(aminoxy)pent-	320669	998320-66-9	53	
			1-enylbenzene				
			Benzene, (1-methylene-2-propenyl)-	37625	002288-18-8	43	
			(CAS) \$ \$ 2-Phenyl-1,3-butadiene				
			Benzene, 1,4,9-decatrienyl-	216843	013393-63-0	43	
			,\$ \$ (1E ,4E)-1,4,9-Decatrienylbenzene #				
20	19.103	1.35	C:\Database\W9N11.L				
			(3S)-2-Hydroxy-3-methyl-3-(4-methy	160490	998160-49-0	35	
			lphenyl)tetrahydrofuran				
			1,3-Cyclopentadiene, 5-(trans-2-et	61095	079209-36-2	27	
			hyl-3-methylcyclopropylidene)-				

21	20.699	1.34	C:\Database\W9N11.L Bicyclo[4.2.1]nona-2,4,7-triene, 7 -isopropenyl- Bicyclo[3.2.1]octa-2,6-diene, 4-(2 -methyl-1-propenylidene)- (CAS) Cyclopropane, 1,1-dichloro-2,2,3,3 -tetramethyl-	84657	998084-65-7	14
22	21.221	1.07	C:\Database\W9N11.L 5H-Benzocycloheptene Fumaric acid, propyl undec-2-en-1- yl ester 4-Methylazulene	55037	998055-03-7	52
				492112	998492-11-2	50
				55036	998055-03-6	50
23	21.506	1.76	C:\Database\W9N11.L Ethyl 4-(chloromethylene)-2,2-diph enyl-3-oxazoline-5-carboxylate 4-(p-Chlorophenyl)-2,6-diphenylpyr idine 4-(o-Chlorophenyl)-2,6-diphenylpyr idine	567372	000000-00-0	53
				568131	001498-82-4	43
				568132	998568-13-2	43
24	21.744	0.89	C:\Database\W9N11.L 9-Epipresilphiperfolane-9,15-epoxi de methyl (8S,6Z,9Z)-[7,8-dideuterio] trideca-6,9-dien-3-ynoate 1-Acetoxy-1,2-dihydro-3-oxo-3H-pyr rolizin-5-carbaldehyde	238468	998238-46-8	27
				237599	998237-59-9	22
				200416	998200-41-6	22
25	22.335	1.13	C:\Database\W9N11.L 1,4-Dimethylnaphthalene 2,3-Dimethyl-1,4-dihydronaphthalen 2-Methyl-5-phenyl-2,4-pentadiene	84705	000000-00-0	64
				84704	998084-70-4	64
				84693	998084-69-3	64
26	22.545	1.00	C:\Database\W9N11.L Acetic acid, chloro-, octadecyl es	579089	005348-82-3	45

25	22.335	1.13	C:\Database\W9N11.L		
			1,4-Dimethylnaphthalene	84705	000000-00-0 64
			2,3-Dimethyl-1,4-dihydronaphthalen	84704	998084-70-4 64
			2-Methyl-5-phenyl-2,4-pentadiene	84693	998084-69-3 64
26	22.545	1.00	C:\Database\W9N11.L		
			Acetic acid, chloro-, octadecyl ester	579089	005348-82-3 45
			Chloroacetic acid, octadecyl ester		
			Chloroacetic acid, tridecyl ester	398314	018277-85-5 43
			Tridecyl chloroacetate #		
			1-Octadecanol (CAS) Stenol	383086	000112-92-5 43
			Stearol Lanol Al		
			dol		62
27	22.674	1.30	C:\Database\W9N11.L		
			Undecane n-Undecane Hendecane	80956	001120-21-4 50
			n-C ₁₁ H ₂₄ UN 2330		
			Undecane (CAS) n-Undecane Hendecane	80958	001120-21-4 45
			n-C ₁₁ H ₂₄ UN 2330		
			AI3-21126		
			Undecane n-Undecane Hendecane	80954	001120-21-4 43
			n-C ₁₁ H ₂₄ UN 2330		
28	23.149	1.29	C:\Database\W9N11.L		
			Naphthalene, 1,4-dimethyl- (CAS)	81073	000571-58-4 76
			1,4-Dimethylnaphthalene		
			Naphthalene, 1,5-dimethyl- (CAS)	81078	000571-61-9 76
			1,5-Dimethylnaphthalene		
			Naphthalene, 2,6-dimethyl- 2,6-Dimethylnaphthalene	81130	000581-42-0 76
29	23.801	0.98	C:\Database\W9N11.L		
			Junipene	193447	000475-20-7 96
			Junipene	193449	000475-20-7 95
			Widdrene	193737	000470-40-6 93

29	23.801	0.98	C:\Database\W9N11.L			
			Junipene	193447	000475-20-7	96
			Junipene	193449	000475-20-7	95
			Widdrene	193737	000470-40-6	93
30	24.276	2.90	C:\Database\W9N11.L			
			1-Octadecanesulphonyl chloride	590842	998590-84-2	49
			Pentadecane (CAS) \$\$ n-Pentadecane	216738	000629-62-9	46
			\$\$ CH ₃ (CH ₂) ₁₃ CH ₃ \$\$.n - penta - decane			
			Octadecane, 1-chloro- \$\$ n-Octadec yl chloride \$\$ Octadecyl chloride	433162	003386-33-2	46
31	24.432	1.26	C:\Database\W9N11.L			
			(1S*,2S*,5R*,10R*)-1,6-dimethyl-10	243860	124780-75-2	43
			-ethoxy-11-oxatricyclo[5.3.0.1(2,5)undec-6-en			
			5-Cyano-1-methylcyclohexene	26488	998026-48-8	27
			4-Methyl-6-(2',6',6'-trimethylcycl ohex-1'-en-1'-yl)hex-2-yne-1,4-dio	325081	998325-08-1	22
32	24.867	1.24	C:\Database\W9N11.L			
			4,6,8-TRIMETHYLAZULENE \$\$ 4,6,8-TR	110491	000941-81-1	93
			IMETHYLAZULENE #			
			Naphthalene, 2,3,6-trimethyl- (CAS	110537	000829-26-5	90
) \$\$ 2,3,6-Trimethylnaphthalene			
			Naphthalene, 1,6,7-trimethyl- \$\$ N	110522	002245-38-7	83
			aphthalene, 2,3,5-trimethyl-			
33	25.783	0.92	C:\Database\W9N11.L			
			Phytol \$\$ 2-Hexadecen-1-ol, 3,7,11	455612	000150-86-7	43
			,15-tetramethyl-, [R-[R*,R*-(E)]]-			
			Hentriacontane \$\$ n-Hentriacontane	721660	000630-04-6	43
			\$\$ Untriacontane			
			2-Hexadecen-1-ol, 3,7,11,15-tetram	455611	000150-86-7	43
			ethyl-, [R-[R*,R*-(E)]]- (CAS) \$\$			

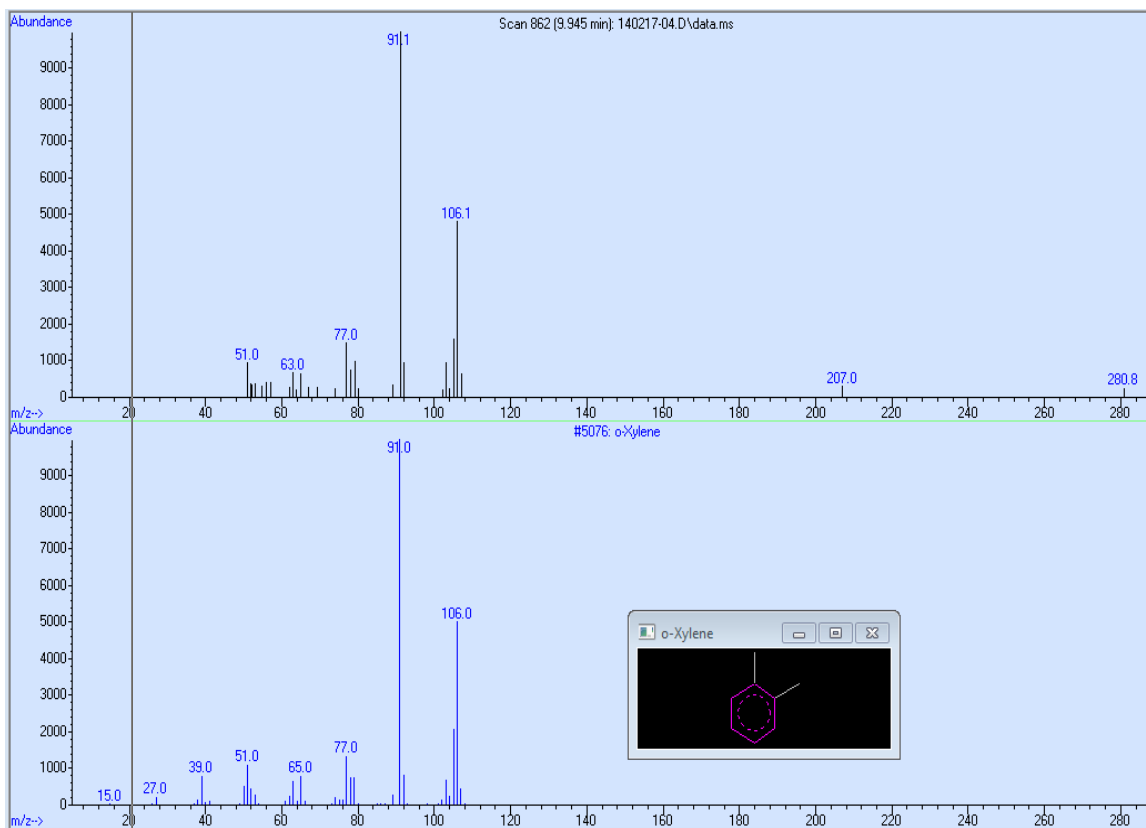
34	27.209	1.85	C:\Database\W9N11.L				
			Undecane \$\$ n-Undecane \$\$ Hendecan	80956	001120-21-4	50	
			e \$\$ n-C11H24 \$\$ UN 2330				
			Methoxyacetic acid, 2-pentadecyl e	466207	998466-20-7	49	
			ster \$\$ 1-Methyltetradecyl methoxy				
			acetate #				
			Methoxyacetic acid, 2-tetradecyl e	427621	998427-62-1	49	
			ster \$\$ 1-Methyltridecyl methoxyac				
			etate #				
35	27.609	0.97	C:\Database\W9N11.L				
			1-(Prop-1-enyl)naphthalen-2-ol	142560	998142-56-0	51	
			(E)-5,5-Dimethyl-1-phenyldec-3-en-	142919	000000-00-0	48	
			1-yne				
			ALLYL 2-NAPHTHYL ETHER	142462	998142-46-2	47	
36	28.587	1.77	C:\Database\W9N11.L				
			Eicosane (CAS) \$\$ n-Eicosane \$\$ Ic	416887	000112-95-8	55	
			osane \$\$ n - eicosane \$\$ n - icos				
			ane				
			Carbamic acid, (2-hydroxy-1-methyl	457093	117828-58-7	43	
			-4,6-tridecadienyl)-, ethyl ester,				
			[S-[R*,R*-(
			Eicosane \$\$ n-Eicosane \$\$ Icosane	416882	000112-95-8	42	
			# \$\$ n-Icosane				
37	28.750	2.40	C:\Database\W9N11.L				
			1-Octadecanesulphonyl chloride	590842	998590-84-2	45	
			Sulfurous acid, butyl tetradecyl e	551732	998551-73-2	43	
			ster				
			Sulfurous acid, butyl tridecyl est	517563	998517-56-3	43	
			er				
38	30.243	2.70	C:\Database\W9N11.L				
			Eicosane (CAS) \$\$ n-Eicosane \$\$ Ic	416887	000112-95-8	49	
			osane \$\$ n - eicosane \$\$ n - icos				
			ane				

39 32.395 1.44 C:\Database\W9N11.L
Eicosane (CAS) \$\$ n-Eicosane \$\$ Ic 416887 000112-95-8 47
osane \$\$ n - eicosane \$\$ n - ico
ne
Eicosane (CAS) \$\$ n-Eicosane \$\$ Ic 416886 000112-95-8 42
osane \$\$ n - eicosane \$\$ n - ico
ne
Eicosane \$\$ n-Eicosane \$\$ Icosane 416885 000112-95-8 42
\$\$ n-Icosane

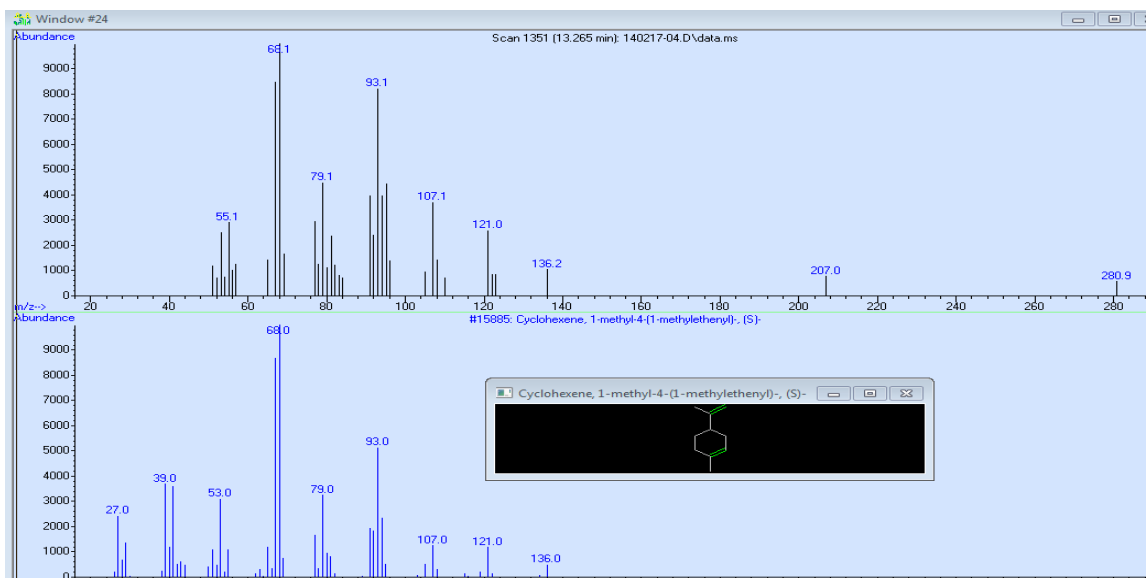
40 35.328 0.94 C:\Database\W9N11.L
Tetrapentacontane, 1,54-dibromo- \$ 817510 998817-51-0 38
\$ 1,54-Dibromotetrapentacontane #
Ethanol, 2-(tetradecyloxy)- \$\$ Myr 347897 002136-70-1 30
istyl monoethoxylate \$\$ 2-Tetradec
yloxyethanol
HAHNFETT 819412 000000-00-0 30

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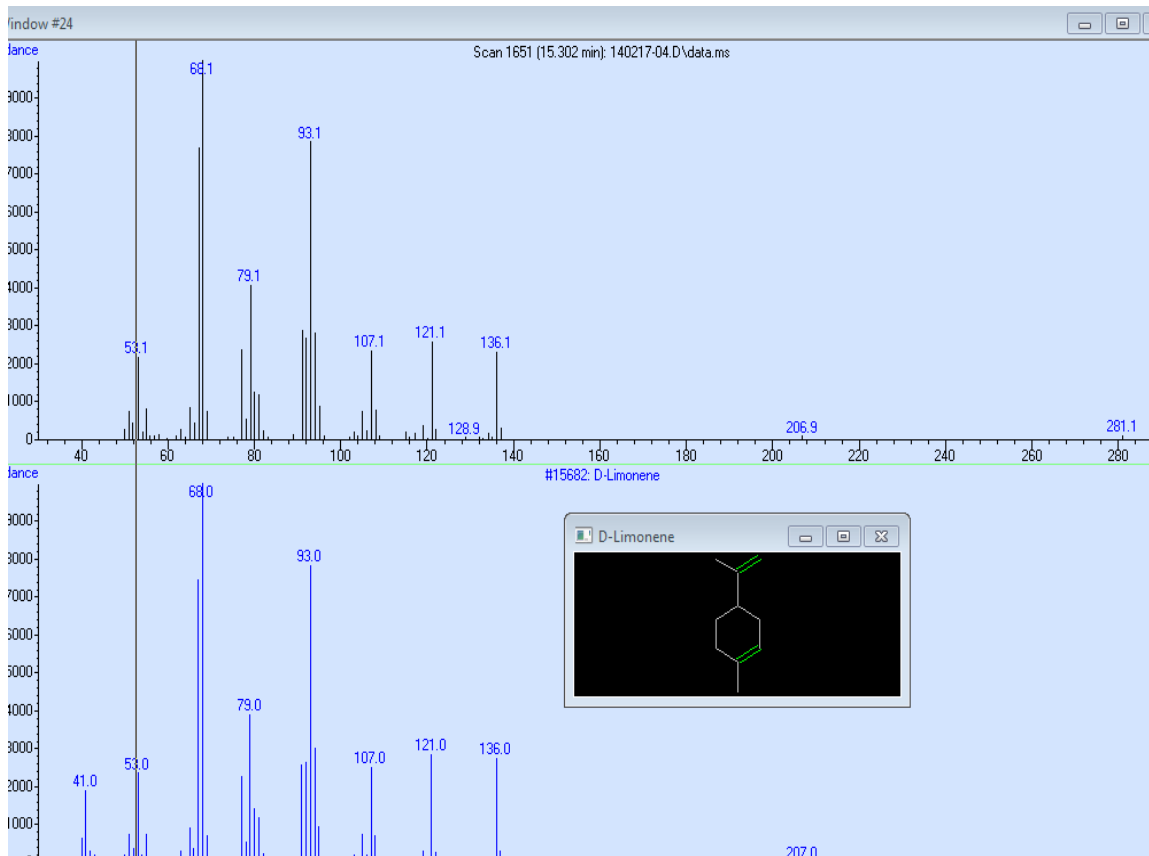
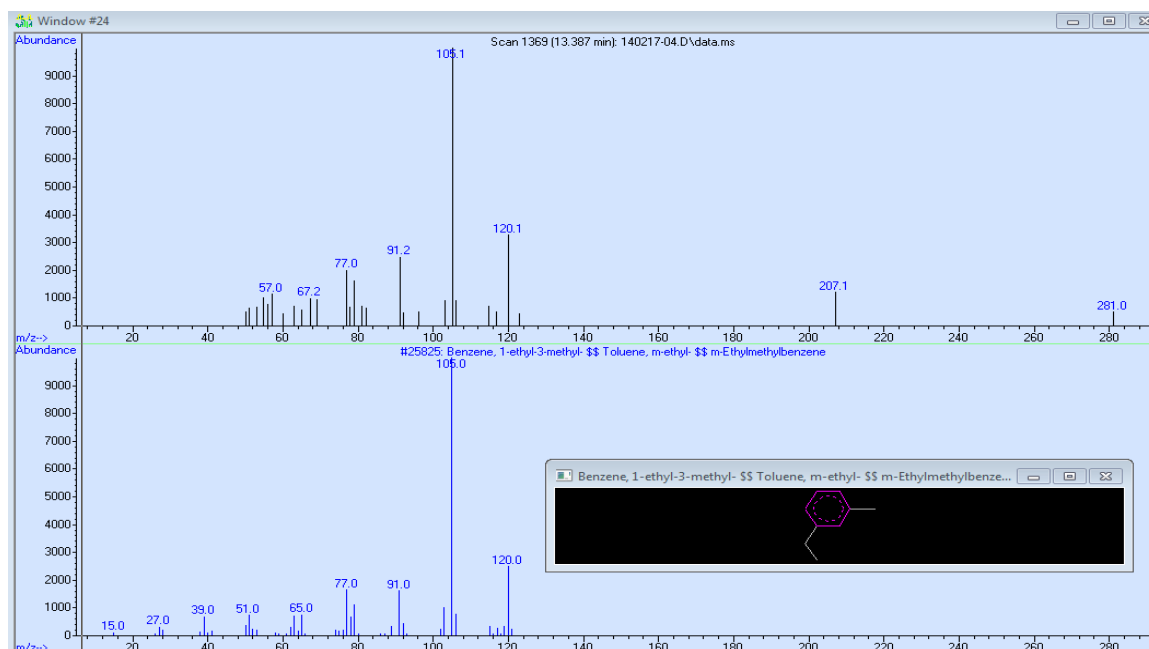
Appendix B GC-MS analysis at different retention time and peak area



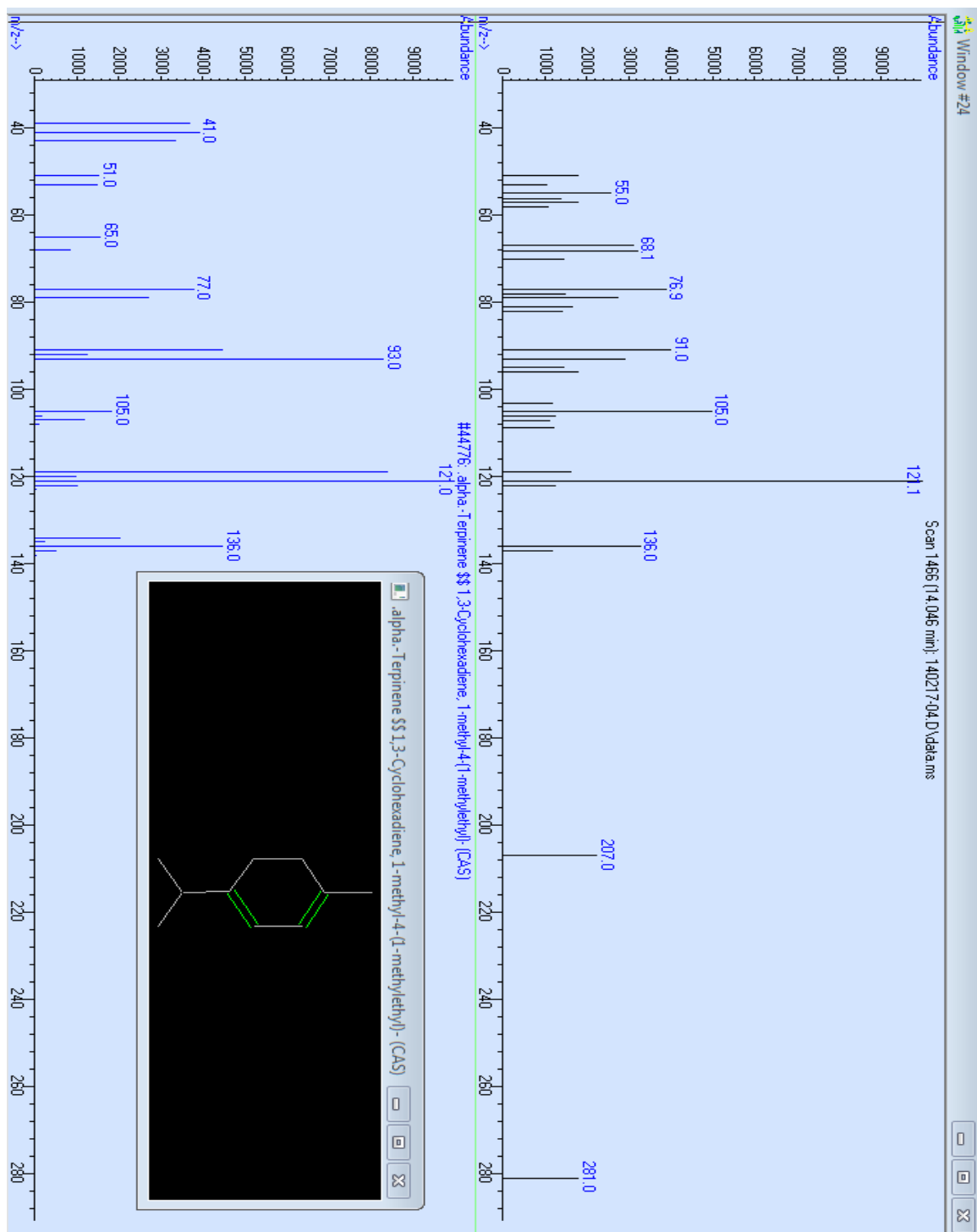
(a)



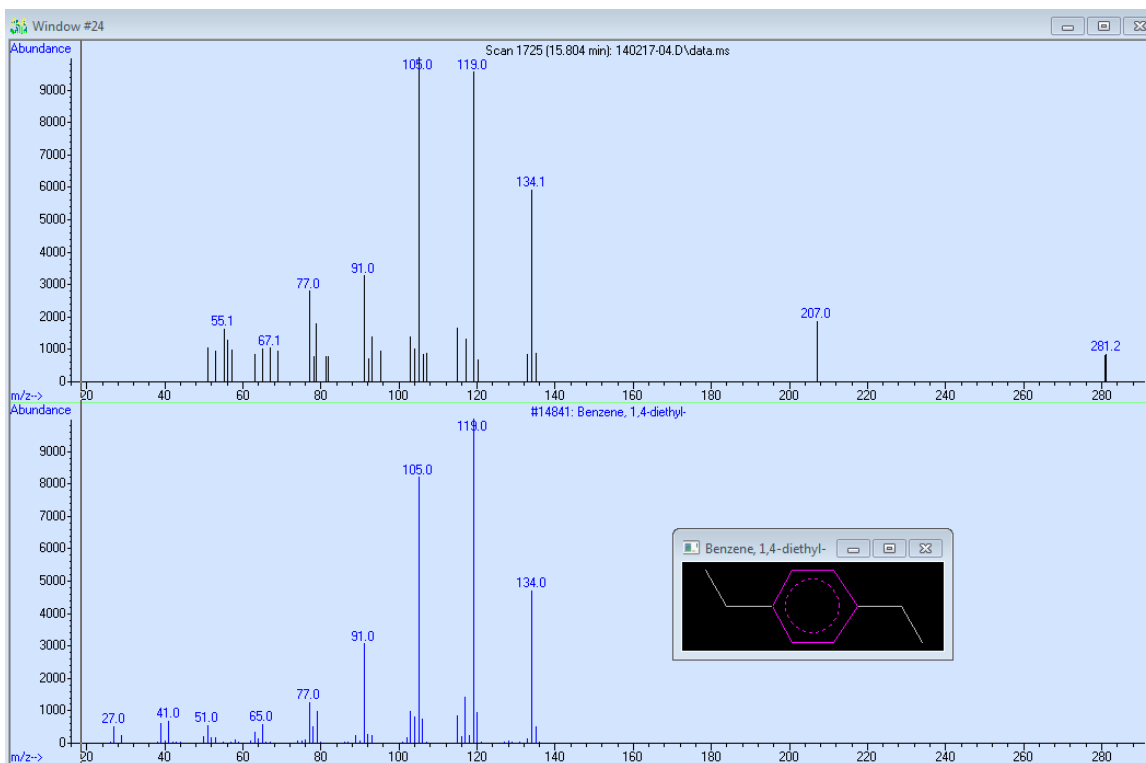
(b)



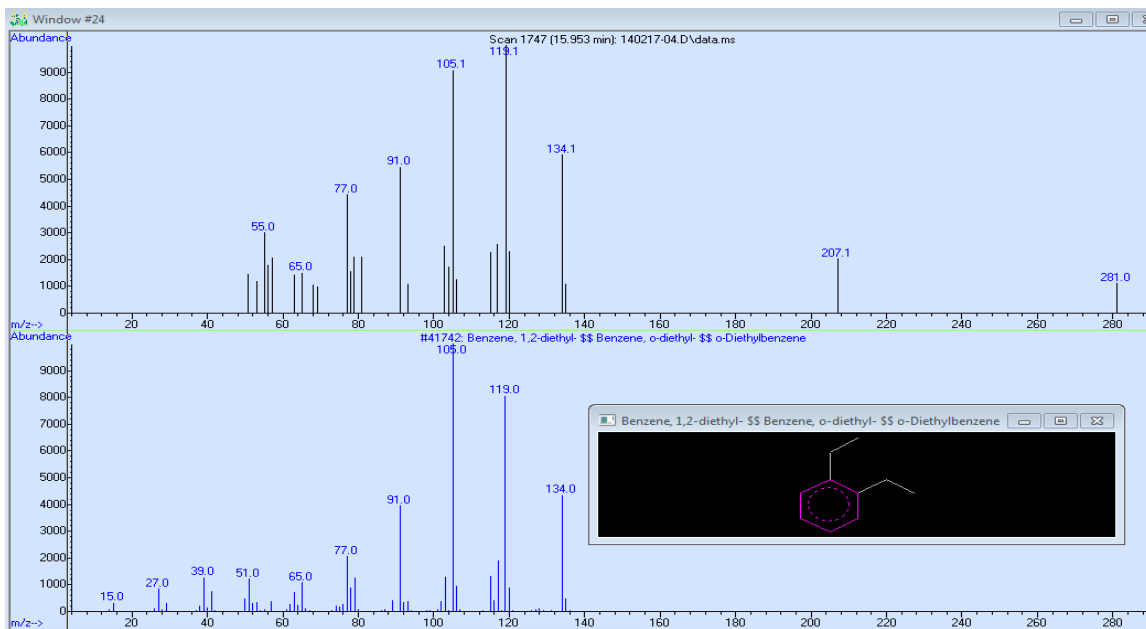
(c)



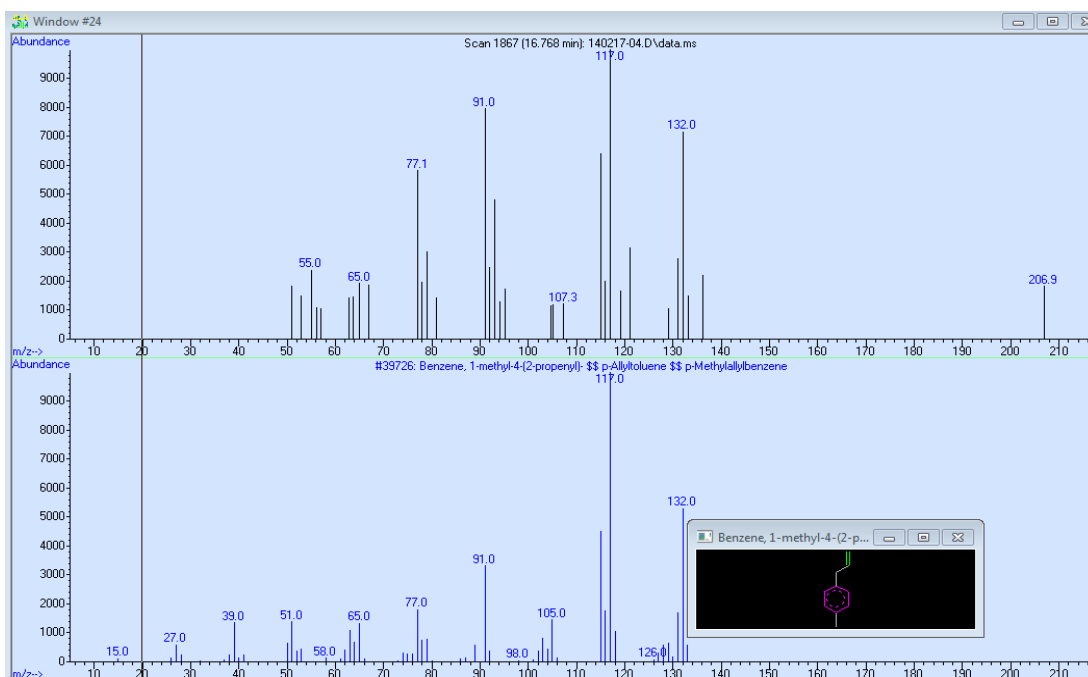
(d)



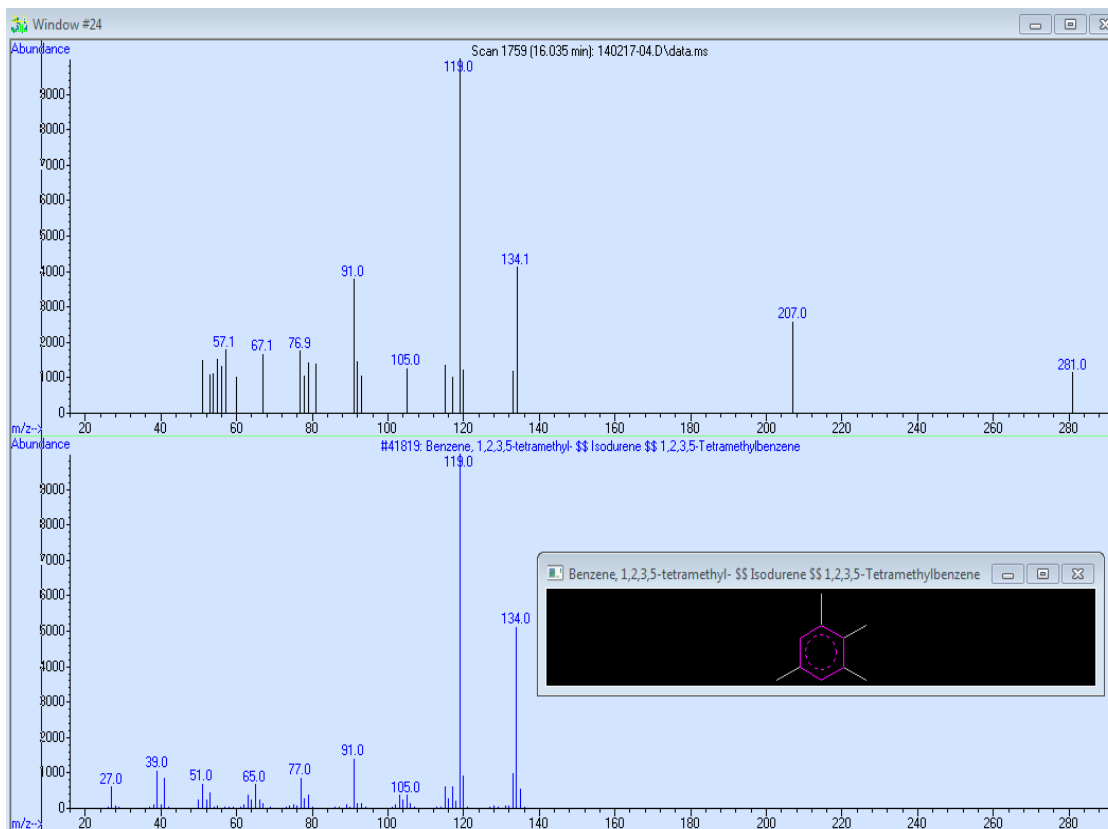
(e)



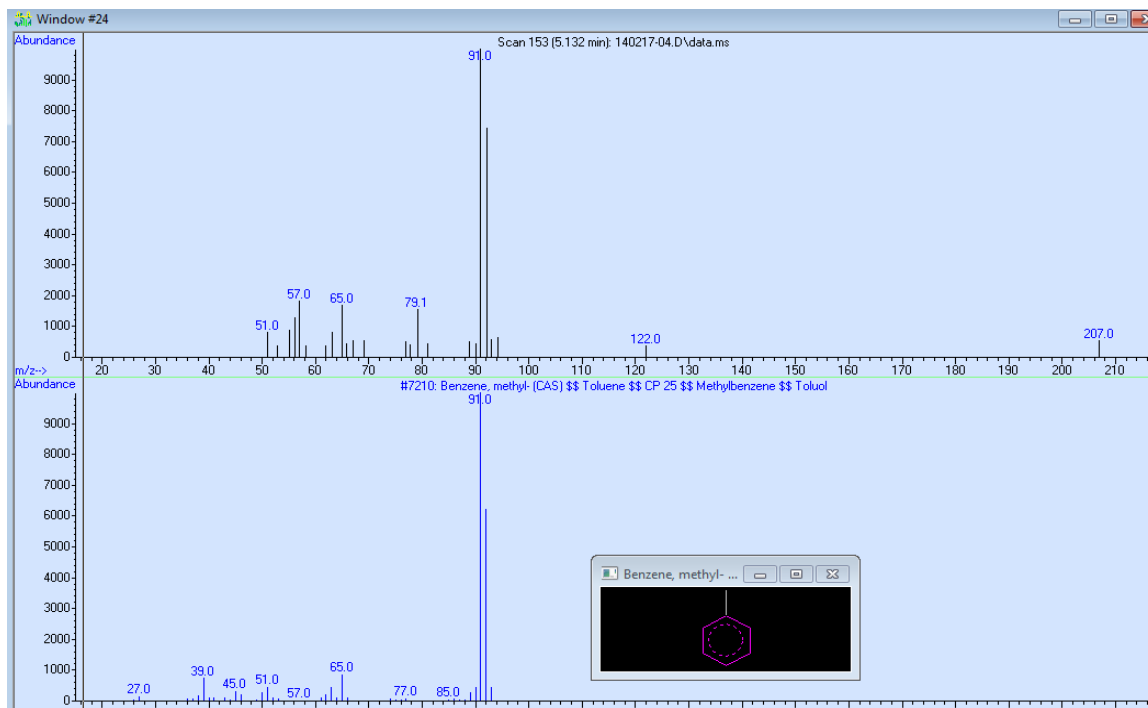
(f)



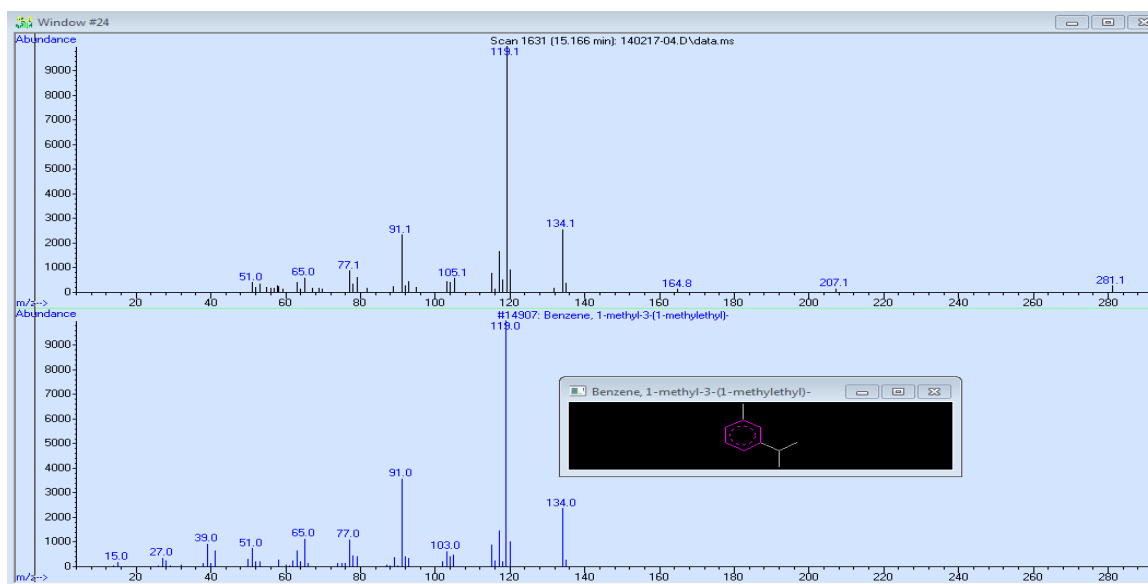
(g)



(h)



(i)



(j)

Figure B. (a-j) GC-MS analysis graph at different retention time and peak area

Appendix C FTIR infrared spectrum analysis

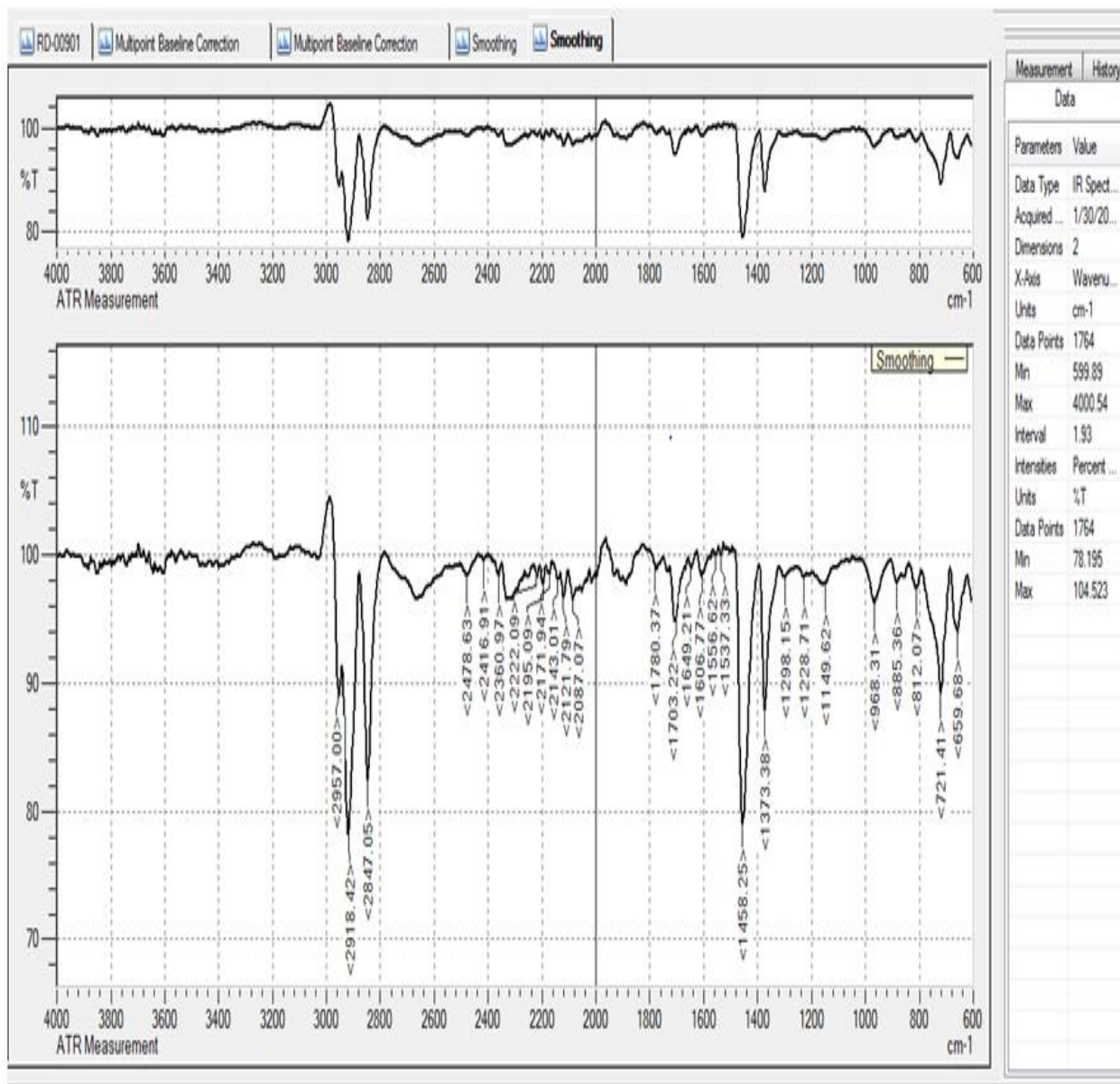


Figure C FTIR infrared spectrum analysis

Appendix D pyrolysis extracted data analysis by using design expert soft ware

Table D Analysis of experimental design (actual) data of fuel oil from waste tyre at different extraction time and temperature

Std.	Run	Block	Factor 1 Time (hr)	Factor2 Temperature (°C)	Response Yield(%)
1	27	Block 1	500	75	50.7
2	18	Block 1	500	60	52.5
3	20	Block 1	500	45	51.7
4	12	Block 1	600	45	50
5	6	Block 1	550	45	51.4
6	22	Block 1	500	60	50.6
7	5	Block 1	550	60	54.5
8	10	Block 1	500	75	55
9	2	Block 1	500	75	50.5
10	13	Block 1	600	60	51.2
11	21	Block 1	600	45	50.2
12	15	Block 1	550	75	54.1
13	26	Block 1	550	75	54.8
14	1	Block 1	500	60	50
15	4	Block 1	600	75	53.8
16	8	Block 1	600	60	53.7
17	9	Block 1	550	60	50
18	17	Block 1	600	75	54.3
19	25	Block 1	600	60	51.5
20	14	Block 1	500	60	50.9
21	3	Block 1	500	75	54.3
22	19	Block 1	550	60	53.1
23	23	Block 1	550	45	52.4
24	11	Block 1	550	45	52
25	16	Block 1	600	45	49.7
26	24	Block 1	600	75	52
27	7	Block 1	550	60	53.8

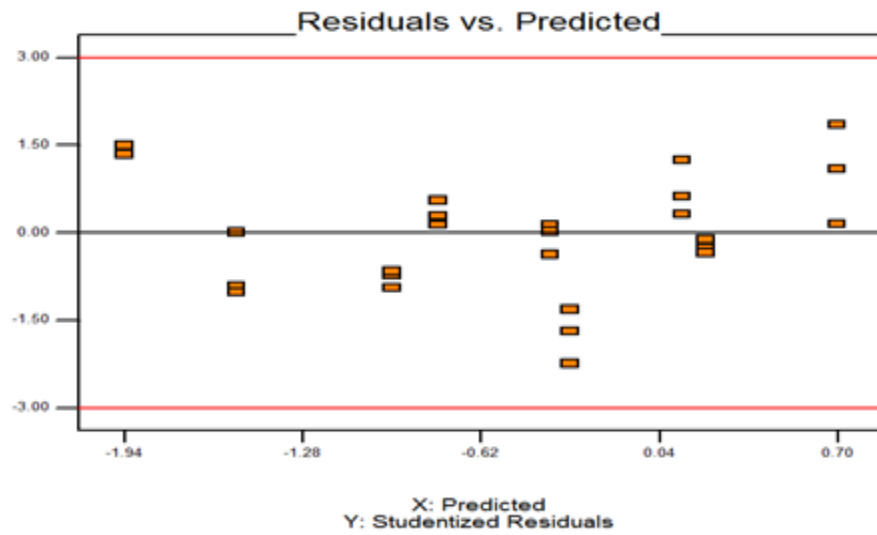


Figure D1 Residua versus predicted graph

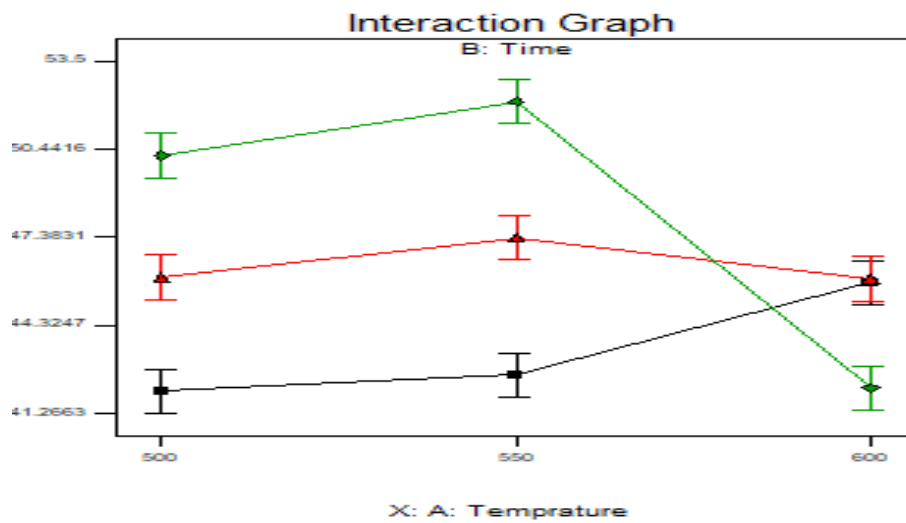


Figure D 2 interaction graph