Extraction of Pyrolytic Fuel from Non-biodegradable Solid Waste

by

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A Project submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering in the Department of Mechanical Engineering

Khulna University of Engineering & Technology
Khulna 9203, Bangladesh
November, 2013

Declaration

This is to certify that the project work entitled "*Extraction of Pyrolytic Fuel from Non-biodegradable Solid Waste*" has been carried out by *Md. Hasan Ali* in the Department of *Mechanical Engineering*, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above project work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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Acknowledgements

At first it is the author's immense pleasure to express his praiser and gratitude to the Merciful Allah, who makes him capable to successfully complete this study. The author is profoundly indebted to his supervisor Professor Dr. Md. Nawsher Ali Moral of Mechanical Engineering Department, Khulna University of Engineering & Technology, Bangladesh, for his proper guidance, inspiration, suggestion and all kinds of supports in performing and completing the dissertation works in time. The author also wishes to express his heart-felt gratitude to his advisor who tolerated his shortcomings; showed patience in author's all kind of activities relevant to research works, remove intricacy in research works and made him confidence enough in the research field. The author would like to express his sincere appreciation and gratitude to Professor Dr. Mohammad Mashud, Head of Mechanical Engineering Department, Khulna University of Engineering & Technology, Bangladesh for his cooperation to create sufficient laboratory facilities for carrying out part of the research works in this University and potential encouragement from the beginning.

Warmest and sincere thanks are extended to Mr. Pollob Kumar Shaha, Technician of Heat Engine Laboratory, for his expertise in precise fabrication of the fixed-bed fire-tube heating pyrolysis reactor system.

The author would like to express his sincere gratitude and thanks to the Vice Chancellor of Khulna University of Engineering & Technology for financial support during research period. Also, the patience, understanding, moral support and cooperation of the author's parents and family are deeply acknowledged. May Allah bless and reward all of them.

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Abstract

Under the project work waste tire and tube of bicycle/rickshaw were converted to useful fuel oil by the process of pyrolysis. In doing so fixed bed fire tube heating pyrolysis technology has been applied.

Thermal pyrolysis is one of the renewable technologies where waste tire and tube were pyrolysed into fuel oil, carbon black, and combustible gas under the action of reasonable technological conditions. This technology could not only reasonably and effectively dispose waste tire and tube without pollution, but also is effective in producing fuel that can reduce energy crisis. In the present work, thermal pyrolysis of waste bicycle tire and tube were carried out in a batch reactor made up of mild steel within the temperature range of 300°C to 600°C. The optimum pyrolytic oil of 45.29% by weight was obtained at 450°C for tire and 43.89% by weight for tube at 550°C. A higher temperature and smaller particle size increase the heating rate resulting in a decreased char yield. The cracking of the hydrocarbons with an increase of the hydrogen content in the gaseous product is favored by a higher temperature and by using smaller particle size. The residence time is another vital parameter of the converting process. The effect of raw materials on the production of pyrolytic fuel is also studied. The physical properties of the oil obtained were determined. After proper treatment these oil can be used as substitute of alternative fuel.

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CHAPTER I

Introduction

1.1 General

Energy crisis and environmental degradation are the main problems that mankind is facing now a days. This is due to the growing population, rapid industrialization and disposal of diverse solid wastes, which are generated on a regular basis. To solve this energy crisis and environmental degradation, scientists are putting much effort on the potentials of utilizing appropriate technologies to recover energy and useful by-products from domestic and industrial solid wastes. Thus considerable research has been done to recover energy from waste materials, including materials that are not bio-degradable. Such materials include biomass, municipal solid wastes, industrial wastes, agricultural wastes and other low grade fuels as well as high energy density materials such as rubber and plastics. Rubber containing wastes such as tire and tube waste are causing a big environmental problem because it is an artificial polymer and also not biodegradable. Rubber containing waste takes significantly much longer time as compared to biomass materials in case of photo degradation [1].

These discarded wastes pose a threat to the environment and human health if not handled properly. Thus timely action regarding recycling of used tire and tube is necessary to solve the problem keeping in view the increasing cost of raw materials, resource constraints and environmental problems including fire and health hazards associated with the stockpiles of the used tires and tube. Therefore, Pyrolysis is an interesting and challenging area of research. Besides that, pyrolysis of tire and tube waste has several advantages that can help resolve the energy crisis. So a number of studies have been conducted to investigate the pyrolysis of waste tires and tubes in both laboratory and industrial scale, under either inert or partial oxidizing atmosphere and may be optimized to produce high energy density oils, solid char and gases. In addition to that, the oil products can be stored until required or readily transported to where it can be most efficiently utilized [2]. And it is well known that waste tire and tube possess high volatiles and low ash content, with a heating value that is greater than that of coal and biomass. So waste tire and tube can be a source of energy and valuable chemical product, and their thermal decomposition makes the recovery of useful compounds possible. Conventional methods for tire shredding and metal separation, allows seamless incorporation of this technology for oil production and waste tire disposal. Therefore in recent years there has been an increased interest in production of oil fuel from waste tire and tube by pyrolysis method. This innovative technology, because of its portability and scalability, uniquely address the challenges faced when converting tires to low sulfur oil [3].

Bangladesh is one of the developing and most densely populated (914 persons/km^2) countries, with a total population of 135 million. About 77% people live in rural areas, but 50% of them do not own any land. More than 2.5% of adult (15–64 years old) male population (43 million) lives on rickshaw (light three-wheeled hooded vehicle) pedaling. Private car is just like a dream to 99% of ladies and gentlemen and they become passengers for the rickshaw pedalers and almost all other men use bicycle for their fast movement. It is estimated that 20.50 million (30.75x10^3 metric ton) of bicycle/rickshaw tires become scrap every year and wait for disposal [4]. The estimated value is about 37 wt% of total tire waste production in Bangladesh. Moreover, bicycle is also a common carrier for movement all over the world. It is estimated that 30,750 metric tons bicycle/rickshaw tires, 5160 metric tons motorcycle tires, and 28,900 metric tons bus and truck tires become scrap and are disposed of every year [5].

The disposal of solid tire and tube wastes from human activity is a growing environmental problem for modern society, especially in developing countries. This organic solid waste is non-biodegradable. One common way of disposal is landfilling. Landfilling for disposal of used tire and tube are connected with some problems: it needs a considerable amount of space because the volume of tires and tubes cannot be compacted. Dumped scrap tire and tube in massive stockpiles provide ideal breeding grounds for disease carrying mosquitoes and other vermin. Also, landfilling is a potential danger because of the possibility of accidental fires with high emissions of hazardous gases [4].

The pyrolysis of solid tire and tube wastes has received increasing attention since the process conditions may be optimized to produce high energy density liquids, char and gas. In addition, the liquid products can be stored until required or readily transported to where it can be most efficiently utilized.

Three products are typically obtained from the tire and tube rubber: liquids, char and gas. Tire pyrolysis liquids (a mixture of paraffins, olefins and aromatic compounds) have been found to have a high gross calorific value (GCV) of around 41–44 MJ/ kg, which would encourage their use as replacements for conventional liquid fuels [4]. In addition to their use as fuels, the liquids have been shown to be a potential source of light aromatics such as benzene, toluene and xylene (BTX), which command a higher market value than the raw oils. Similarly, the liquids have been shown to contain monoterpene such as limonene [1-methyl-4-(1-methylethenyl) - cyclohexene], a high value light hydrocarbon. Limonene has extremely fast growing and wide industrial applications including formulation of industrial solvents, resins and adhesives, as a dispersing agent for pigments, as a fragrance in cleaning products and as an environmentally acceptable solvent. It is very common in cosmetic products and also used as flaming combustible liquid. Furthermore, the biological activity of limonene, such as its chemopreventive activity against rat mammary cancer, has been recently investigated.

In order to enhance the marketability of tire and tube pyrolysis liquids, Stanciulescu and Ikura separated limonene-enriched fraction using vacuum distillations and reacted with methanol to produce limonene ethers. Methyl limonene ether is a high value product and has a very pleasant fragrance. It can be used alone or as an odor-improving additive. The former researcher groups extensively investigated separation of limonene from tire and tube-derived pyrolysis liquids using various techniques. Pyrolytic char may be used as a solid fuel or as a precursor for activated carbon. Some of the previous researcher groups studied the composition of evolved pyrolysis gas fraction and reported that it contains high concentrations of methane, ethane, butadiene and other hydrocarbon gases with a GCV of approximately 37 MJ/m^3, sufficient to provide the energy required by the pyrolysis process [4].

A variety of scrap tire and tube are available in the modern society. These are bicycle and rickshaw tires and tubes, motorcycle and auto-rickshaw tires and tubes, car and taxi tires and tubes, microbus and jeep tires and tubes, tractor tires and tubes, bus and truck tires and tubes. Tires contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cords, steel or fabric belts, and steel-wire reinforcing beads. Other components in the tire are: carbon black, extender oil, which is a mixture of aromatic hydrocarbons, sulphur, accelerator, typically an organo-sulphur compound, zinc oxide and stearic acid. There are many different manufacturers and countless different formulations available all over the world; the composition of the tire varies depending on the tire grade and manufacturers. Consequently, the tire and tube pyrolysis products may also vary in terms of yield and chemical composition depending on the source and grade of the tires and tubes.

There have been many pyrolysis woks in international literature for automotive tire and tube wastes but there is no work for the influence of rubber content in bicycle/rickshaw tires and tubes on the product yields and compositions. Thus it is an emerging issue to investigate the pyrolysis behaviors of the bicycle/rickshaw tire and tube wastes including pyrolytic product yields and product characteristics.

Very different experimental procedures have been used to obtain liquid products from tire and tube wastes by pyrolysis technology including fixed-bed reactors, fluidized-bed pyrolysis units, vacuum pyrolysis units, spouted-bed reactors etc., and ranging from laboratory to commercial scale plants. Pyrolysis yields and characteristics of the products obtained from tire tube wastes depend on type and size of feedstock, size and system configuration of reactor, efficiency of heat transfer, vapor residence time, etc. A fixed-bed consists of individual particles of different shapes and sizes, which are in contact with each other or with the void in between. Maximum liquid yields are obtained with high heating rate, at reaction temperature around 500°C and with short vapor residence time. The heat transfer rate requirement imposes particle size limitations on the feed. The cost of size reduction in financial and energy terms have been clearly realized and similarly liquid yields from the very smaller size feed is low due to the fact that too quick devolatilization occurs and secondary reaction takes place in the reactor. Moreover, longer vapor residence time contributes to secondary reactions, which leads to less oil and more gas product. A number of research works have been performed for the effect of reactor temperature on the product yields and product compositions but there have been very limited studies in the international literature for the effect of feed size and vapor residence time in tire wastes pyrolysis regime. However, more understanding for optimum operating conditions in relation to range of reactor temperature, larger feed size and vapor residence time, which make influence on the yields and composition of the derived products are essential to develop a more efficient pyrolysis unit.

One of the main objectives of the present work is to study the characteristics of the total pyrolysis liquids derived from used bicycle/rickshaw tires and tubes. In the present study, a approach in heating system for fixed-bed pyrolysis technology to the recovery of hydrocarbons from used tires and tubes; we have investigated fixed-bed pyrolysis with a fire-tube heating reactor. This process of heating has proved very effective in the technology for fire tube steam boilers. The thermal recycling of bicycle/ rickshaw tire and tube wastes by pyrolysis technology has been carried out in the internally heated fire-tube heating reactor system under N_2 atmosphere. The effects of operating temperature feed size and vapor residence time on the yields and compositions of product liquids were investigated. A detailed characterization of the whole pyrolysis liquids obtained at optimum operating conditions has been carried out including physical properties, elemental analyses, GCV etc.

1.2 Problem statement

In general, there is a lack of awareness and concern among the industry in particular and the public in general on the environmental and health impacts due to improper management of waste tires and tubes in Bangladesh. The major chunk of these environmentally associated problems takes place because of the lack of a formal, well-coordinated management system for waste tires and tubes. Thus, the disposal of vehicle tire and tube represents a major environmental issue throughout the world. For many years landfill was the main practical means for dealing with the problem of waste tire and tube. However the practice is rapidly declining as tires and tubes do not degrade easily in soil as they are bulky, taking up valuable landfill space and prevent waste compaction. Open dumping is another method of disposing the waste tires and tubes. It also has many hazardous effects on the environment. For an example when it results in an accidental fire, it causes a great deal of environmental pollution and most of the time it also pollutes the soil and contaminates underground water. So far today, waste tires and tubes have been mainly dumped in massive stockpiles, which provided ideal breeding grounds for disease carrying mosquitoes and other vermin [6].

The utilization of these waste materials is indeed an important option for checking the economic and environmental concerns of the modern society which develops with the growing production and utilization of tires and tube across the world [7]. As every tire is destined to go as waste stream for disposal/recycling/reclamation, despite its passage through retreading process, the number of used tires being discarded is going to increase significantly. Timely action regarding recycling of used tires and tubes is necessary in view of solving the problem of disposal, increasing cost of raw material, resource constraints and environmental problems including fire and health hazards associated with the stockpiles of the used tires and tubes. The problem has drawn attention of planners, environmentalists, consumers and industry in the developed countries like the countries of Western Europe, USA, Japan, Australia etc. where billions of used tires and tube are stock piled. These stockpiles are also direct loss of energy and resources in addition to fire and health hazards and other environmental issues [8]. Further incineration was studied for the thermal treatment of these wastes, because it involves combustion of waste at highly controlled temperatures. There are various general public concerns regarding the health consequences of incineration of wastes because incineration of the tire and tube waste emits a lot of toxic compounds such as dioxin, mercury, cadmium, nitrous oxide, hydrochloric acid, sulfuric acid, fluorides and particulates that can be inhaled and magnify or stay permanently in our lungs. They can cause an array of dieses like asthma and cancer. It is known that heavy metals like arsenic, lead, mercury, chromium and organic chemicals such as polycyclic aromatics hydrocarbons, dioxins and furans, radioactive materials are not destroyed by incineration [9].

Moreover, different techniques are used for tire and tube recycling such as retreading, reclaiming, incineration, grinding, etc. which have significant drawbacks and limitations [10]. A possible solution to overcome tire and tube waste problems would be pyrolysis which has currently received renewed attention from the research organizations. Pyrolysis basically involves the decomposition of the wastes at high temperatures (300-900°C) in an inert atmosphere. Three major products are typically obtained from the organic solid wastes, such as oil, solid char and gases. The pyrolysis of waste tire and tube has a number of advantages as a treatment option since the derived oils may be used directly as fuels or added to petroleum refinery feed stocks. They may also be an important source for refined chemicals. The derived gases are also useful as fuel and the solid char may be used either as smokeless fuel, carbon black or activated carbon. Pyrolysis is the economical reuse of materials from wastes like tires and tubes to obtain improved products and energy. Their high volatile nature, carbon contents and higher heating value makes them excellent material for energy recovery with the appropriate technology [11].

1.3 Environmental impact

The earth's temperature is regulated by atmospheric gases. Mainly carbon dioxide but also other gases such as nitrous oxide, ozone, CFCs and methane, allow the sun's energy to penetrate to the earth, but trap the heat radiated from the earth's surface. Scientists and others are concerned that those gases being added to the atmosphere by human activities will increase the warming at a rate unprecedented in human history. The CO_2 emissions from the use of fossil fuels that provide about 85% of the total world demand for primary energy, cause the observed increase of the CO_2 concentration in the atmosphere [12].

The use of pyrolytic fuel from non-biodegradable solid waste in a closed carbon cycle, as a substitute for fossil fuels, is one of the most promising ways for halting the increase of the CO_2 concentration. Pyrolytic Fuels make no net contributions to atmospheric CO_2 if used sustainably to allow re-growth. Pyrolytic fuels can play a significant role in reducing CO_2 by acting both as a reservoir of carbon, absorbing CO_2 from the atmosphere during growth and as direct substitute for fossil fuels [12].

Acid rain is caused mainly by SO_x, NO_x and HC1 emissions. SO_x and NO_x can be transformed in the atmosphere to H_2SO_4 and HNO_3. SO_x is produced in combustion of sulphur-bearing fuels such as petroleum and coal. SO_x emissions from the utilization of biomass fuel are negligible because biomass contains minimal sulphur. Another acidic gaseous pollutant is HCl, Produced from chlorine and mainly associated with combustion of municipal wastes [13, 14]. HC1 plays also an important role for dioxin formation during combustion [15]. Other high-chlorine bio fuels are straw and some peats.

Special attention is being paid to the NO_x emissions from combustion of nitrogen-containing fuels such as biomass, coal, peat or municipal waste. The NO_x emission from combustion of nitrogen containing fuel comes from two sources: thermal NO_x and fuel NO_x. The former is formed from the nitrogen in the combustion air and its formation is more or less dependent on the temperature and pressure in the combustor [16]. The latter comes from the oxidation of nitrogen in the fuel and is not particularly temperature sensitive. All the nitrogen oxides also enhance the greenhouse effect. During gasification, the fuel-nitrogen mainly forms NH_3. Some HCN and NO may also be formed [17, 18]. During combustion of the gases, ammonia and cyanides undergo oxidation to NOx- The pyrolysis is the initial step in both gasification and combustion. During pyrolysis part of the nitrogen in the fuel is converted to ammonia (NH_3) (the main product), hydrogen cyanide (HCN) and nitric oxide (NO). The conversion of nitrogen may also form N_2. Other part of the nitrogen remains in the char [19].

1.4 Pyrolytic Conversion

Liquid fuel production by fast pyrolysis is a promising technology. High yields of liquid products can be obtained under optimized conditions: very high heating and heat transfer rates that requires a finely ground biomass/tire-tube feed, carefully controlled temperature of around 500°C and rapid cooling of the pyrolysis vapours to give the bio-oil product [17]. Pyrolysis oil consists of water and a complex mixture of organic compounds that are condensed and collected after the pyrolysis step. The time and temperature profile between formation of pyrolysis vapours and their quenching influences the composition and quality of the liquid product. High temperatures will continue to crack the vapours and the longer the vapours are at higher temperatures, the greater the extent of cracking. Vapour residence times of a few hundred milliseconds are necessary for optimum yields of chemicals and food additives, while fuels can tolerate vapour residence times of up to around 2 s [20]. The oils produced by pyrolytic techniques have a relatively higher oxygen content and lower stability than those produced by hydrothermal liquefaction.

The amount of primary tar converted to gases increases markedly with increased temperature. At temperatures above 500°C the primary tar will crack into low molecular gases, such as methane, ethane and hydrogen. Thus a high gas production can be achieved at high temperatures (700-900°C). Rapid pyrolysis at high temperature plays an important role as the initial step in gasification and combustion.

The pyrolysis is a fast reaction at temperatures above 300°C. Pyrolysis of cellulose proceeds through two types of reactions: a gradual degradation, decomposition and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures [21]. The initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration and decarboxylation [22]. The high char yield obtained at low heating rate and low temperature can be explained by a predominance of the dehydration reactions. At temperatures below 300°C the dominating reaction of cellulose is dehydration. The gaseous products are carbon dioxide, water and carbon monoxide, while the cellulose is converted to more stable anhydrocellulose. The anhydrocellulose is more stable than cellulose, which results in a high char production. At temperatures above 300°C cellulose depolymerizes producing mainly levoglucosan. High heating rates provide shorter time for the dehydration to take place, which results in a more unstable material left for depolymerization to primary volatiles and therefore lower final char yields [23]. Also the high char yield at low heating rate has been explained by the vapour-solid interactions (secondary reactions) [24].

A pyrolysis pathway which leads to the selective formation of glycolaldehyde from cellulose has been identified [25]. The glycolaldehyde-fomiing pathway is competitive with the formation of levoglucosan. Conditions which result in the selective formation of levoglucosan from cellulose realize very low yields of glycolaldehyde and vice versa [26, 27, 28]. Temperature exercises only a weak influence on the productivity of two pathways; instead it is primarily the presence of trace amounts of salts and metal ions which determines the product slate.

1.5 Objectives of the Research Work

The aim of the proposed project is to test the pyrolysis technology in small scale at KUET. The main objectives of this research are:

- Selection and construction of a Lab scale fixed-bed fire-tube heating reactor pyrolysis system.
- To pyrolyse the organic solid wastes in a fixed-bed fire-tube heating reactor under different pyrolysis conditions and study of the role of temperature, sweeping gas flow rate and feed size on the product yields and their compositions.
- To determine the physical properties and chemical composition of the product (Pyrolytic-fuel) and compare with the commercial fuel.

CHAPTER II

Literature Review

2.1 Different types of rubber used in tire and tube

Rubber is a versatile product with various usages. It is grown in various countries worldwide and plays a crucial role in the Bangladeshi economy too. India is one of the leading producers of rubber in the world. India is fourth largest producer of natural rubber next to Thailand, Indonesia and Malaysia [1]. The growth of the industry and importance of rubber goes hand-in-hand. It is a known fact that 75% of rubber produced in the world is used in the production of tire [29]. Three major categories of rubber are used for tire and tube making. They are namely natural rubber, synthetic rubber and reclaimed rubber.

2.2 Polyolefins

Polyolefins are one type of synthetic resin produced by the polymerization of olefins or alkenes (molecules with the general formula (CnH2n) such as ethylene, propylene, butene, isoprene, pentene, etc. The name "olefin" means oil-like and refers to the oily character of the materials. Polyolefins may have many applications. Polyolefins is the most widely used plastic and in tonnage terms olefins elastmores such as styrene-butadiene copolymers has a dominant application in making of tire and tube.

2.2.1 Natural rubber

The chemical formula of natural rubber is a polymer of isoprene (2-methyl-1, 3 butadiene). 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 Ficuselastica, which is a native of the Congo, and Guayule, a desert scrub from Mexico and Arizona. Hevea is a native of the Amazon basin and until about 1910 the majority of natural rubber was derived from trees growing wild in this region [30]. It can withstand temperature up to the range of 10-60°C, has tensile strength 200 kg/cm^2 and it has high elasticity ranging from 300 to 1000 % [31,32].

2.2.2 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. Three quarters of all the SBR made goes into tires. The rest goes into products such as footwear, sponge and foamed products, waterproofed materials, and adhesives. Styrene butadiene rubber resembles natural rubber in processing characteristic as well as finished products. It possesses high abrasion-resistance, high load bearing capacity and resilience. On the other hand, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere. Butyl rubber which is used in tire inner tube, is also a synthetic rubber produced by the polymerization of isobutene with a small amount of isoprene. It is impermeable to air and other gases, that are used in tire inner tube and other products which require a good barrier against gases. The thermal stability of these rubbers makes them suitable for use in automotive radiator hoses. Their ozone resistance makes them appropriate for electrical insulation and for weather resistance. Their ability to absorb shock is earning them wide application in automotive suspension bumpers. These rubbers also have a few disadvantages they are incompatible with many natural and synthetic rubbers, they tend to pick up foreign matter and impurities, and they lose elasticity at low temperatures [30, 31, 32].

2.2.3 Reclaimed rubber

Reclaimed rubber is defined as devulcanized 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 tire, tube and miscellaneous waste rubber articles, through the application of heat and chemical agents. This is followed by intense mechanical working, which gives regenerated rubber almost original plasticity. Devulcanized material (i.e. reclaimed rubber) is also used as raw material for new tires manufacturing. The reclaimed rubber is of less tensile strength, lower in elasticity and possesses lesser wear-resistance than natural rubber. However, it is much cheaper, uniform in composition and has better ageing properties [30, 31]

Rubber mostly consists of blends of two or three rubber compounds mixed with tire additives. For example, the tread components can consist of blends of NR and SBR, compounded with carbon black, oils, and vulcanizing chemicals. The sidewall materials consist of a NR/BR blend. The structural formulas of rubber compounds can be distinguished from one another, but the main structures are similar. Polymers are high molecular weight compounds made from multiple low molecular weight building units, or monomers. Polymer structures may consist of 1000- 20000 repeating units of single or double bonded carbon-hydrogen monomers. For instance, NR is a polymer composed of isoprene, butadiene, and styrene and isobutyl units. SBR is a combination of styrene, alkane and alkene units [9].

2.3 Waste generation of tire and tube

Tire and tube are the backbone of the bicycle, rickshaw, bus, truck and many other vehicles. Bicycle and rickshaw continue to be the principal mode of transport for the low and middle income families. This is because the bicycle is both environment and people friendly. The future of the bicycle industry is bright. However, for survival the companies have to successfully restructure and modernize to achieve global competitiveness in terms of quality, cost and distribution system. The tire and tube industry is a major consumer of the domestic rubber production [29]. There is very good domestic as well as export demand of bicycle and rickshaw tire and tube. On the other hand cycling is potentially an important mode of sustainable transport because it is non-polluting, inexpensive, and good for users health and improves the quality of urban life. But the amount of cycling in most cities worldwide remains well below its potential. Bicycle production was up by 3.2% in 2007 to 130 million units, a continuation of the upward trend that has been characterized with the increase in production for most of this decade .India produces approximately 10% of the world annual bicycles [29, 33]. However with increased production of bicycle the production of tire and tube will also be increased which is proportional to the volume production of wastes.

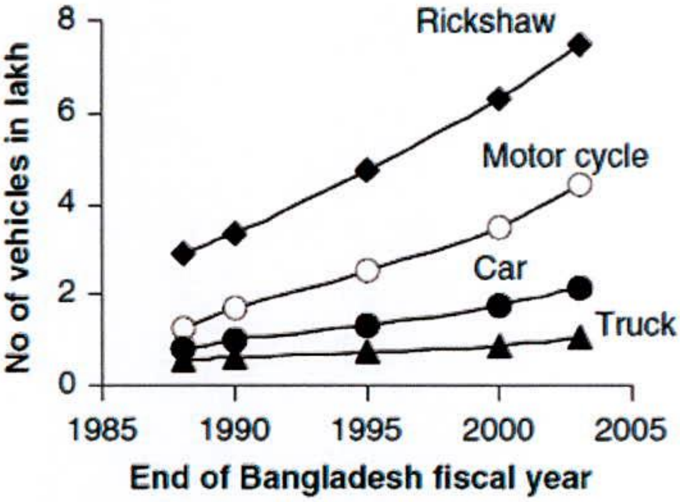


Figure 2.1: Growth rates of transport vehicles [34]

So the generation of solid wastes like tire and tube is increasing steadily. According to the statistical data with the exponential growth in number of automobiles, generation of waste tire and tube increases. In 2009, over 400 million scrap tires were generated and over 3 billion worldwide [3]. So, from the case study by it was predicted that there is an urgent need to identify viable recycling routes for waste tires. As shown in figure 2.2, tire recycling is predicted to remain flat in the UK up until 2012 with the only growth being in energy recovery. A major use in energy recovery is as a fuel source for cement kilns, where tires produce 20% more energy than coal. A considerable shortfall in the capacity of the UK to reprocess its used tires is also predicted due to the lack of economically viable alternatives to landfill [22]. About 80% of people living in rural areas use bicycle. There is also restriction of use of car and motor bikes in different places particularly in educational institutes increasing the demand for the use of cycle. This will produce a lot of tire and tube wastes. Production of these wastes can cause many environmental and hygiene problems. The mass up of this waste in the land filling sites cause problems such as:

- Breeding of insects, mosquitoes etc
- Emissions of pollutants and obnoxious gases
- Requirement of more land filling sites
- Water contamination

Thus, researchers have put many efforts in developing different ways of reusing them.

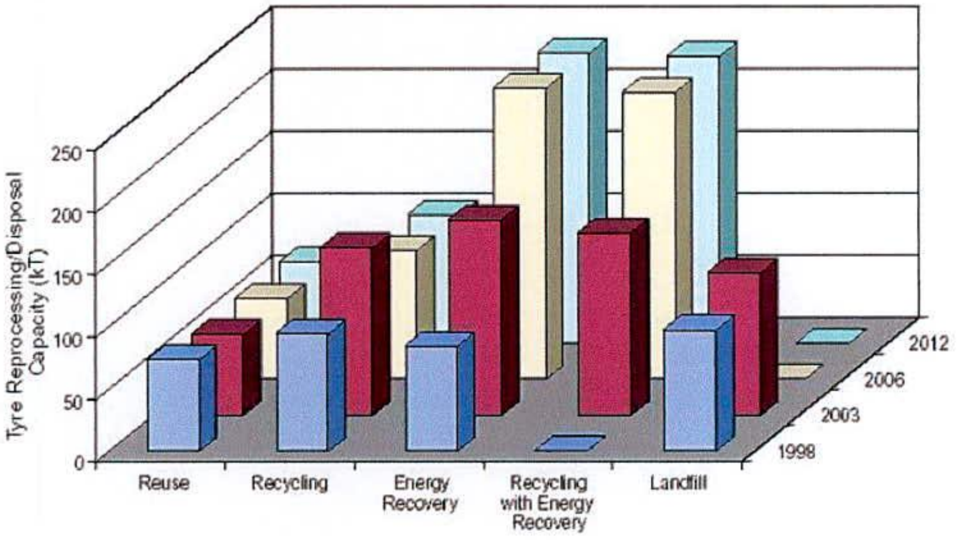


Figure 2.2: Predicted (best case) tire reprocessing capacities by category

2.4 Different types of recycling process to reduce the tire and tube waste

Pyrolysis, gasification and liquefaction are the thermo-chemical processes that can be used to convert waste tire and tube as well as other carbonaceous feed stocks such as coal, wood waste, or municipal solid waste into usable products.

2.4.1 Pyrolysis process

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. Pyrolysis usually occurs at temperature between 300°C and 900°C. In case of pyrolysis, lower temperature produces more oil products and higher temperature produces more gases [35]. This process has a number of advantages. The derived oil from tire and tube 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 [21, 36]. As studied by *Islam M.R et al.* pyrolysis basically involves the thermal decomposition of the tire rubber at high temperatures (300-

900 °C) in an inert atmosphere. The pyrolysis of solid tire wastes has received increasing attention since the process conditions may be optimized to produce high energy density oils, char and gases. In addition, the oil products can be stored until required or readily transportation to where it can be most efficiently utilized. The tire pyrolysis oils production pathway with their wide range of potential opportunities for heat, chemicals, fuels and electricity applications are indicated by figure 2.3 [23].

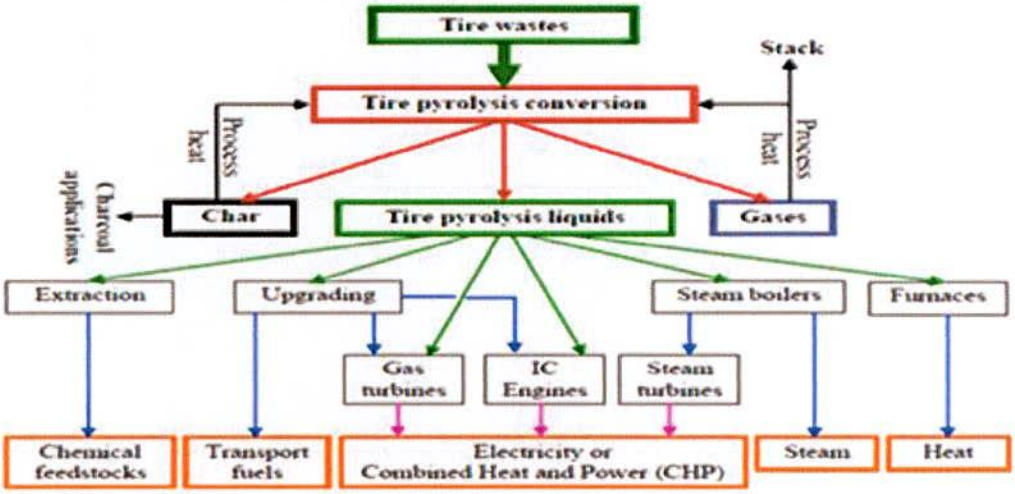


Figure 2.3: Tire pyrolysis conversion and application of products [23]

2.4.2 Thermal pyrolysis

Thermal pyrolysis is the decomposition of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 300-900 °C 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. Several researches have taken place on production of hydrocarbon oils from waste tire and tube by thermal pyrolysis. Solid motorcycle tire waste was thermally pyrolysed in a fixed bed reactor under different operating conditions with different feed size of (2 cm^3, 4 cm^3, 8 cm^3 and12 cm^3). The optimum oil (49%) was obtained at 475 °C with feed size of 4cm_3 [20]. The derived tire pyrolytic oil from thermal pyrolysis of waste tire under static-bed batch reactor at a different range of 450–600 °C was characterized and it was found that the fuel property was similar to light petroleum fuel oil. The temperature has a major influence for increase in the aromatic content of the oils, with a consequent decrease in aliphatic content [21]. *Pakdel H et al.* developed the vacuum pyrolysis process for used tires and got 45% of oil from which 27% was naphtha and showed that the mass spectrometry provides superior quantitative capabilities, while infrared spectroscopy is an excellent complementary technique for simultaneous qualitative analysis of pyrolytic oil [25]. *Kyari et al.* considered pyrolysis analysis of seven different brands of used car tires from several countries throughout the world and characterized the product oils obtained from individual and mixture of seven categories of tire wastes. They reported that there had been major variation in concentration of different compounds presented in the derived oils and gaseous products [26]. During the pyrolysis of car tire it was observed that there was no significant influence of temperature and characteristics of pyrolysis products over 500 °C. The obtained oils are a complex mixture of C_5 - C_{20} organic compounds, with a great proportion of aromatics with high gross calorific values of 42MJ/Kg. The obtained pyrolysis gases composed of hydrocarbons of which C_1 and C_4 are predominant, together with some CO, CO_2 and SH_2 and they have very high gross calorific values (68–84 MJ/ Kg). On the other hand authors have also demonstrated that at 500 °C, 600 °C and 700 °C and at longer reaction time do not decrease solid yields in tire pyrolysis. Therefore, it can be concluded that tire decomposition at 500 °C, 600 °C and 700 °C is complete and that ≈3–4% of char or carbonaceous material is produced [12]. Pyrolysis of waste tire at different degradation rate and product yields has been studied by *Y.M Chang* and proved that the effect on the degradation rate of a pyrolysis temperature of below 400 °C is more sensitive than that above this temperature. The total yield of gas products is 30-53%, oil yield is 28-42%, and char yield is 14-28% by weight. Further, the fuel oil, a part of the oil product, has a maximum level up to 15% by weight at a temperature of 350 °C [27]. The recycling of rubber from old tires by batch hydrogenation has been performed using tubing bomb reactors. Process variables such as temperature, reaction time, initial hydrogen pressure and nature of gas used have been studied and it was shown that, high temperature does not increase rubber conversion but decreases oils yield. A similar trend was found when long reaction times are used. No difference in conversion and yields was found when nitrogen was used. Results are very similar to those obtained when high hydrogen pressures are used concerning to oils quantity but not to oils quality [28].

Experimental and theoretical investigation of combustion and pyrolysis of a single rubber particle was studied by *Zuzana. K et al.* Experiment were carried out by using TGA analyzer and different conditions for particle ignition were investigated, with initial temperature ranging from 500-700 °C and initial concentrations of oxygen varying from 5 to 21 mol%. It was shown, that the combustion time depends on pyrolysis conditions. This fact can be due to different pore structure development inside the particle [29]. Many factors that affect the light oil fraction of oil produced during pyrolysis of waste tyres were investigated with GC-MS, FT-IR, and chromatographic column as separation means. The results showed that carrier gas flow rate, heating rate, and temperature influence the percent of light oil. Compared to N_2 and water vapour as carrier gas, CO_2 can better improve the fraction of light oil and reduce the fraction of heavy oil. Fast flow rate can give greater benefit to increase of the percentage of light oil. In contrast to this, fast heating rate is not favorable to improve the yield of light oil. The depth of pyrolysis was seriously related to the temperature. The content of PAH compounds in the pyrolytic oil always increased under the condition of less than 800 °C as the temperature was raised [37]. Pyrolysis of rubber appears to be a logical choice, all the more because, apart from minor fugitive sources and equipment leaks, this process products virtually no emissions. One of the problems with thermal pyrolysis is that of wide oil product distribution with poor economical value. Therefore, catalytic pyrolysis, an alternative technique to thermal pyrolysis, is under extensive exploration [38].

2.4.3 Gasification:

Gasification of organics occurs at operating conditions between the complete absences of oxygen and stoichiometric (i.e., sufficient oxygen to complete the oxidation reaction).Gasification involves drying and paralysing a feedstock, and oxidizing the solid char to heat the reaction and provide carbon monoxide (CO) to the gas. Gasification is generally carried out at higher temperatures (700-1400 °C) than pyrolysis and in the presences of a partially oxidative reactive atmosphere. In the early 1980s, the waste industry saw gasification as promising. Gasification processes maximized the effect of carbon-hydrogen ratios. Furthermore, the product gas was suitable for use in existing boilers [39]. Gasification of scrap tires seems to be an attractive method since the gaseous fuel product can be stored, transported and easily fueled for existing boilers and combustors with little modification. The characteristics of syngas evolution during pyrolysis and gasification of waste rubber have been investigated; Gasification resulted in more than 500% increase in hydrogen yield as compared to pyrolysis at 800 °C [40]. One of the disadvantages of the conventional gasification system is the high temperature that is required for decomposition of the feed stock and for the reforming reactions, which affect the overall energy efficiency of the process [41].

2.4.4 Liquefaction:

Liquefaction is the thermochemical conversion of an organic solid into petroleum-like oil. Liquefaction typically involves the production of oil composed of heavy molecular compounds from a pyrolytic gas stream. It encourages the production of oil, which can be upgraded to transportation fuels. The oil has properties similar, but not identical, to those of petroleum-based fuels. Essentially, liquefaction is manipulation of the pyrolysis process in order to produce oil with characteristics similar to petroleum-based oils (e.g., fuel oils) [39]. Tires could be liquefied singly, or in combination with other waste materials and/or coal in co-processing schemes, in one or two stage processes. The idea of including tires into a coal liquefaction process has been proven to be more advantageous on a development plant scale. Liquefaction provides an effective approach for converting the organic content into oils. Pyrolysis offers an alternative approach and is simplified since solvent is not needed.

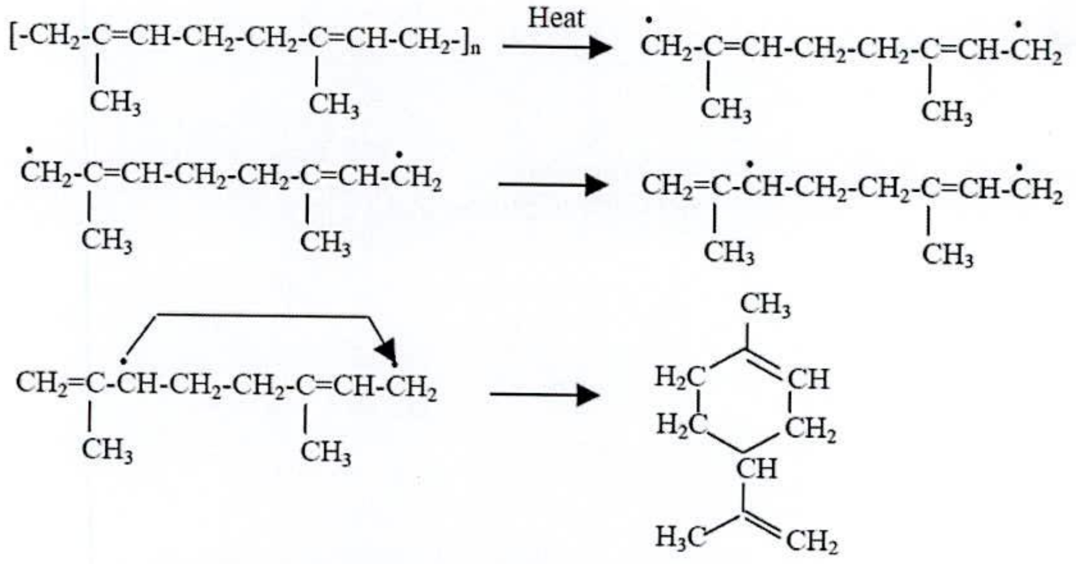
D.M. Money et al. studied the liquefaction process of scrap automobile tires by using different solvents and solvent mixes (process derived recycle solvent (PDRS) or tire pyrolysis oil (TPO) or a mixture of the two solvents). Experiments were carried out at different temperatures (360, 380, 400 °C) and for different reaction periods (400 °C, 1 or 2 hr).The results have shown that tire can be depolymerised and dissolved in PDRS, with dissolution of all the organic content under relatively moderate reaction conditions which are similar to those used in coal liquefaction. When. TPO was used as solvent; dissolution was less than PDRS under comparable conditions, especially at 380 °C when retrograde reactions occurred due to the low H-donor capacity of the TPO. No significant pressure build up was noted in any of the liquefaction experiments. Liquefaction was found to be a superior process than pyrolysis and hydropyrolysis which minimizes gas formation and maximizes oil yields [42]. Work by *Harrison and Ross* [43] showed that the addition of TPO at this level would not be detrimental to coal dissolution and suggest that coal and scrap tires could be used as a feed to the dissolution stage of two stage coal liquefaction, which could use a recycle solvent augmented by TPO to dissolve the feed, without detriment to the extent of dissolution of the individual components of the feed.

Liquefaction could also provide an effective way of dealing with scrap tyres independently, but problems with filtration caused by the presence of carbon black would need attention if excessive filtration times are to be avoided.

2.5 Reaction mechanisms occurred during pyrolysis of tire

Pyrolysis of tire depends on the various parameter and reactor type. Tire is made up of different type of rubber compounds such as natural rubber (NB), butadiene rubber (BR), or styrene butadiene rubber (SBR)and these rubbers basically consists of different types of polymer. During the pyrolysis of tire different types of polymerization reactions are formed inside the reactor.

Tamura et al. have also shown that isoprene and dipentene are formed in high concentration in natural rubber pyrolysis and have suggested that both are produced by depolymerization from the polymer radicals occurring by β-scission at double bonds. The polymer radicals are liable to form six-membered rings, especially under mild pyrolysis conditions, so the dipentene is formed predominantly at lower temperature [44]. *Bhowmick* also examined pyrolysis of natural rubber using TGA. They showed that degradation started at ~330 °C in nitrogen, with a peak weight loss at ~400 °C. They found that decomposition of tire is by radical generation via polymer chain scission and results in the formation of isoprene, dipentene and other smaller compounds [45].The thermal decomposition mechanism of waste tyre has been described by *M Rofiqul et al* and they found that polyisoprene has depolymerized forming dimeric species. Correspondingly the dimmer species, a short-life radical, could be stabilized through a two-step process driving to limonene by pyrolytic isomerization, as it happens from propylene to cyclopropane according to the following mechanism [46, 47].



Scheme 2 Reaction mechanism during pyrolysis of tyre

The solid char consists of carbon black, some solid hydrocarbons, and lower amounts of tire rubber additives such as zinc, sulfur, clays, silica, and metal oxides [48, 49]. Therefore, there is no obvious mechanism for char loss with increasing temperature, excepting only the higher temperature volatilizes some of the solid hydrocarbons content of the char [48, 50]. Competing with char loss reactions, certain amount of char or coke like carbonaceous material is formed in the pyrolysis of many polymeric materials, due to secondary repolimerization reactions among the polymer derived products [51-54]. Since solid yields do not decrease in the temperature range of 475-575°C, it may be concluded that tire decomposition is completed and carbonaceous material has been formed. The decrease in liquid yield and increase in gas yield above the temperature of 475°C are probably due to the decomposition of some oil vapor into permanent gases [55], and secondary repolimerization and/or carbonization reactions of oil hydrocarbons into char [8]. The increase in gas yields at higher temperatures is also provided by the char loss reactions. Thus, at higher temperatures the gas yields gradually become dominating. However, 475°C seems to be the optimum temperature to obtain liquid product from thermal recycling of bicycle/rickshaw, motorcycle, car and truck tire rubber by pyrolysis technology, since decomposition is complete and the liquid yields become maximized at this temperature. Pyrolysis product yields and their distributions over the whole range of temperature depend not only on the feedstock composition and operating temperature used for the experiments, but also on the specific characteristics of the system used, such as size and type of reactor, efficiency of heat transfer from the hot reactor surface to and within the tire mass, feed particle size, vapor residence time, etc. Therefore, results from different authors are difficult to compare. Moreover, sometimes contradictory data can be found in the literature. Some of the research groups [55, 56, 57, 58] found very similar product distributions to those of the present study *i.e.* solid yield decreases and gas and liquid yields increase up to an intermediate temperature and then solid yield remains almost constant while gas yield increases, and liquid yield decreases with further increase in temperature. Gonzalez et al. [56] pyrolyzed automobile tire wastes of 0.2-1.6mm diameter particles size in N_2 atmosphere for both isothermal and non-isothermal case. The temperature range studied was 350-700°C in isothermal regime and the non-isothermal experiments were performed with heating rates of 5-20°C/min until a final temperature of 600°C. Run times were 30min for their isothermal experiments. The maximum liquid and char yields were 55.6 and 37.6 wt% at 550°C for isothermal run, and 55.4 and 39 wt% at heating rate of 15°C/min for non-isothermal run. Dai et al. [56] studied pyrolysis of automotive tire waste in a circulating fluidized-bed reactor for temperature range of 360-810°C, feed size of 0.32-0.8mm and residence time of 1-5 sec and reported that the optimum conditions were: 500°C, 0.32mm and 1 sec with liquid yields of 50% and char yields of 32%. Chang [57] pyrolyzed tire wastes of particle size 2mm in diameter with N_2 atmosphere over a temperature range of 200- 800°C in a reactor, whose structural construction was similar to the Dupont TGA of model V2.2A-9900. He reported that the yield of liquid had a maximum level up to 40 wt% at 350°C with char yield of 17 wt%. Islam et al. [58] pyrolyzed automotive scrap tire in an externally heated fixed-bed reactor with N_2 atmosphere for feed sizes of 0-1cm, 1-2cm and 3-5cm, a temperature range of 350-550°C and reaction time of 25-110min. A cylindrical biomass source heater was used to heat the reactor and the gas-preheating chamber. They controlled the temperature of the reactor by varying the supply of air by means of an air blower. A maximum amount of liquid product was obtained at 450°C for a sample size of 3-5cm and reaction time of 75min. Cunliffe and Williams [48] also found similar results that the oil yield decreases from 58.1-53.1 wt% and gas yield increases over a temperature range of 450-600°C while char yield remains almost constant with a mean value of 37.8 wt%. The decreases in oil yields with increasing temperature and corresponding increases in gas yields have also been found by other researchers [59-61].

On the other hand Ucar et al. [62] pyrolyzed passenger car tire (PCT) and truck tire (TT) separately in a fixed-bed reactor at the temperatures of 550, 650 and 800°C under N_2 atmosphere, and found that the product distributions for both feed do not change significantly with increasing temperature. They obtained maximum liquid yields of 48.4±2.4 and 56±1.8 wt%; with char yields of 41.7±2.7 and 33.8±2.4 wt% at 650°C for car and truck tire feed, respectively. Similar results have been reported by other research groups. Laresgoiti et al. [63, 64] carried out pyrolysis tests in an unstirred stainless steel 3.5 dm^3 autoclave from 300 to 700°C every 100°C, and found that solid yield decreases while gas and liquid yields increase from 300 to 500°C, but not from 500 to 700°C. In their studies the maximum liquid yield was 38±1.8 wt% at 500°C with char yield of 44.8±0.6 wt%. Roy et al. [65] studied tire pyrolysis in the range 350-700°C, and found no influence of temperature on the pyrolysis yields over 500°C. The thermochemical conversion of rubber from scrap tires by pyrolysis and hydropyrolysis was studied by Mastral et al. [66]. They observed that neither the total conversion nor liquid yield increased with increasing temperature above 500°C for the pyrolysis at a heating rate of 300°C/min. On the contrary Williams et al. [50] studied pyrolysis from 300 to 720°C and observed that char and gas yields decreased while liquid yield increased in the whole temperature range, although the effect of temperature was slighter over 600°C, and varied depending on the heating rate used. Barbooti et al. [67] pyrolyzed scrap automotive tire particles of size 2-20mm, under a temperature range of 400-460°C and with a N_2 gas flow rate of 0.2-0.5 m^3/h in a fixed-bed batch reactor. They also observed that the solid yields sharply increased and liquid yields decreased for all size particles until a temperature of 430°C. The char yield for small particle decreased while the yield for relatively larger particles (16 and 20mm) almost remained constant with further increase in temperature (450-460°C). In the temperature range of 430-450°C, the yield of liquid was almost constant, but further increase of temperature from 450 to 460°C caused fast increase in liquid yield for all particle size. The gas yields decreased over the whole range of temperature. Under their system configuration the optimum conditions were: reactor temperature 430°C, gas flow rate 0.35 m^3/h and particle size 10mm with product yields of solid char and pyrolytic liquid 32.5 and 51 wt%, respectively.

CHAPTER III

Experimental Set-up and Procedure

3.1 Materials and methods

The raw materials used as feedstock for the pyrolysis were the waste tire and tube of bicycle/rickshaw. The different tires and tubes have been collected from the nearby bicycle repairing shops, Khulna city, Bangladesh. The collected tire wastes were washed by detergent to remove the mud, sand, and other contaminations with the tire body. The steel thread was removed from the tire. In order to maintain uniformity of the components in the representative samples of tires and tubes, very same tires were chopped cross-section wise into four different sizes as 1 cm × 2 cm × 0.25 cm = 0.5 cm^3; 2 cm × 2 cm × 0.250 cm = 1 cm^3; 3 cm × 2 cm × 0.25 cm = 1.5 cm^3 and 4 cm × 2 cm × 0.25 cm = 2 cm^3. The cross-section pieces, which were representative of the whole tire, contained no steel cords but the textile fabrics. The sample pieces were dried to remove moisture.

3.2 Experimental Set-up

Batch type fixed-bed fire-tube pyrolysis reactor was selected for the study. It was made of MS sheet having a length of 57 cm, the outer diameter of the unit was 16.7 cm and inner diameter of 16.0 cm. One end of the unit was sealed and the other end was connected to the feeding system. Figure 3.1 shows the schematic diagram of the experimental unit which consists of a reactor furnace system for maintaining constant temperature inside and condenser for collecting pyrolytic liquid. The major components of the unit are

(i) A fixed-bed fire-tube heating reactor
(ii) A power system (heater)
(iii) A gravity feed type reactor feeder
(iv) Two water-cooled condensers, each of them having a liquid collecting steel bottle
(v) N_2 gas cylinder
(vi) Char collecting bag
(vii) Temperature indicator
(viii) K-type thermocouples, with temperature controller

A distributor plate was fitted to support the feedstock which is at a distance of 30 mm from the bottom of the reactor. The distributor plate was made of stainless steel having 84 holes of 3 mm diameter each. The N_2 gas inlet was 4cm below the distributor plate. Eight equally spaced stainless steel, 10 mm diameter fire-tubes containing insulated electric coil of a total capacity 2.0 kW were fixed inside the reactor. The reactor was thermally insulated with asbestos and glass wool. The reactor height from the distributor to the gas exit was 57 cm and its diameter was 16 cm.

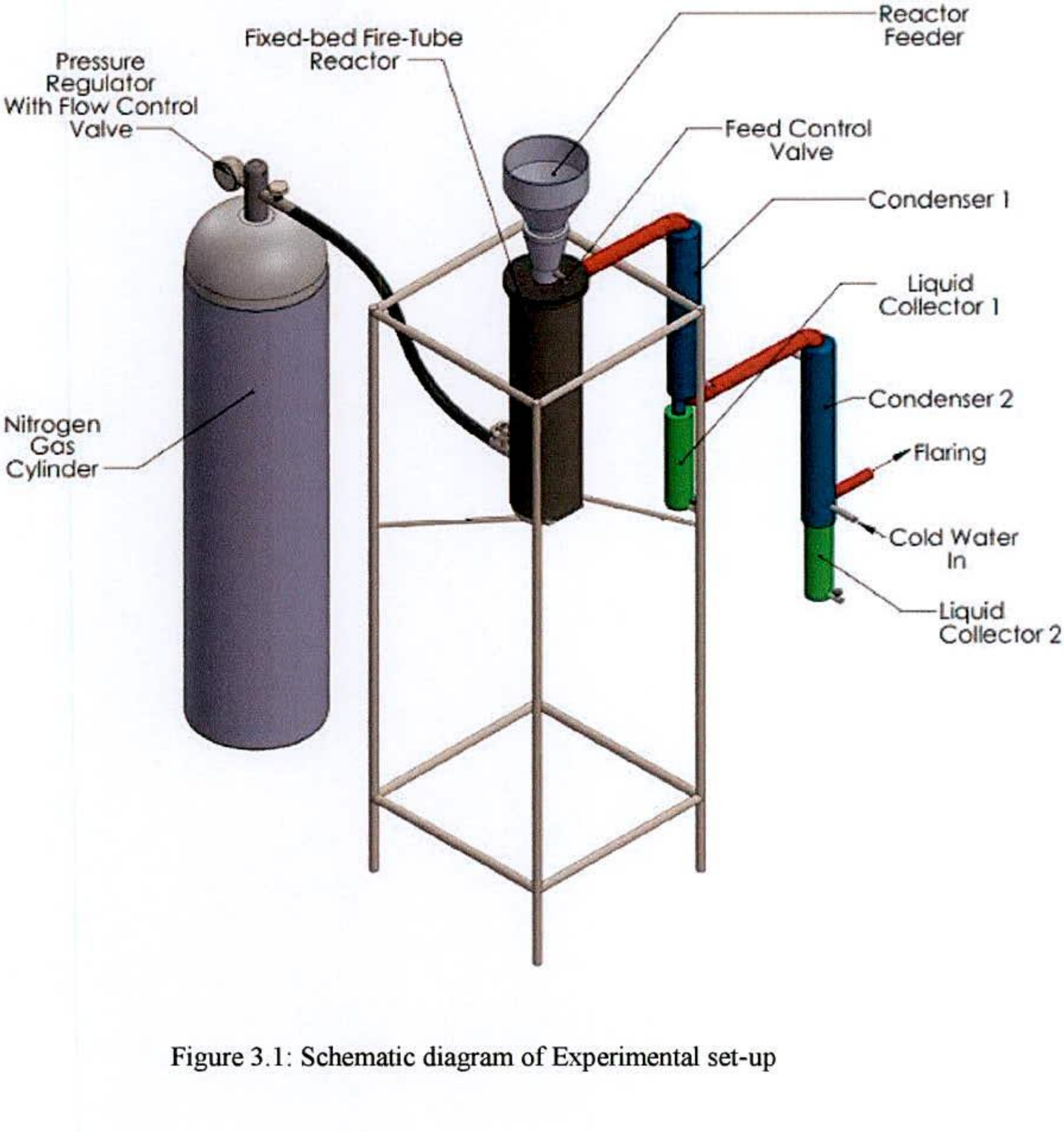


Figure 3.1: Schematic diagram of Experimental set-up

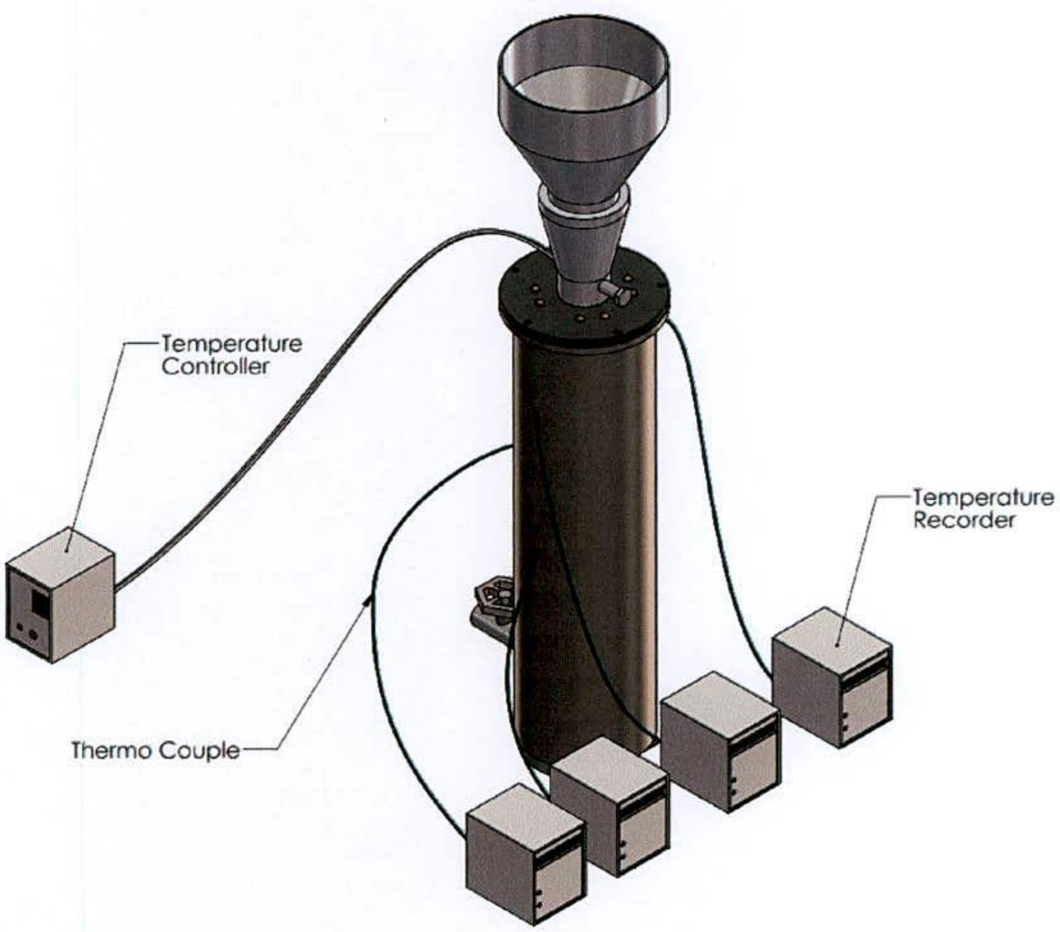


Figure 3.2: Schematic diagram of Reactor

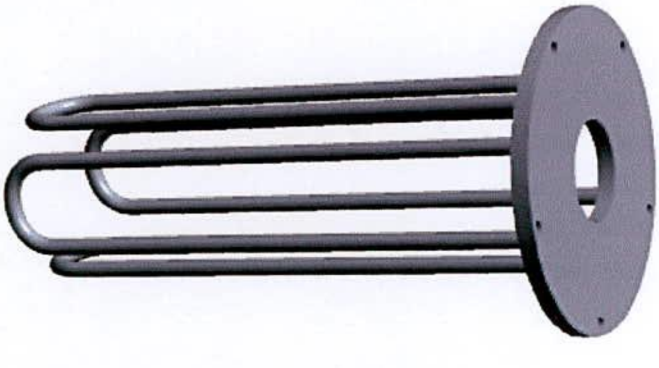


Figure 3.3: Schematic diagram of heater

Figure 3.4: Photograph of the fixed-bed fire-tube heating pyrolysis system

3.3 Experimental Procedure

The batch type fixed-bed fire-tube heating pyrolysis system was constructed and placed (installed) in the Heat Engine Laboratory of Department of Mechanical Engineering, Khulna University of Engineering & Technology. The experiments were performed for different temperature and feed volume (size of raw material). The experiments were performed separately for tire and tube. In case of tire 1.7 kg of sample were taken in the reactor in each run. 1.8 kg of sample was taken in the reaction chamber in each run in the case of tube pyrolysis. Feeding of the raw materials were maintained by the action of gravity. Before the start of the experiment, the reactor was purged by the flow of N_2 for 2 minutes to remove the inside air. The reactor heater was switched on, and the temperature of the reactor was allowed to rise to a desired value of 300, 350, 400, 450, 500, 550 or 600 °C indicated by the temperature recorder. The thermocouple sensors were placed in the reactor chamber to record the temperature. The temperatures were noted from the digital recorder during experiment. At the same time, the temperature was controlled by a temperature controller. During pyrolysis of tire and tube, a reddish/bright brown visible vapor usually flared into the atmosphere. When the decomposition was completed, colorless gas came out from the reactor. The colorless flaring was the significance of the completion of the thermal decomposition of the sample (tire) inside the reactor. After completion of all runs usually no further visible vapor product came out. Nitrogen gas was supplied in order to maintain the inert atmosphere in the reactor and also to sweep away the pyrolyzed vapor product to the condensers. Pyrolysis vapor product was passed through two sets of condenser pipes to quench into liquid and then collected in the steel bottles. The uncondensed gases were flared to the atmosphere. The bottles were completely filled up with liquid so that no air could be trapped into the bottles. When pyrolysis of the feed material in the reactor was completed, the vapor exit port was closed and, the reactor heater was switched off and N_2 gas supply was also stopped. After cooling down the system, the char product was pushed out from the reactor chamber. Char was collected in the char collection bag and weighed. The liquid was then weighed and gas weight was determined by subtracting the sum of the liquid and char weight from the total weight of feedstock. Afterwards, the system had been made ready for the next run just repositioning the valves.

Initially, the experiments were performed by varying the temperature within the range of 300-600°C at every 50°C interval for a particular feed size of tire. Once the temperature of maximum liquid yield was selected, additional experiments were conducted at the optimum temperature of 450°C by varying the feed size to find out the optimum process conditions. Same procedure was followed for pyrolytic conversion of tube within the temperature range of 300-600°C. Before analyzing the liquid product, heavy condensate and impurities were removed by gravity action.

CHAPTER IV

Experimental Data

The raw materials used were the waste tire and tube of bicycle/rickshaw. During experiments 1.7 kg tire and 1.8 kg tube were taken in the reactor chamber separately in each case. The experiments were conducted for four different size of raw material which are 1 cm × 2 cm × 0.25 cm = 0.5 cm^3; 2 cm × 2 cm × 0.25 cm = 1.0 cm^3; 3 cm × 2 cm × 0.25 cm = 1.5 cm^3 and 4 cm × 2 cm × 0.25 cm = 2 cm^3. The experiments were performed by varying the temperature within the range of 300-600°C at every 50°C interval for each feed size of tire and tube. The data collected during pyrolytic conversion of tire and tube is shown in Table 4.2 through 4.11.

Table 4.1: Details of Sample

SI. No.	Tire and tube		Weight	
	Sample Size (cm × cm × cm)	Volume (cm^3)	Tire (kg)	Tube (kg)
1	1 × 2 × 0.25	0.5	1.7	1.8
2	2 × 2 × 0.25	1.0	1.7	1.8
3	3 × 2 × 0.25	1.5	1.7	1.8
4	4 × 2 × 0.25	2.0	1.7	1.8

Table 4.2: Experimental data of pyrolysing 1.7 kg of tire having volume of 0.5 cm^3 (Size 1 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.35	1.25	0.10	66
2	350	0.48	1.10	0.12	54
3	400	0.68	0.89	0.13	46
4	450	0.72	0.79	0.19	42
5	500	0.71	0.75	0.24	39
6	550	0.70	0.72	0.26	35
7	600	0.65	0.69	0.36	31

Table 4.3: Experimental data of pyrolysing 1.7 kg of tire having volume of 1.0 cm^3 (Size 2 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.37	1.22	0.11	62
2	350	0.51	1.06	0.13	53
3	400	0.70	0.85	0.15	44
4	450	0.75	0.75	0.20	40
5	500	0.73	0.72	0.25	37
6	550	0.70	0.70	0.30	32
7	600	0.66	0.68	0.36	31

Table 4.4: Experimental data of pyrolysing 1.7 kg of tire having volume of 1.5 cm^3 (Size 3 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.39	1.19	0.12	60
2	350	0.54	1.00	0.16	52
3	400	0.70	0.80	0.20	43
4	450	0.77	0.71	0.22	39
5	500	0.75	0.71	0.24	35
6	550	0.71	0.70	0.29	30
7	600	0.66	0.68	0.36	28

Table 4.5: Experimental data of pyrolysing 1.7 kg of tire having volume of 2.0 cm^3 (Size 4 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.38	1.19	0.13	59
2	350	0.53	1.04	0.13	50
3	400	0.70	0.82	0.18	40
4	450	0.75	0.74	0.21	37
5	500	0.73	0.71	0.26	33
6	550	0.69	0.69	0.32	28
7	600	0.66	0.69	0.35	27

Table 4.6: Experimental data of pyrolysing 1.8 kg of tube having volume of 0.5 cm^3 (Size 1 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.35	1.37	0.08	73
2	350	0.40	1.29	0.11	64
3	400	0.52	1.10	0.18	55
4	450	0.65	0.92	0.23	46
5	500	0.69	0.85	0.26	43
6	550	0.71	0.81	0.28	40
7	600	0.70	0.79	0.31	36

Table 4.7: Experimental data of pyrolysing 1.8 kg of tube having volume of 1.0 cm^3 (Size 2 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.37	1.35	0.08	72
2	350	0.42	1.26	0.12	63
3	400	0.55	1.06	0.19	55
4	450	0.68	0.88	0.24	46
5	500	0.71	0.83	0.26	42
6	550	0.73	0.79	0.28	40
7	600	0.72	0.77	0.31	35

Table 4.8: Experimental data of pyrolysing 1.8 kg of tube having volume of 1.5 cm^3 (Size 3 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.39	1.31	0.10	72
2	350	0.45	1.22	0.13	61
3	400	0.57	1.02	0.21	53
4	450	0.70	0.85	0.25	45
5	500	0.74	0.80	0.26	42
6	550	0.76	0.76	0.28	40
7	600	0.75	0.73	0.32	35

Table 4.9: Experimental data of pyrolysing 1.8 kg of tube having volume of 2.0 cm^3 (Size 4 cm × 2 cm × 0.25 cm) for various temperatures

No. of Observation	Temperature (°C)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	300	0.40	1.30	0.10	70
2	350	0.47	1.19	0.14	60
3	400	0.58	1.00	0.22	52
4	450	0.70	0.86	0.24	44
5	500	0.76	0.77	0.27	41
6	550	0.79	0.72	0.29	38
7	600	0.77	0.70	0.33	35

Table 4.10: Experimental data of 1.7 kg tire for various sample size

No. of Observation	Feed Size (cm^3)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	0.5	0.65	0.75	0.30	60
2	1.0	0.70	0.75	0.25	52
3	1.5	0.77	0.73	0.20	43
4	2.0	0.71	0.73	0.26	39

Table 4.11: Experimental data of 1.8 kg tube for various sample size

No. of Observation	Feed Size (cm^3)	Product yield			Residence Time (min)
		Oil, kg	Char, kg	Gas, kg	
1	0.5	0.63	0.86	0.31	60
2	1.0	0.67	0.85	0.28	52
3	1.5	0.74	0.80	0.26	43
4	2.0	0.79	0.76	0.25	39

CHAPTER V

Results and Discussion

5.1 Presentation of Result

Under the study of pyrolytic conversion of waste tire and tube in batch type fixed-bed fire-tube heating reactor system, the unit was tested in the temperature range of 300°C to 600°C. The experimental data are shown in Table 4.2 to Table 4.11 and the results calculated from the data are shown in Table 5.1 to Table 5.10, from which figs 5.1 to 5.14 have been drawn.

Table 5.1: Effect of temperature on product distribution of pyrolysis of 0.5 cm^3 (1 cm × 2 cm × 0.25 cm) tire

No. of Observation	Temperature (°C)	Weight of tire (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.7	20.59	73.53	5.88
2	350		28.24	64.71	7.05
3	400		40.00	52.35	7.65
4	450		42.35	46.47	11.18
5	500		41.76	44.12	14.12
6	550		41.18	42.35	16.47
7	600		38.23	40.59	21.18

Table 5.2: Effect of temperature on product distribution of pyrolysis of 1.0 cm^3 (2 cm × 2 cm × 0.25 cm) tire

No. of Observation	Temperature (°C)	Weight of tire (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.7	21.76	71.76	6.48
2	350		30.00	62.35	7.65
3	400		41.18	50.00	8.82
4	450		44.12	44.12	11.76
5	500		42.94	42.35	14.71
6	550		41.18	41.18	17.64
7	600		38.82	40.00	21.18

Table 5.3: Effect of temperature on product distribution of pyrolysis of 1.5 cm^3 (3 cm × 2 cm × 0.25 cm) tire

No. of Observation	Temperature (°C)	Weight of tire (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.7	22.94	70.00	7.06
2	350		31.76	58.82	9.42
3	400		41.18	47.06	11.76
4	450		45.29	41.76	12.95
5	500		44.12	41.76	14.12
6	550		41.76	41.18	17.06
7	600		38.82	40.00	21.18

Table 5.4: Effect of temperature on product distribution of pyrolysis of 2.0 cm^3 (4 cm × 2 cm × 0.25 cm) tire

No. of Observation	Temperature (°C)	Weight of tire (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.7	22.35	70.00	7.65
2	350		31.18	61.18	7.64
3	400		41.18	48.23	10.59
4	450		44.12	43.53	12.35
5	500		42.94	41.76	15.3
6	550		40.59	40.59	18.82
7	600		38.82	40.59	20.59

Table 5.5: Effect of temperature on product distribution of tube pyrolysis of 0.5 cm^3 (1 cm × 2 cm × 0.25 cm) tube

No. of Observation	Temperature (°C)	Weight of tube (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.8	19.44	76.11	4.45
2	350		22.22	71.67	6.11
3	400		28.89	61.11	10.00
4	450		36.11	51.11	12.78
5	500		38.33	47.22	14.45
6	550		39.44	45.00	15.56
7	600		38.89	43.89	17.22

Table 5.6: Effect of temperature on product distribution of tube pyrolysis of 1.0 cm^3 (3 cm × 2 cm × 0.25 cm) tube

No. of Observation	Temperature (°C)	Weight of tube (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.8	20.56	75.00	4.44
2	350		23.33	70.00	6.67
3	400		30.56	58.89	10.55
4	450		37.78	48.89	13.33
5	500		39.44	46.11	14.45
6	550		40.56	43.89	15.55
7	600		40.00	42.78	17.22

Table 5.7: Effect of temperature on product distribution of tube pyrolysis of 1.5 cm^3 (2 cm × 2 cm × 0.25 cm) tube

No. of Observation	Temperature (°C)	Weight of tube (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.8	21.67	72.78	5.55
2	350		25.00	67.78	7.22
3	400		31.67	56.67	11.66
4	450		38.89	47.22	13.89
5	500		41.11	44.44	14.45
6	550		42.22	42.22	15.56
7	600		41.67	40.56	17.77

Table 5.8: Effect of temperature on product distribution of tube pyrolysis of 2.0 cm^3 (4 cm × 2 cm × 0.25 cm) tube

No. of Observation	Temperature (°C)	Weight of tube (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.8	22.22	72.22	5.56
2	350		26.11	66.11	7.78
3	400		32.22	55.56	12.22
4	450		38.89	47.78	13.33
5	500		42.22	42.78	15.00
6	550		43.89	40.00	16.11
7	600		42.78	38.89	18.33

Table 5.9: Effect of feedstock size on product distribution of tire pyrolysis

No. of Observation	Feed Size (cm^3)	Weight of tire (kg)	% of Product yield		
			Oil	Char	Gas
1	0.5	1.7	38.24	44.12	17.64
2	1.0		41.18	44.12	14.70
3	1.5		45.29	42.94	11.77
4	2.0		41.76	42.94	15.3

Table 5.10: Effect of feedstock size on product distribution of tube pyrolysis

No. of Observation	Feed Size (cm^3)	Weight of tube (kg)	% of Product yield		
			Oil	Char	Gas
1	0.5	1.8	35.00	47.78	17.22
2	1.0		37.22	47.22	15.56
3	1.5		41.11	44.44	14.45
4	2.0		43.89	42.22	13.89

Table 5.11: Physical properties of pyrolytic oil derived from tire tube at optimum temperature of 450° for tire and 550° for tube respectively

Properties	Oil extracted from tire	Oil extracted from tube	Diesel
Density (Kg/m^3)	917.9	918.4	820 t0 860
Kinematic Viscosity in @100°CeSt	5.31	2.94	2 to 4.5
Flash Point °C	39	42	≥ 55
Fire Point °C	4	6	65
Pour Point °C	-3	-6	-40 to -1
Gross Calorific Value (MJ/Kg)	34.61	34.51	44 to 46
Boiling Point °C	362	360	N/A

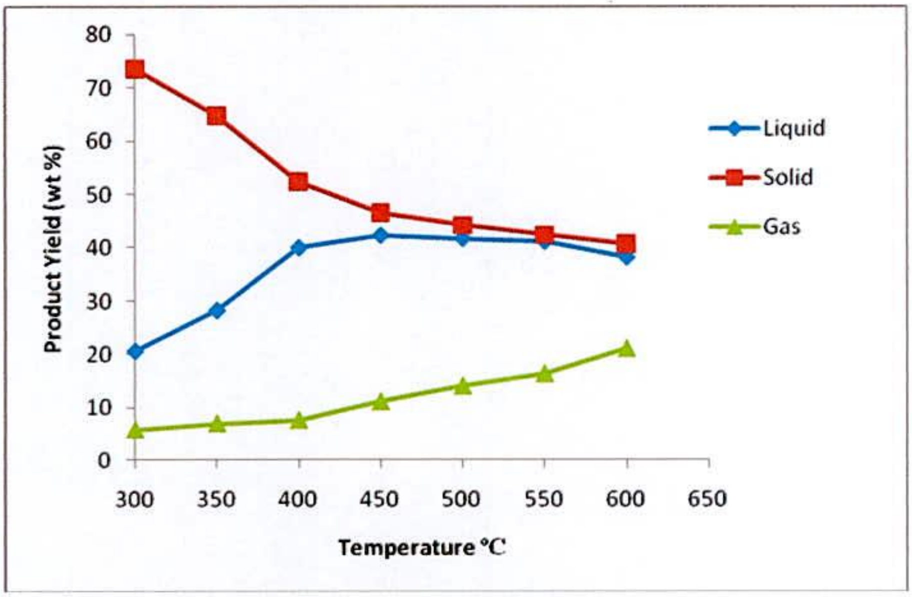


Figure 5.1: Effect of temperature on product yields (feed size 0.5 cm^3) for tire pyrolysis

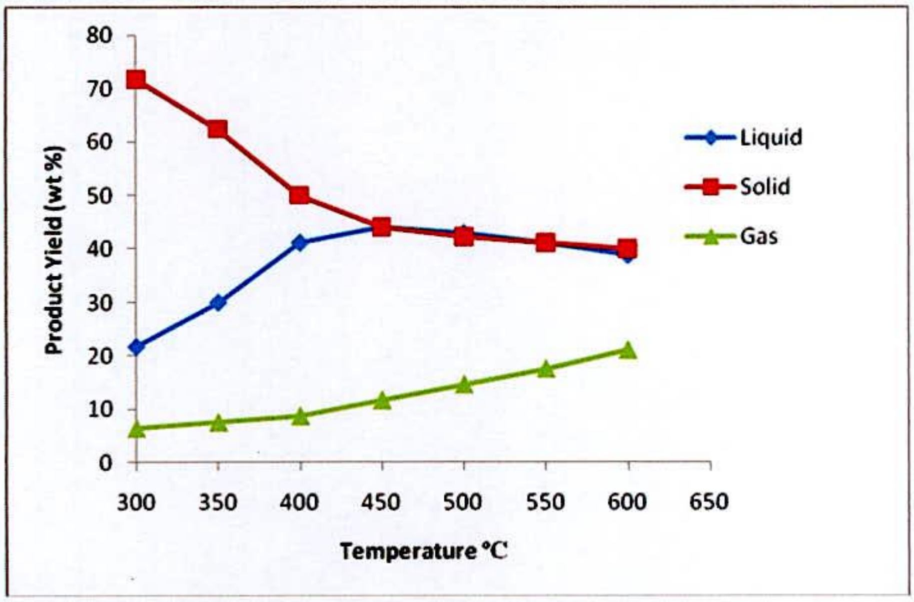


Figure 5.2: Effect of temperature on product yields (feed size 1.0 cm^3) for tire pyrolysis

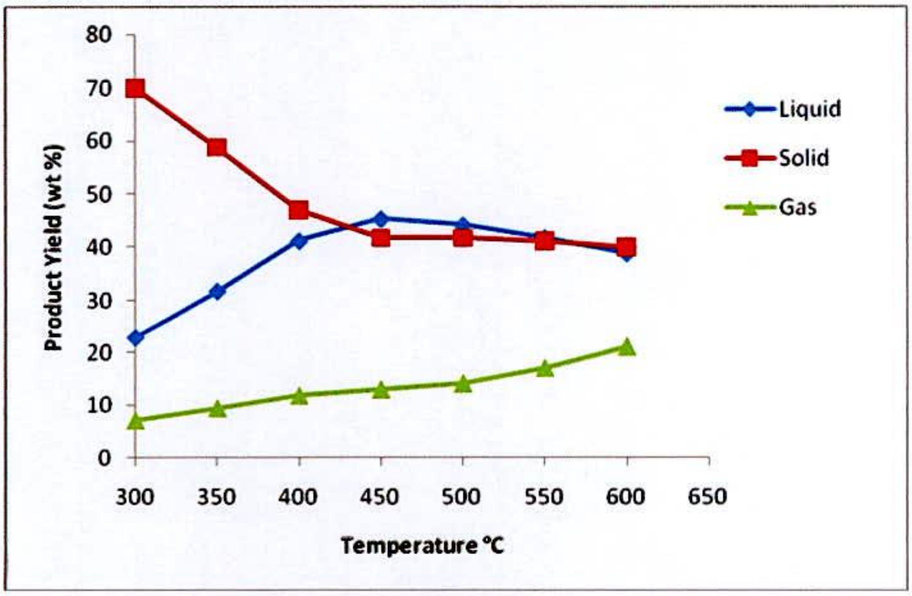


Figure 5.3: Effect of temperature on product yields (feed size 1.5 cm^3) for tire pyrolysis

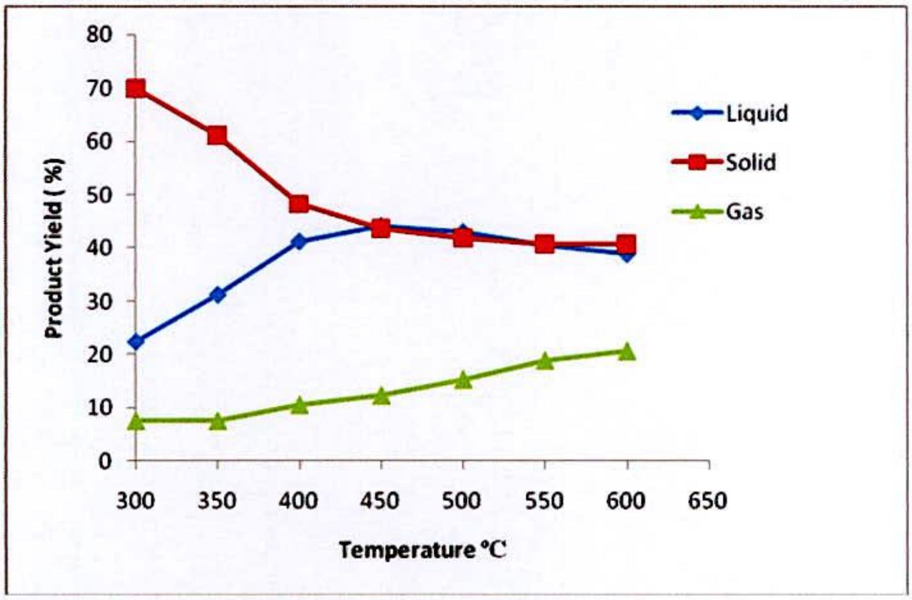


Figure 5.4: Effect of temperature on product yields (feed size 2.0 cm^3) for tire pyrolysis

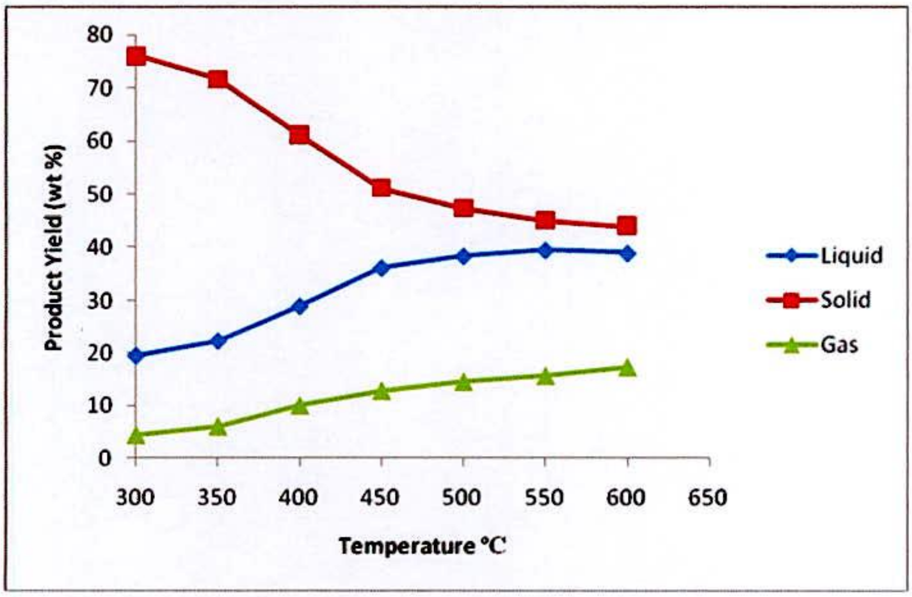


Figure 5.5: Effect of temperature on product yields (feed size 0.5 cm^3) for tube pyrolysis

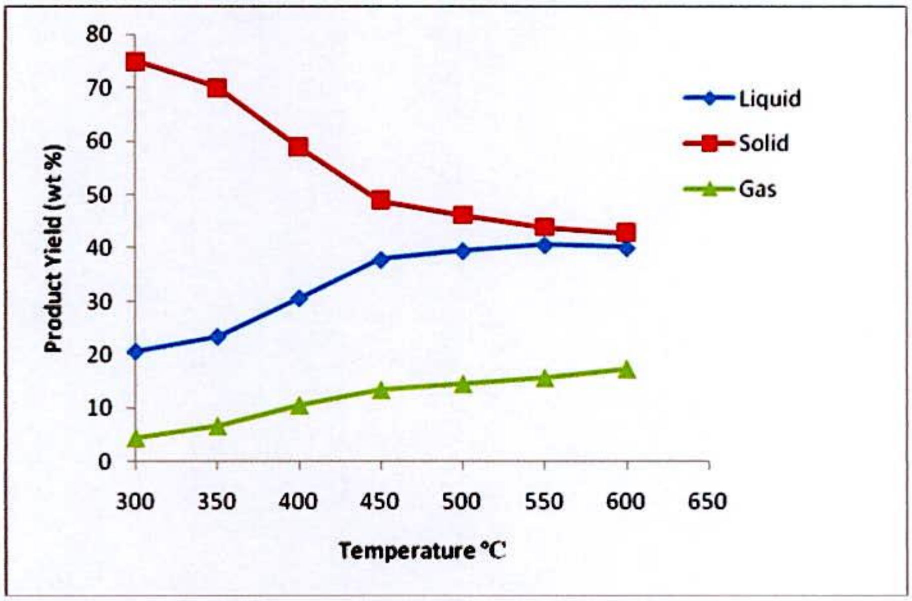


Figure 5.6: Effect of temperature on product yields (feed size 1.0 cm^3) for tube pyrolysis

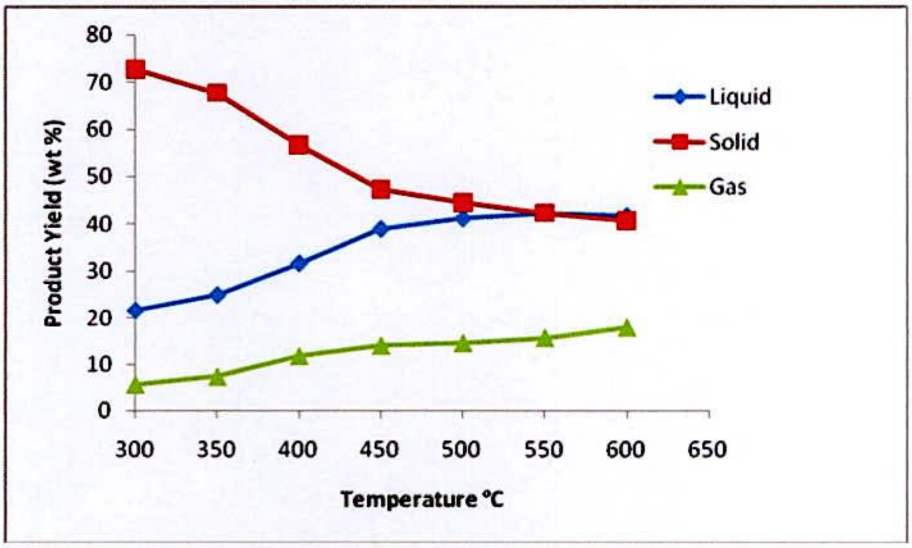


Figure 5.7: Effect of temperature on product yields (feed size 1.5 cm^3) for tube pyrolysis

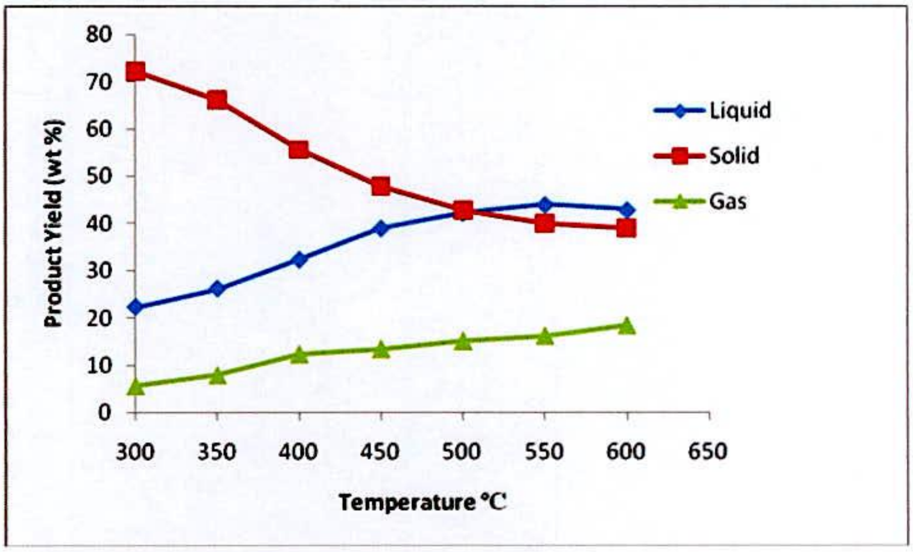


Figure 5.8: Effect of temperature on product yields (feed size 2.0 cm^3) for tube pyrolysis

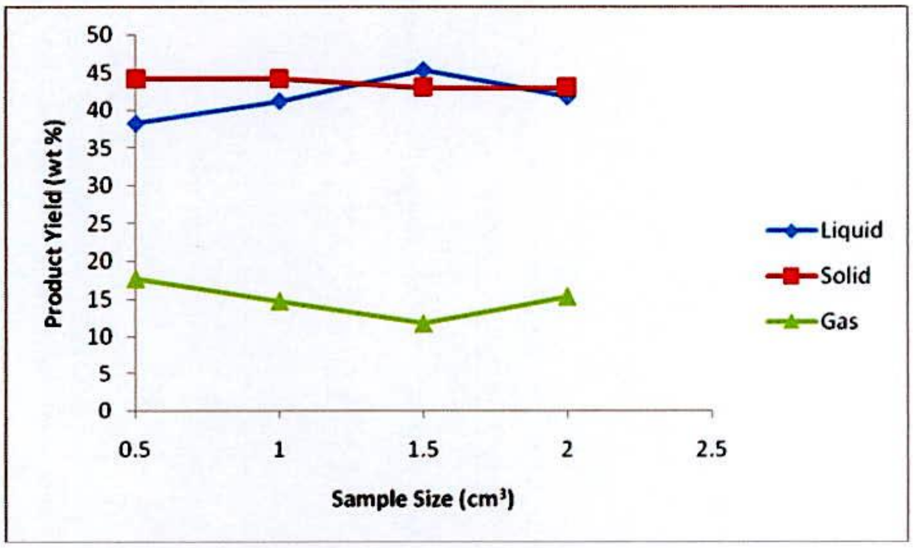


Figure 5.9: Effect of feed size on product yields at 450°C of tire pyrolysis

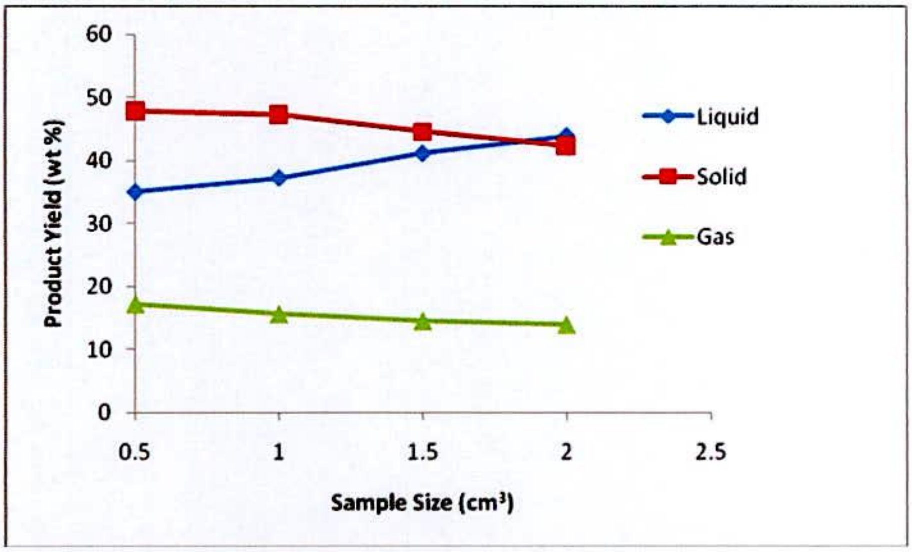


Figure 5.10: Effect of feed size on product yields at 550°C of tube pyrolysis

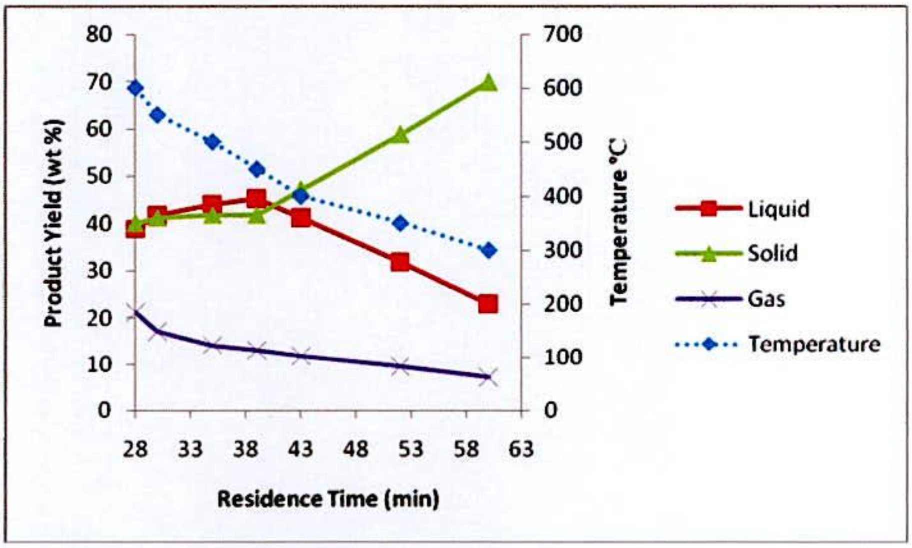


Figure 5.11: Effect of Residence time and temperature on product yield (feed size 1.5 cm^3) for tire pyrolysis

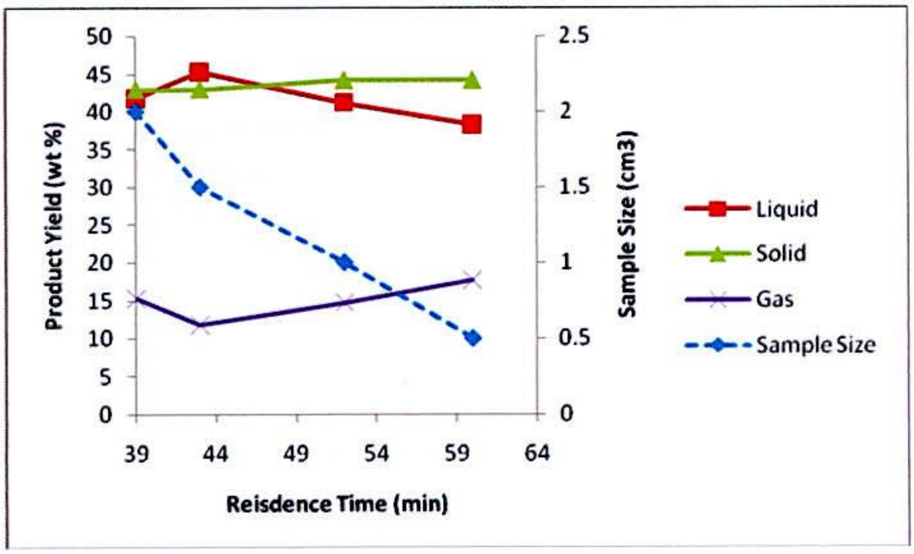


Figure 5.12: Effect of Residence time and sample size on product yield for tire pyrolysis

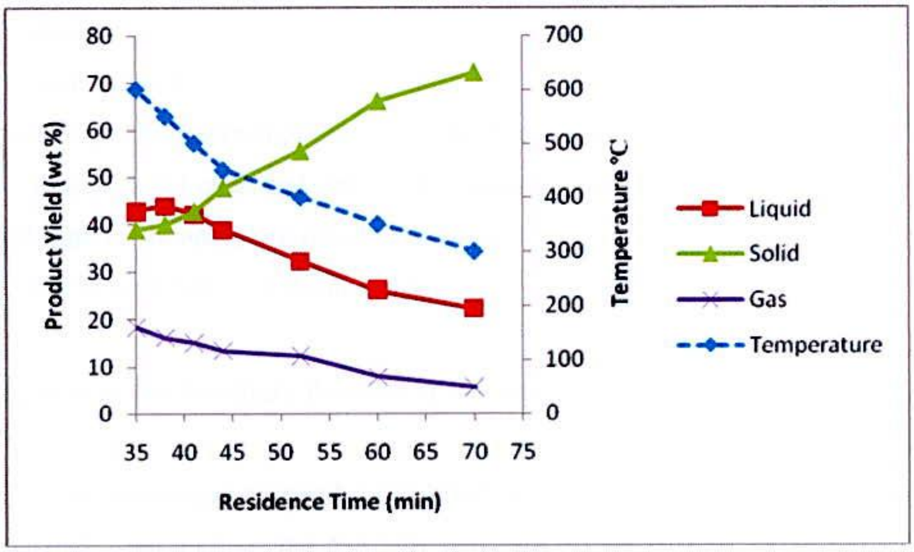


Figure 5.13: Effect of Residence time and temperature on product yield (feed size 2.0 cm^3) for tube pyrolysis

5.4 shows the same nature. Among the four samples the best result was found for feed size of 1.5 cm^3 (3 cm × 2 cm × 0.25 cm), the result of which has been shown in fig. 5.3. Here the maximum yield of liquid oil was observed to 45.29% by weight at a temperature of 450°C and then decreases to 38.82% by weight at a temperature of 600°C.

The gas yield increases over the whole temperature range to a maximum value of 21.18% at 600°C, while char yield decreases up to 450°C and then remains almost constant. This is probably due to better cracking of the tire at this temperature and rubber of the tire is not totally decomposed (pyrolysis is not complete) at a temperature less than 450°C. Further it is observed that solid yield decreases, liquid and gas yields increases. This is probably due to complete thermal decomposition of the rubber of the tire. It was apparent that at lower temperature the tire was partially pyrolysed to give less oil and volatiles with maximum retention of material in solid form as char. This results agree fairly with work of [20, 29,48, 55, 56, 57, 58, 59, 60, 61].

In case of thermal pyrolysis of tube three different products were obtained, which are oil, char and gas. The effect of temperature on product yield is shown in figs. 5.5 to 5.8. It is observed from figs. 5.5 to 5.8 that when the temperature increases from 300 to 600°C, the yield of liquid increases first to a maximum value at 550°C, and then decreases to a minimum value at 600°C for all sizes of tube feedstock.

All the curves from figs. 5.5 to 5.8 shows the same nature. Among the four samples the best result for waste tube was found for feed size of 2.0 cm^3 (4 cm × 2 cm × 0.25 cm), the result of which has been shown in fig. 5.8. Here the maximum yield of liquid oil was observed to 43.89% by weight at a temperature of 550°C and then decreases to 42.72% by weight at a temperature of 600°C.

The gas yield increases over the whole temperature range to a maximum value of 18.33%, while char yield decreases up to 550°C and then remains almost constant. This results agree fairly with work of [20, 29,48, 55, 56, 57, 58, 59, 60, 61].

(b) Effect of sample size on pyrolytic conversion of tire and tube

The effect of sample size on product yield of tire under optimum reactor temperature (450°) is presented in Table 4.10 and Table 5.9 and also in fig. 5.9. The weight fractions of liquid oil, char and gas produced were plotted together with sample size in the fig. 5.9.

Figure 5.9 shows that liquid yield from tire first slightly increases up to a maximum value of 45.29% for sample size of 1.5 cm^3 and then decreases for larger sample while the char yield increases and gas yield decreases through all the sample sizes from 0.5 to 2.0 cm^3. Smaller sample size provides more reaction surface causes high heating rate and too quick decomposition of the rubber sample occurs. From fig. 5.9 it is observed that liquid yield is a maximum for sample size of 1.5 cm^3 (3 cm × 2 cm × 0.25 cm = 1.5 cm^3).

The oil vapor comparatively get enough time for secondary reaction in the reactor and consequently increase in gas yields and, decrease in liquid and char yields. On the other hand, the heating rate in larger sample is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller pieces. Thus, the rubber core of the larger pieces becomes carbonized and/or cannot be decomposed completely resulting increase in char yields and decrease in liquid and gas yields.

The effect of sample size on product yields of tube under optimum reactor temperature (550°) is presented in Table 4.11 and Table 5.10. The weight fractions of liquid oil, char and gas produced were plotted together with sample size in the fig. 5.10. Figure 5.10 shows that liquid yield from tire first slightly increases up to a maximum value of 45.29% for sample size of 2 cm^3 and then decreases for larger sample while the char yield increases and gas yield decreases through all the sample sizes from 0.5 to 2.0 cm^3. Smaller sample size provides more reaction surface causes high heating rate and too quick decomposition of the rubber sample occurs. It is observed in fig. 5.10 that liquid yield is a maximum for sample size of 2.0 cm^3 (4 cm × 2 cm × 0.25 cm = 2 cm^3). This results agree fairly with work of [20, 29,48, 55, 56, 57, 58, 59, 60, 61].

(c) Effect of Residence time

The effect of residence time on the product yield is shown in figs. 5.11 to 5.12 for tire and in figs. 5.13 to 5.14 for tube pyrolysis. In all figures from 5.11 to 5.14, it is observed that at low temperature, more residence time was required to complet the conversion which results in incomplete deploymerisation of the sample that leads to production of more char and less amount of oil. At higher temperature, less residence time was required to complete the conversion, which leads to more oil and less char. There is no obvious mechanism for gas loss with residence time. It was also observed that at low temperature with longer residence time contributes to secondary reaction of primary products, which leads to less oil and more char products. This results agree fairly with work of [20, 29,48, 55, 56, 57, 58, 59, 60, 61].

5.2.3 Analysis of Pyrolytic fuel/oil

The liquid obtained from pyrolysis of tire and tube is oily organic compounds and appears as dark-brown-color with a strong acrid smell. Careful handling of the liquid is required since it reacts easily with human skins, leaving permanent yellowish brown marks and an acrid smell for a few days, which is difficult to remove by detergent. No phase separation was found to take place in the storage bottles. The liquids were characterized in terms of both fuel properties and chemical compositions.

Pyrolytic liquid obtained under the different liquid yield conditions were well mixed and homogenized prior to analysis being made. Physical properties such as specific gravity, density, Kinematic viscosity, flash point, fire point, pour point, GCV, boiling of the tire and tube oil were determined. The oil obtained after thermal pyrolysis of waste bicycle tire and tube appears dark brown in color with strong acidic smell resembling petroleum fractions. The oils were characterized in terms of fuel properties. The fuel properties of oil derived from tire and tube were analyzed and compared with that of diesel which has been summarized in Table 5.11 and Table 5.12

The fuel properties of the pyrolytic liquid in comparison to commercial automotive diesel, which is mostly consumed, are shown in Table 5.11 and Table 5.12. The table shows that the density of pyrolytic liquid was found 917.9 kg/m^3 for tire and 918.4 kg/m^3 for tube are higher than that of the commercial diesel (820-860 kg/m^3) and petrol (700-800 kg/m^3) fuel but lower than that of heavy fuel oil (980 kg/m^3 at 20°C). This is attributed to the presence of heavier compounds in the both the pyrolysis oil. The kinematic viscosity of tube pyrolytic oil is nearly same as to the diesel. The viscosity of liquid products from the waste tire (5.31@100°CeSt) was slightly higher than that of the diesel (2 to 4@100°CeSt) but too much lower than that of heavy fuel oil (200@100°CeSt). But the viscosity of liquid products from the tube (2.94@100°CeSt) was lower than that of the diesel (2 to 4@100°CeSt). Low viscosity of the liquids of 4.62-4.90 cSt at 30°C is a favorable feature in the handling and transporting of the liquid [18, 20]. The flash point obtained from the pyrolytic oils derived from tire and tube were less than that of diesel. The flash point of the liquid derived from tire was ≤9°C. On the other hand the flash point of the liquid derived from tube was ≤10°C. The flash point is low when compared with petroleum-refined fuels; for example, kerosene has a required minimum flash point of 23°C, diesel fuel of 55°C and light fuel oil 79°C. The low flash points of the liquids derived from tire and tube are not surprising since the product obtained is unrefined with a mixture of components having a wide distillation range. The pour point of the tire and tube liquids derived from tire and tube is comparatively low compared to the automotive diesel fuel but the laboratory experience of the present study shows that it is not problematic even at 7°C. Gross calorific values of both the pyrolytic oil (34.61MJ/kg for tire and 34.51 MJ/kg for tube) were less than that of diesel and gasoline.

The important requirement for diesel fuel is its ignition quality, viscosity, percentage of and water, sediment, and sulfur contents. Therefore, the pyrolytic oils were requiring preliminary treatments such as decanting, centrifugation, filtration, desulphurization, and hydrotreating to be used as fuel. The treated pyrolytic oil could be used directly as fuel oil or blended with diesel fuel, which will reduce the viscosity and, increase the pH value and flash point of the resulting blend. Consequently, the atomization will be improved, ensuring a complete burnout of the fuel [18]. Based on its fuel properties, the pyrolytic oil derived from tire and tube may be considered as a valuable component for use with automotive diesel fuel. Moreover, the oil may be directly used as fuel for industrial furnaces, power plants, and boilers [17].

5.2.4 Solid char fraction during pyrolysis of tire and tube

The solid char fractions obtained at optimum reactor conditions were of equal size and shape as original tire pieces, which were easily disintegrable into black powder and steel cords. The GCV of char fraction is 22–25 MJ/kg, which is comparable with that of the good quality coal.

The liquid and char yields from the wastes of bicycle/rickshaw tire and tube wastes are almost same compared to those of the previous studies [48, 50, 55, 56, 58, 60, 61, 65, 67]. These variations in the product yields are due to mainly the compositional differences in tire and tube feeds. The bicycle/rickshaw tire and tube wastes, which were used as feedstock in the presented study, have lower volatile and higher ash content than those of car and truck tire wastes result in lower liquid yields.

CHAPTER VI

Conclusion and Future Scope

6.1 Conclusion

Under the study, the recovery of value added products obtained from pyrolysis of waste tire and tube pyrolysis were investigated. Thermal pyrolysis of waste tire and tube has been studied. Within the range of experimental limit the following conclusions can be drawn.

i. The maximum yield of pyrolytic oil from the waste tire was 45.29% by wt at a temperature of 450°C when the tire size was 1.5 cm^3 (3 cm × 2 cm × 0.25 cm) having weight of 1.7 kg.

ii. The maximum yield of pyrolytic oil from the waste tube was 43.89% by wt at a temperature of 550°C when the waste tube size was 2 cm3 (4 cm × 2 cm × 0.25 cm) having weight of 1.8 kg.

iii. In case of tire the product of pyrolytic oil was found to increase upto temperature 450°C and then remains almost constant upto temperature 600°C.

iv. In case of tube the product of pyrolytic oil was found to increase upto temperature 550°C and then remains almost constant upto temperature 600°C.

v. Physical properties of pyrolytic oil derived from both waste tire and tube are comparable with that of diesel fuel.

vi. Thermal cracking of raw material during pyrolysing is an essential parameter for the product yield which in turn depends on the relative size of sample and the reactor. So for lab scale reactor the sample size can be considered as a parameter for better performance of pyrolytic conversion of non-bio-degradable waste tire and tube.

6.2 Future Scope

- Better experimental model can be made to improve the quality and quantity of products.
- Different catalysts can be used to obtain more yields of the oil products.
- Fractionating columns can be used for separation of the oil fuel into different fractions.
- Different kinetic methods and models can be used for designing a suitable reactor to maximize the oil product.
- Optimization of the process to achieve an economical and eco-friendly method.

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