Extraction of Liquid Fuel from Pyrolysis of Waste Tyres with Catalyst

by

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Declaration

This is to certify that the project work entitled "*Extraction of Liquid Fuel from Pyrolysis of Waste Tyres with Catalyst*" has been carried out by *Md. Shameem Hossain* in the *Department of Energy Technology*, Khulna University of Engineering & Technology, Khulna, Bangladesh. The project work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

28.10.15

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DEDICATION

This project work is dedicated to my parents.

Approval

This is to certify that the project work submitted by *Md. Shameem Hossain* entitled "*Extraction of Liquid Fuel from Pyrolysis of Waste Tires with Catalyst*" has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of *Master of Engineering* in the Department of *Energy Technlogy*, Khulna University of Engineering & Technology, Khulna, Bangladesh in October' 2015.

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Md. Shameem Hossain

Summary

Bangladesh is a developing and most densely populated country in the world with a total population of about 156.6 million. Her per capita energy consumption is much below the world average. Energy consumption mix is estimated as: indigenous biomass 60%, natural gas 27.45%, oil 11.89%, coal 0.44% and hydro 0.23%. More than 77% of the country's population lives in rural areas and meeting most of their energy needs from traditional biomass fuels. Around 32% have access to electricity, while in rural areas the availability of electricity is only 22%. Only 3–4% of the households have connection of natural gas for cooking. About 2–3% households use kerosene for the same and the rest (over 90%) depend on biomass for their energy needs. Thus, it is crucial to find out alternative and sustainable resources to mitigate the energy crisis.

Recent environmental issues and energy security have been emerged as public and political concern which led to alternative way of thinking and renewable energy sources may be an indigenous source of that kind of thinking. As energy demand is becoming acute day by day, scientists are giving efforts on the potentials of utilizing appropriate technologies to recover energy and useful by-products from domestic and industrial solid wastes. Researchers have been conducted for biodegradable and non-biodegradable waste materials. Rubber and plastic containing waste is non-biodegradable. About 20.50 million bicycle/rickshaw tyres become scrap every year and wait for disposal which is about 37% (wt) of total tyre waste production in Bangladesh. It is estimated that 30,750 tons bicycle/rickshaw tyres, 5160 tons motorcycle tyres, and 28,900 tons bus/truck tyres become scrap and are disposed of every year.

Disposal of waste tyres causes typical problems for environment. Dumped scrap tyre. in massive stockpiles is one of the possible causes of ideal breeding grounds for disease carrying mosquitoes and other vermin with the aid of rain water deposited in the free space of tyre wall. On the other hand, tyres left in open air may result in significant disturbances and dangerous situations like risk of fire. Different means are available for disposal of waste tyres and one relatively effective way is pyrolysis of there.

In the present work, waste bus-tyres were pyrolysed in a fixed bed reactor with catalyst and without catalyst. The objectives were to investigate the composition of derived oil from waste tyre and the effect on oil extraction in presence of catalyst. The influences of pyrolysis temperature, catalyst/tyre ratio (CT ratio), heating rate, operating time, sample size etc. on yield were investigated. The pyrolysis of tyre was carried out within the temperature range of 300°C to 600°C. The optimum pyrolytic oil of 42.0 % (wt) was obtained for tyres pyrolysis and 36.67% (wt) for catalytic pyrolysis at 450°C. A higher temperature and smaller particle size increases the heating rate that resulting a decreased char yield. The cracking of hydrocarbons, resulting increased H_2 content in the gaseous product, is favored by a higher temperature and smaller particle size. The physical properties of the pyrolytic oil were examined. It showed that increase in catalytic temperature and CT ratio resulted in high yield of gas at the expense of oil yield. When CT ratio is increased from 0.13 to 0.30, the yield of gas increased from 13.33% to 15.33 % (wt), and oil yield decreased from 36.67% to 28.0% (wt) at temperature 450°C. High CT ratio favored to increase the concentration of light naphtha in the pyrolytic oil. Fractional distillation of 97% (wt) of the pyrolytic oil from catalytic pyrolysis below 350°C with CT ratio of 0.3 and pyrolysis temperature of 450°C shows that after proper treatment these oil can be used as substitute of alternative fuel or chemical feedstock to Naphtha.

Nomenclature

wt %	Weight Percent
°C	Degree Celsius
MJ/kg	Mega joule per Kilogram
Kg/m^3	Kilogram per cubic meter
KgOE	Kilogram of Oil Equivalent
GCV	Gross Calorific value
SBR	Styrene Butadiene Rubber
BR	Butadiene Rubber
IR	Isoprene Rubber
HDPE	High Density Poly Ethylene
LDPE	Low Density Poly Ethylene
PP	Poly Propylene
PVC	Poly Vinyl Choloride
PET	Poly Ethelene Terapthalate
PS	Poly Styrene
EPT	Ethylene Propylene Terpolymer
IIR	Isobutylene Iso-prene Rubber
UV	Ultraviolet
NR	Natural Rubber
PBR	Polybutadiene Rubber
EPA	European Pollution Authority
MJ	Mega Joule
FCC	Fluid Catalytic Craking
TGA	Thermo Gravimetric Analysis
KW	Kilowatt
N2	Nitrogen Gas
CT ratio	Catalyst -Tyre ratio
ASTM	American Society for Testing Materials
FTIR	Fourier Transform Infra –Red
CARS	Centre for Advanced Research in Sciences
TCR	Total Capital Requirement
FCI	Fixed Capital Investment.
O-H	Hydroxyl stretching
N-H	Amines
C-H	Carbon Hydrogen (Alkanes group)
C=C	Carbon Hydrogen double bonding
C-O	Carbonyl Stretching
O-H	Alcohol, Phenol group
C≡C	Carbon Hydrogen Triple Bonding (Alkynes)

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CHAPTER I

INTRODUCTION

1.1 General

The standard of living and quality of life of a nation depend on its per capita energy consumption. Bangladesh is a developing country and is one of the most densely populated countries in the world with a total population of 156.6 million. Her per capita energy consumption in 2012 stands at 214 kgOE (kilograms of oil equivalent), which is much below the world average of 1778 kgOE. The energy consumption mix was estimated as: indigenous biomass 60%, natural gas 27.45%, imported oil 11.89%, coal 0.44% and hydro 0.23%. More than 77% of the country's population lives in rural areas but 50% of them do not own any land, meeting most of their energy needs from traditional biomass fuels. Around 32% have access to electricity, while in rural areas the availability of electricity is only 22%. Only 3–4% of the households have connection of natural gas for cooking purposes. About 2–3% households use kerosene for the same purpose and the rest (over 90%) of people depend on biomass for their energy needs [1]. Thus, it is crucial to find out alternative and sustainable resources to mitigate the energy crisis of Bangladesh

Recently environmental issues and energy security have been emerged as the public and political concern which has led to alternative way of thinking. Renewable energy sources may be an indigenous source of that kind of thinking [2]. As the energy demand is becoming acute day by day scientists are giving efforts on the potentials of utilizing appropriate technologies to recover energy and useful by-products from domestic and industrial solid wastes. To do so researches have been conducted for biodegradable and non-biodegradable waste materials. 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 waste such as tyre is an organic solid waste which is non-biodegradable. So, disposal of used tyres causes some typical problems for environment as well as to our surroundings. Dumped scrap tyre in massive stockpiles is one of the possible causes of ideal breeding grounds for disease carrying mosquitoes and other vermin with the aid of rain water, which is deposited in the free space of the tyre wall. On the other hand, tyres left in open air may result in significant disturbances and dangerous situations such as risk of fire.

It is estimated that 20.50 million bicycle/rickshaw tyres become scrap every year and wait for disposal [1]. The estimated value is about 37% (by weight) of total tyre waste production in Bangladesh. Moreover, buses and bicycle are also a common carrier for movement all over the world. It is estimated that 30,750 metric tons bicycle/rickshaw tyres, 5160 metric tons motorcycle tyres, and 28,900 metric tons bus and truck tyres become scrap and are disposed of every year [3].

The disposal of solid tyre 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 tyres are connected with some problems: it needs a considerable amount of space because the volume of tyres cannot be compacted. Also, landfilling is a potential danger because of the possibility of accidental fires with high emissions of hazardous gases [1].

These discarded wastes pose a threat to the environment and human health if not handled properly. Thus, timely action regarding recycling of used tyre 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 tyres. Waste tyre can be a source of energy and valuable chemical product, and their thermal decomposition makes the recovery of useful compounds possible. Conventional methods for tyre shredding and metal separation, allows seamless incorporation of this technology for oil production and waste tyre disposal. Therefore, in recent years there has been an increased interest in production of oil fuel from waste tyre by pyrolysis method [5].

Pyrolysis, an attractive method to recycle scrap tyres, has recently been the subject of renewed interest. Pyrolysis of tyre can produce oils, chars, and gases. The oil from pyrolysis is known as pyrolysis oil or pyrolytic oil or pyrolytic liquid, in addition to the steel cords, all of which have the potential to be recycled. Tyre 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 [1]. The liquids have been shown to contain monoterpene such as limonene [1-methyl-4-(1-methylethenyl)-cyclohexene], a high value light hydrocarbon. Besides that, pyrolysis of tyre 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 tyres 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 [4].

Roy et. al. [6-8] compared the derived oil from tyre pyrolysis with petroleum naphtha; the conclusion was the naphtha from the derived oil had a higher octane number than petroleum naphtha but must be hydrofined and reformed in order to be used as a clean fuel. However, the high concentration of aromatic hydrocarbons [9-10] limited the derived oil from tyre pyrolysis to be used as 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 feedstock's in the chemical industry. For example, benzene is surfactants, dyestuffs and pharmaceutical, and toluene is used in the production of pesticides, dyestuffs, surfactants and solvents. O-Xylene is used to produce plasticizers, dyes and pigments, m-xylene derivatives are used in the fibre industries and p-xylene derivatives are used in the production of polyester fibers [11]. However, their concentrations are not sufficiently high to enable their extraction from the oil and utilization as a chemical feedstock, so catalysts are introduced to produce more single ring aromatic compounds. *Williams and Brindle* [12-13] have conducted some important research in this field by using zeolite USY catalysts with different Si/Al ratios and pore sizes to study the influences of pyrolysis temperature, catalytic temperature and CT ratio on the yields of products and the composition of derived oils. They obtained the oil with high concentration of certain single ring aromatic compounds such as benzene, toluene and xylenes after catalysis.

Pyrolytic char may be used as a solid fuel or as a precursor for activated carbon. Some 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 [1].

A variety of scrap tyre is available in the modern society. These are bicycle and rickshaw tyres, motorcycle and auto-rickshaw tyres, car and taxi tyres, microbus and jeep tyres, tractor tyres, bus and truck tyres. Tyres 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 tyre 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. Therefore, the composition of the tyre varies depending on the tyre grade and manufacturers. Consequently, the tyre pyrolysis products may also vary in terms of yield and chemical composition depending on the source and grade of the tyres [14].

There are various experimental method that can produce liquid product by pyrolysis technology from waste tyres such as fixed-bed reactors, fluidized-bed pyrolysis units, vacuum pyrolysis units, spouted-bed reactors etc. Products of tyre pyrolysis varies its characteristic and quality depend on type and size of feedstock, size and system configuration of reactor, efficiency of heat transfer, vapor residence time, catalyst etc. The influences of pyrolysis temperature, catalytic temperature, heating rate and CT ratio on the yield and fraction of the derived oils were investigated. The property of the derived oil had also been analyzed by Gas-Chromatography (GC)–Mass Spectroscopy (MS) for the purpose of potential use as chemical feedstock, such as benzene, toluene and xylenes. 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 Scope of Present Investigation

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 refuse, which are generated daily. By the year 2100, the world population is expected to be in excess of 12 billion and is estimated that the demand for energy will be increased by five times from what is now. The increasing human population on the earth caused ever increasing demand of energy. To alleviate part of these energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for the possible recovery of recourses from non-conventional sources, like municipal and industrial organic waste, refused plastic, used tyres, etc. Searching for the alternative fuel to the meet the increasing fuel demand the present investigation will put emphasis in the followings:

- Study of the wastes tyre of automobile as feed materials for the availability in this country at cheap price.
- Proper disposal of ever increasing scrap tyres with potential material recovery.
- Emphasis on the production of the liquid fuel.
- Study for the high quality oil production.
- Study for the effect of catalyst on tyre pyrolysis.
- Using maximizing liquid or solid production by using catalyst.

1.3 Objectives of the Research Work

The main objective of the proposed project is to analyze catalytically by pyrolysis technology in small scale at KUET Lab. Under the study, waste tyres automobile will mainly be used as raw material. The specific objectives of this project are-

- Selection and erection of a fixed bed fire tube laboratory scale plant for pyrolysis of tyres in presence of catalyst.
- To pyrolyse the organic waste tyres in the proposed plant under pyrolytic conditions and studies the role of catalyst temperature, CT ratio and feed size on the product yields and their compositions.
- To analyze the quantity of liquid, solid and gaseous product and
- To analyze the physical and chemical composition of the liquid product and contrast them with the commercial fuel.

CAPTHER II

THEORITICAL ASPECTS

2.1 Tyre Fundamentals

Tasawan Suparat [15] studied a type of ring shape covering of the circumference of a wheel. It is an essential part of most ground vehicles and is used to protect the wheel from wear and tear as well as to provide a friction between the vehicle and the road to improve acceleration and handling. The important functions of tyre are supporting vehicle direction; an absorbing road shocks. A tyre carcass is composed of several parts. The cross section of a tyre is shown in Figure 2.1

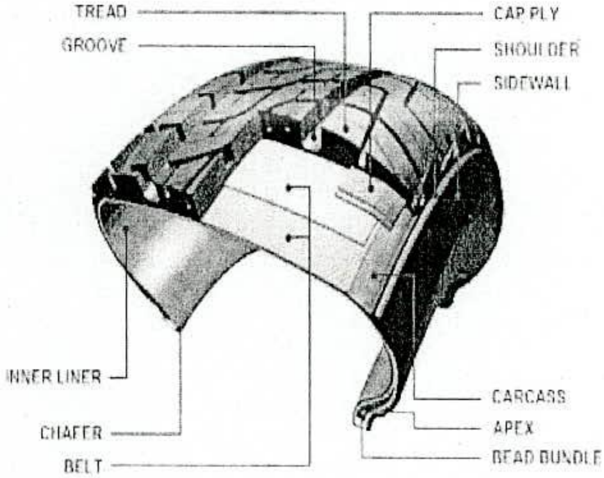


Figure: 2.1 Cross section of tyre

Belt: Layers of rubber and closely spaced steel chords, provide strength while remaining flexible.

Tread: Tread is the part of the tyre that is in contact with the road surface and is made of rubber with additions (carbon black and other chemicals). It not only has to provide grip and cornering stability but must resist abrasion, cutting, and impacts, as well as to withstand high temperatures.

Groove: A channel within the tread. A tyre groove helps to improve driving stability, pulling ability, and braking ability.

Cap ply: steel cords stabilized the shape of the tyre against internal pressure.

Shoulder: The section that is in transition between the edge of the tread and the sidewall.

Sidewall: Bridge between tread and bead, often reinforced with steel chords/fabrics to provide strength/flexibility, transfers torque from shaft to tread.

Carcass: Scaffolding of the tyre provides coherence, made of fabric embedded in rubber, optionally steel chords.

Apex: Filler providing coherence on between bead, inner and body ply.

Bead bundle: Rigid bands of steel wire in rubber compound, establishes press fit of the tyre to the wheel.

Chafer: Protects the steel cords against wear and cutting by the rim, prevents dirt and moisture from getting into rim.

Inner liner: Airtight rubber sheet to hold high pressure air inside.

Tyres are made of vulcanized rubber and various reinforcing materials. The most commonly used rubber matrix is the natural rubber and synthetic rubbers which use in different purpose. Natural rubber is an essential element of a tyre since it has unique elastic properties. Synthetic rubber or elastomers such as Styrene Butadiene Rubber (SBR), Butadiene Rubber (BR), Isoprene Rubber (IR), Ethylene Propylene Terpolymer (EPT), and Isobutylene Isoprene Rubber (IIR) are added to natural rubber to achieve the desired elastically. In addition to the rubber to achieve the desired elasticity. In addition to the rubber compound tyres contain:

1. Reinforcing fillers such as carbon black. It is used to strengthen the rubber and make tyre have more abrasion resistance.
2. Reinforcing fibers such as textile or steel fibers. it is usually in the form of a cord which used to provide the reinforcing strength or tensile component in tyres. The materials are used for making textile is natural cotton and synthetic textile such as nylons and polyesters.
3. Extender such as petroleum oils. It is used to control viscosity, reduce internal friction during processing, and improve low temperature flexibility in the vulcanized product.

4. Vulcanizing agents such as organo-sulphur compounds. It is used as the catalyst for the vulcanization process; and Zinc oxide and stearic acid, used to activate the curing (cross-linking) system and to preserve cured properties.

The raw materials used in tyre manufacture are shown in Table 2.1[16]. The proportion of each raw material very slightly depending on the type of tyre (car, truck, airplane etc.) being produced.

Table-2.1: A Typical Composition by Weight of Tyre.

Component	Car tyre	Truck tyre
Rubber/ elastomers	48	45
Carbon black	22	22
Black metal (mainly steel)	15	25
Textile	5	-
Zinc oxide	1	2
Sulphur	1	1
Additives	8	5

2.2 History of Tyre Invention

During the 19th century, Charles Goodyear studied on making rubber more resistant to various chemicals. He started his working by mixing rubber with various dry powders and aimed to find a way to make natural rubber sticker. In 1839, he achieved to obtain the best product by applying steam heat under pressure, for four to six hours at 132°C

Following the discovery of vulcanization, manufacture began producing tyres from solid rubber which yielded a strong material to resist cuts and abrasions. Although this was a great progress, the tyres were too heavy and rigid. In order to decrease vibration and improve traction, Robert W. Thomson, first produced the pneumatic rubber tyre which consisted of rubber filled in with air. His idea could not be commercialized since it was introduced too early for its time. John Boyd Dunlop from Ireland, who did not know about Thomson's earlier invention, one more introduced the pneumatic tyre to the market in 1888. This time; pneumatic tyre caught the public's attention because bicycles were becoming extremely popular and the lighter tyre provided a much better ride [17].

The following is a brief discussion about some characteristics of whole and processed waste tyres intended to help designers create new products from them, For most practical purposes, tyre and tyre products function as homogenous mixture, but processing can impact physical characteristics as size and shape are altered and as reinforcing wire and fabrics are removed. Therefore, variations are discussed in subsequent sections where they may be important.

Density: Tyres are slightly heavier than water and will sink in water entrapped air provide enough buoyancy to allow them to float. This generally occurs only with whole tyres or fine crumb rubber particles, however, tyres and tyre products are much lighter than soil or stone. The density of whole and studied tyres depends upon size, depth and compaction.

Durability: Tyre rubber contains carbon black, antioxidants, and UV stabilizers to enhance resistance to wear, chemical decomposition, and sunlight, respectively. These characteristics are independent on particles size. Strength of whole tyres is further enhanced by reinforcing wire and (like nylon or polyester), but this additional strength is lost as wire and fabrics are removed from smaller particles. Abrasion resistance is illustrated by the long life of tyres in contact with roads.

Moisture Absorption: Tyres and shred can trap water on the surface and in irregular contours, but they are relatively imperative to actual absorption.

Temperature Tolerance: Tyre rubber is capable of withstanding a full range of ambient temperature extremes without undergoing permanent property change. Some properties like flexibility change as a function of temperature. But this change is reversible and repeatable.

Flammability: Tyre sheds have a reported flash point of 306°C, higher than some other materials used for architectural purpose such as wood, paper, foam and fabric. The flash point is the temperature at which materials will initially ignite and the temperature to support continuing combustion (fire point) is even higher. When crumb rubber is combined with a binder has a lower flash point.

Color: Passenger tyres are predominantly black, but white pigment is used to provide visible sidewall lettering as a result, shreds and crumb rubber made from passenger tyre have a mixture of black and white coloring. Truck tyres do not have white pigment. So resulting products are completely black. Color can be important performance characteristic.

2.3 Description of Rubber Component

Rubber, an elastic substance, obtained from the exudations of certain tropical plants (natural rubber) or derived from petroleum and natural gas (synthetic rubber). Because of its elasticity, resilience, and toughness, rubber is the basic constituent of the tyres used in automotive vehicles, aircraft, and bicycles. More than half of all rubber produced goes into automobile tyres; the rest goes into mechanical parts such as mountings, gaskets, belts, and hoses, as well as consumer products, such as, shoes, clothing, furniture, and toys. The rubber components briefly described in the following sub-section,

2.3.1 Polyolefins

Polyolefins are one type of synthetic resin produced by the polymerization of olefins or alkenes (molecules with the general formula (C_nH_{2n}) 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 are the most widely used plastic and in tonnage terms olefins elastomers such as styrene-butadiene copolymers has a dominant application in making of tyre.

2.3.2 Different Types of Rubber Used in Tyre

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. 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 tyre [18]. Three major categories of rubber are used for tyre and tube making. They are namely natural rubber, synthetic rubber, reclaimed rubber, vulcanized rubber and devulcanized rubber.

Natural rubber, or polyisoprene is the basic elastomer used in tyre making, Styrene-butadiene co-polymer (SBR) is a synthetic rubber which is often substituted in part for natural rubber based on the comparative raw materials cost. Polybutadiene is used in combination with other rubbers because of its low heat-buildup properties. Halobutyl rubber is used for the tubeless inner liner compounds, because of its low air permeability. The halogen atoms provide a bond with the carcass compounds which are mainly natural rubber. Bromobutyl is superior to chlorobutyl, but is more expensive. Carbon black forms a high percentage of the rubber compound. This gives reinforcement and abrasion resistance. Silica, used together with carbon black in high performance tyres, as a low heat buildup reinforcement. Sulphur crosslinks the rubber molecules in the vulcanization process. Vulcanizing accelerators are complex organic compounds that speed up the vulcanization. Activators assist the vulcanization. The main one is zinc oxide. Antioxidants and anti ozonants prevent sidewall cracking due to the action of sunlight and ozone. Textile fabric reinforces the carcass of the tyre.

2.3.3 Natural Rubber

The chemical formula of natural rubber is a polymer of isoprene (2-methyl-1, 3 butadiene) the purified form of natural rubber can also be produced synthetically. Natural rubber is an ideal polymer for dynamic or static engineering applications. Natural Rubber is an elastic substance obtained from the latex sap of trees, especially those trees which belong to the genera Hevea and Ficus. Technically speaking, natural rubber is an elastomeric or an elastic hydrocarbon polymer. Natural rubber is one of the types of rubber that also include vulcanized rubber which is finished into a variety of rubber products. Natural rubber is also known by the names of India rubber, gum elastic, 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 [19]. It can withstand temperature up to the range of 10-60°C, has tensile strength 19615 kPa and it has high elasticity ranging from 300 to 1000 % [20].

2.3.4 Synthetic Rubber

Synthetic rubber is made by the polymerization of a variety of petroleum-based precursors called monomers. More than half of the world's synthetic rubber are styrene-butadiene rubbers (SBR) derived from the copolymerization of styrene and 1, 3-butadiene. Three quarters of all the SBR made goes into tyre production. The rest goes into products such as footwear, sponge and foamed products, waterproof 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 tyre 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. Other synthetic rubbers are prepared from isoprene (2-methyl-1, 3-butadiene), chloroprene (2-chloro-1, 3-butadiene), and isobutylene (methyl propene) with a small percentage of isoprene for cross-linking. These and other monomers can be mixed in various proportions to be copolymerized to produce products with a range of physical, mechanical, and chemical properties. The monomers can be produced in pure form and the addition of impurities or additives can be controlled by design to give optimal properties. Polymerization of pure monomers can be better controlled to give a desired proportion of cis and trans double bonds [21].

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 temperature [22].

2.3.5 Reclaimed Rubber

Reclaiming is a procedure in which scrap tyre rubber or vulcanized rubber waste is converted using mechanical and thermal energy and chemicals into a state in which it can be mixed, processed, and vulcanized again. The principle of the process is devulcanization. Historically and practically, in the concept of rubber reclaiming, devulcanization consists of the cleavage of intermolecular bonds of the chemical network, such as carbon-sulfur (C-S) and/or sulfur-sulfur (S-S) bonds, with further shortening of the chains also occurring. Devulcanized materials (i.e. reclaimed rubber) is also used as raw material for new tyres manufacturing. The reclaimed rubber is of less tensile strength, lower in elasticity and possesses lesser wear resistance than natural rubber.

2.3.6 Vulcanized Rubber

Vulcanization is the thermo-chemical process that incorporates sulfur and sulfur crosslinks into a mixture of rubber molecules in order to provide the elasticity and other properties that are desired in manufactured rubber products. In the process of vulcanization, the added sulfur allows some C-H bonds to be broken and replaced by C-S bonds. The process of vulcanization cross-links the chains or polyisoprene to each other. The cross-linked molecules create a three-dimensional network of rubber. Each cross-link is a chain of about eight sulfur atoms between two long chains of polyisoprene.

Vulcanized rubber is about 10 times stronger than natural rubber and is also about 10 times more rigid. However, it is still very elastic, which means that is can be stretched reversibly. Polymers, that are elastic, are sometimes called elastomers. The optimum amount of sulfur to be added to the rubber is about 10% by weight. Adding an excess of sulfur produces a very brittle and inelastic substance called ebonite. Man-made or synthetic rubber can also be vulcanized.

2.3.7 Devulcanized Rubber

Devulcanization is the process of cleaving the monosulfidic, disulfidic, and polysulfidic crosslinks (carbon-sulfur or sulfur-sulfur bonds) of vulcanized rubber. Ideally, devulcanized rubber can be revulcanized with or without the use of other compounds. The different types of devulcanization processes also modify other properties of the rubbers. These processes cause diminution of some properties over those of the parent rubber. Ideally, devulcanization would yield a product that could serve as a substitute for virgin rubber, both in terms of properties and in terms of cost of manufacture.

Rubber mostly consists of blends of two or three rubber compounds mixed with tyre 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 [23].

2.3.8 Waste Generation of Tyre

Tyre is the backbone of the bicycle, rickshaw, bus, truck and many other vehicles. Buses and trucks continue to be the principal mode of road transport for the heavy load and long drive in our country. However, for survival the companies have to successfully restructure and modernize to achieve global competitiveness in terms of quality, cost and distribution system. The tyre industry is a major consumer of the domestic rubber production [17]. However, with increased production of buses the production of tyre will also be increased which is proportional to the volume production of wastes. The growth rates of transport vehicles are shown in Figure 2.2 [24]:

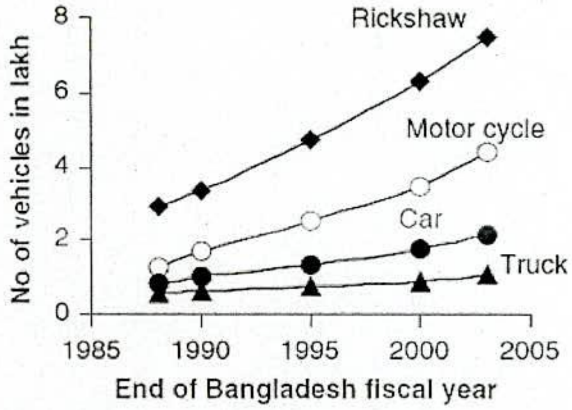


Figure 2.2: Growth rates of transport vehicles

The generation of solid wastes like tyre and tube is increasing steadily. According to the statistical data with the exponential growth in number of automobiles, generation of waste tyre increases. In 2009, over 400 million scrap tyres were generated and over 3 billion worldwide. So, from the case study, it was predicted that there is an urgent need to identify viable recycling routes for waste tyres. As shown in Figure 2.3, tyre 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 tyres produce 20% more energy than coal. A considerable shortfall in the capacity of the UK to reprocess its used tyres is also predicted due to the lack of economically viable alternatives to landfill [25]. 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 bicycle. This will produce a lot of tyre 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.

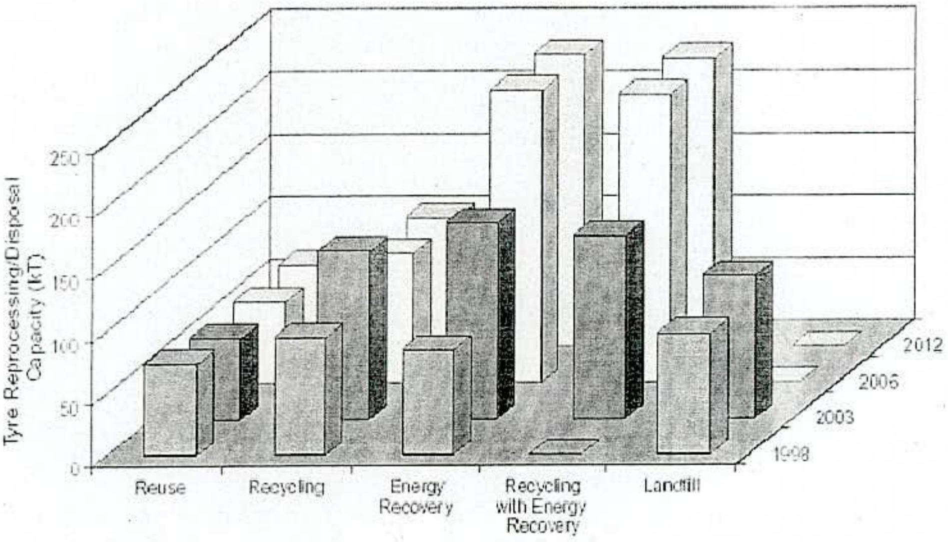


Figure 2.3: Predicted (best case) tyre reprocessing capacities by category

2.4 Waste Products and Their Classification

Wastes are materials for which a user doesn't find any primary use and wants to dispose the product. Based on their effects on human health and environment, wastes are classified into following different categories, such as:

1. General Solid Waste
    - i. Biodegradable Waste
    - ii. Non- Biodegradable Waste
2. Liquid Waste
3. Special Waste
4. Hazardous Waste

General Solid Waste

General solid wastes are grouped into two categories

- I. Biodegradable
- II. Non -Biodegradable

Bio-degradable waste: This is a type of waste that can be broken down by microbes or other living organism in a reasonable amount of time. Ex: MSW, Wood, Vegetable waste.

Non Bio-degradable products: These are products which either cannot be broken down my microbes or it takes a long duration for them to do so, Ex: Plastic, Polyethelene

Liquid Waste

For a waste to be classified as a liquid waste it must have the following characteristics:

- Has an angle of repose less than 5°C above horizontal
- Becomes free flowing at below 60°C or when it is transported
- Is generally not capable of being picked up by a spade or shovel

Special Waste

'Special Waste' is a category of wastes that have unique regulatory requirements. These should be managed in a streamlined way to minimize harm to the environment and human health. These can be any of the following groups:

- Clinical and related waste
- Asbestos Waste

Hazardous Waste

Wastes exhibiting characteristics like toxicity, corrosiveness, flammability and reactivity are categorized under hazardous waste. European Pollution Authority (EPA) has classified hazardous waste as:

- Container the previously contained goods that are deemed dangerous for transportation, from which resides have not been washed or vacuumed out.
- Coal tar or pitch waste
- Lead acid or nickel cadmium batteries.
- Lead plant waste from residential and educational
- Nuclear waste.

2.5 Difficulties with the Wastes Tyres

Tyres are made of vulcanized rubbers with styrene butadiene rubber (SBR), natural rubber (NR) and polybutadiene rubber (PBR), carbon black, steel, textile cord and little amount of others additives. The dumping of waste tyres is one of the main environmental issues all over the world. The toughness and resistance of the material to biological make their removal and reprocessing difficult [26]. One common way of disposal for these waste tyres is landfilling, Tyres are bulky and 75% of the space a tyre occupies is void, so that the landfilling of waste tyres has several difficulties. It needs a considerable amount of space because of the volume of tyres cannot be compacted. Tyres tend to float or rise in a landfill and come to the surface. Under the ground, the void space of waste tyres captures various gases such as methane which has a tendency to burn suddenly with a vast explosion. If the waste tyre is scattered on land in vain then it come with rain water and may be a good place for breeding mosquitoes or others bacteria. This causes various harmful diseases to human beings [27]. If the scrap tyres burn directly in brick field or any other incineration plant then various harmful gases such as CO_2 CO, SOx, NOx, etc. will produce which cause environment pollution. Thus, an environmental friendly and economic technology should be developed to recover the energy from tyres wastes. It will also help to reduce disposal problem for the waste tyres effectively. Different alternative techniques have been using for recycling the waste tyres such as retreating, reclaiming, incineration, grinding, etc. However, all of them have significant drawbacks and limitations [23].

As reported in [28], at this moment, the most significant methods and technologies adopted for waste tyre recovery and disposal are:

- Reusing the original form
- Reconstruction of waste tyres
- Shredding operations to use them in powdered or scrapped form.
- Thermal treatment to perform material and or energy recovery
- Utilization in building applications
- Other treatments
- Landfilling, heaping and abandonment.

From the prescriptive frame, it comes out that the general criteria normally applied to the waste management problem encourage, first the minimization of waste production during the manufacturing process, secondly reusing in the original form, recycling the material and or energy recovery and, finally, as the last choice, disposal. It is worth noticing that, because of their structural characteristics, waste tyres are hard to recycle in the conventional ways used for other waste flows, like glass, paper and plastics, So thermal treatments, aimed at matter and energy recovery, are a promising disposal method as an alternative to landfilling [29].

2.6 Effects of Waste Tyre on Environment

Tyres represent a serious environmental concern on several fronts. Part of the risk lies with their chemical makeup. Toxins released from tyre decomposition, incineration or accidental fires can pollute water, air and soil. For many years landfill was the main practical means for dealing with the problem of waste tyre. However, the practice is rapidly declining as tyres 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 tyres [30]. The EPA classifies tyres as municipal solid waste rather than hazardous waste. Nevertheless, tyres that are thrown away instead of recycled can cause serious environmental problems. The issues arise when the chemicals they contain are released into the environment. The breakdown of tyres release hazardous wastes. Tyres contain oils that contaminate the soil; they also consist of heavy metals such as lead that can persist in the environment and accumulate over time. Another major concern of discarded tyres is increased fire risk. When heated, tyres become a fuel source. In fact, nearly 50% (by weight) of recycled scrap tyres find a second life in fuel generation. Fires fueled by tyres can be more difficult to control and extinguish. In addition, the smoke contains toxic chemicals and particulate matter that poses human health consequences, such as, worsening of existing respiratory conditions. Discarded tyres present environmental risk that may not be as obvious as waste generation. This effect can, in turn, increase the risk for vector-borne diseases such as encephalitis. Rodents may also find habitat in tyres. The U.S. Centers for Disease Control and Prevention recommends removing discarded tyres from anyone's property because of their possible health hazards [31].

Atmospheric ozone O_3 is, by far, the most damaging factor on rubbers. The failure of rubber tyres in service is often the direct result of O_3. Atmospheric ozone degrades polydiene rubbers by reacting directly with the polymer chain. Ozone attacks the double bond of the polymer and forms an intermediate organoperoxide (carbonyl) and an aldehyde (if terminal carbon) or ketone. The intermediate organoperoxide bonds with secondary ozonides to form stable organoperoxides and organohydroperoxides. Induced surface cracking or alternatively fatigue or mechanical failure is initiated by the surface cracks produced by O_3 attack. Once released to the environment, metal ions associated with a tyre's composition are relatively mobile and can migrate to ground and surface waters through soil leaching and runoff. But in most cases, the concentrations of metals that leached from tyres and tyre chips are very minute. Consequently, the impact of metal on the environment from tyre leaching is relatively small. Metals and metal oxides recovered from the thermal oxidation of tyres have a higher potential to impact the environment and should be recovered or stabilized [32].

2.7 Analysis of Properties of Pyrolytic Oil:

To study the behavior of any chemical substance its properties are determined. These are two type of properties i.e , Physical and chemical properties. The analyses of the properties of pyrolytic oil are briefly explained below:

2.7.1 Physical Properties

The physical properties of pyrolytic oil can be determined by following the standard test methods for Kinematic viscosity, Density, Flash point, Pour point, Distillation etc. These are briefly described below:

Kinematic Viscosity

The kinematic viscosity is a measure of the resistance to gravity flow of a fluid. Viscosity of oil is an important property since it affects for example the flow of the liquid through the pipelines. The lower the viscosity of the oil, the easier it is to pump and to atomize and achieve finer droplets. This is the major criterion upon which the oil are graded. The kinematic viscosity of the pyrolysis liquids was determined using Glass Capillary Kinematic Viscometer, according to ASTM-D445 test methods.

Density

The density of oil is a measure of its aromaticity in hydrocarbon oils, but not in biomass derived oils, it is necessary parameters used to calculate the volumetric output of pump and injectors needed to supply a given rate of delivered energy, because the heat rate of combustion is determined on a weight basis. The density of the pyrolysis liquids is much higher, than petroleum derived hydrocarbon oils. Unlikely hydrocarbon oils the higher density of pyrolysis oils refers the high oxygen content, rather than a high pyrolytic aromatic content. The pyrolysis liquid having relatively higher density typically has lower water contents. The density of the liquid was measured using methods ASTM D-4052.

Flash point

The flash point of a volatile material is the lowest temperature at which it can vaporise to form an ignitable mixture in air. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the ignition source is removed. This is a measure of the volatility of the oil as well as its ease of ignition. The higher this number, the safer the oil is to handle because the risk of accidental vapor ignition is reduced. The flash point of the liquid was determined according to ASTM –D93 test methods.

Pour point

The pour point is the lowest temperature at which the liquid is observed to flow under prescribed conditions. The parameter is an indication of the minimum temperature at which the oil can be pumped without heating of the storage tank. The standard test method for the determination of the pour point is ASTM D97.

Distillation

Distillation is a process of separating the component substances from a liquid mixture by selective evaporation and condensation. Distillation may result in essentially complete separation (nearly pure components), or it may be a partial separation that increases the concentration of selected components of the mixture. In either case the process exploits differences in the volatility of mixture's components. Distillation is also used as a purification process in which non-volatile components are separated from volatile ones. The standard test methods for the determination of the distillation are ASTM D86.

2.7.2 Chemical Properties

The chemical properties of pyrolytic oil can be determined by the following the tests such as Gross calorific value (GCV), FTIR. These are briefly described below:

Gross Calorific Value (GCV)

The gross calorific value is a measure of the quantity of heat released in total combustion and therefore measure the energy content of a fuel. It is the most important fuel property of any fuel. The Gross calorific value (GCV) of the pyrolysis liquids were determined by a Oxygen bomb calorimeter.

Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy

The functional group compositions of the pyrolysis liquids were analyzed by Fourier Transform Infra-Red (FTIR) spectroscopy to identify the basic compositional group. The standard FTIR spectra of hydrocarbons were used to identify the functional groups of the components of the pyrolysis oil.

2.8 Cost Analysis:

Cost analysis is the process of developing and analyzing cost data from separate business elements and estimating incremental and total resources needed to support current and future business strategies. A decision making tool used to evaluate and prioritize resource needs at based on cost estimates and their expected return on investment. The cost analysis of a pyrolytic plant is described in the following section.

2.8.1 Cost Analysis of Pilot Plant

Techno-economic assessment

Islam et. al. [5] showed the production cost for crude pyrolysis oil from solid tyre waste feedstock for three cases: medium commercial scale, small commercial scale and pilot scale plants. The production cost was determined by estimating the capital cost and the operating costs for collection and shredding process of tyre wastes.

2.8.2 Capital Costs

The capital cost of a plant is determined by summing the costs related to the major pieces of base equipment. Capital cost was calculated as a Total Capital Requirement (TCR) by adding to the Fixed Capital Investment (FCI). The capital charges were determined by the formula given by Eq. No. (1)

$$ACC=\frac{TCR}{\{1-(1+i)^{N}\}}\times i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where ACC, the annual capital cost, *i*, the interest rate and N, the plant life time

2.8.3 Operating Costs:

The majority of the fixed operating costs (maintenance, over-heads, taxes and insurance) were based on percentages of the Fixed Capital Investment (FCI). There are different parameters used in cost estimation. These are given in the Table -2.2. The analysis of unit production cost of oil is the basis for assumptions.

Table-2.2: Parameters used in Annual Cost Estimation of a Tyre Pyrolysis Plant.

Plant Capacity	200kg/day, Waste tyre
Location, time, currency	Bangladesh, 2013,Tk
Annual operating cost	3600h@ 16 h/day
Maintenance charge	2.5 % of FCI
Overheads	2% of FCI
Taxes and Insurance	1.5% of FCI
Other fixed operating costs	1 % of FCI
Feed stock cost	15 Tk./kg
Labour cost	300 Tk./day
Total labours	2 (working 225 days/ yr)
Electricity price	3.20 (Tk./kWh)
General overheads	60% of total salaries
Interest rate	10%
Plant life	5 years

Calculation:

Fixed capital investment (FCI)= Tk. 160000

Total Capital Requirement (TCR) = (FCI + the start up costs, 10 % of FCI + the working capital, 5% of FCI)

= Tk. (160000 +16000 +8000) = Tk.184000

Using Eq.(1) , ACC= Tk.48548.81 , Fixed operation cost = Tk. 78.700

Variable operating cost (Electricity, Feed stock, General overheads) = Tk. 945180

Total operating cost = (Fixed operating cost + Variable operating cost)

= (78700 +945180) = Tk.1023880

Total annual production cost of oil = (Annual capital cost + Total operating cost).

= Tk. (48548.81+1023880) = Tk.1072428.81

Total annual oil production = (200 × 225×0.45) = 20,250 kg

Unit production cost of oil (Tk./kg)= Tk.52.95 per kg

CHAPTER III

LITARATURE REVIEW

3.1 Pyrolytic Conversion

Liquid fuel production by fast pyrolysis is a promising technology today. Generally, all biodegradable and non biodegradable materials can be converted to liquids by pyrolysis. High yields of liquid products can be obtained under optimized conditions: very high heating and heat transfer rates that requires a finely ground biomass/tyre feed, carefully controlled temperature of around 500°C and rapid cooling of the pyrolysis vapours to give the bio-oil product [33] . 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 time of a few hundred milliseconds are necessary for optimum yields of chemicals and food additives, while fuels can tolerate vapour residence time of up to around 2s [34]. 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.

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 [35]. The initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration and decarboxylation. 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 [36]. Also, the high char yield at low heating rate has been explained by the vapour-solid interactions [37].

3.2 Various Recycling Process to reduce Wastes Tyre

Pyrolysis, gasification and liquefaction are the thermo-chemical processes that can be used to convert waste tyre and tube as well as other carbonaceous feed stocks such as coal, wood waste, or municipal solid waste into usable products [14].

3.2.1 Pyrolysis Process

Pyrolysis is the thermo chemical decomposition of organic materials at temperatures between 400 and 650 °C in the absence of O_2. The decomposition process releases volatile species, while the solid, non-volatiles are collected as bio-char. A portion of the gas phase volatiles condense into a black, viscous fluid termed bio-oil [37] that has a variety of synonyms including pyrolysis oil, bio-crude oil, bio-fuel oil, wood liquid, wood oil, liquid smoke, wood distillates, pyroligneous tar, and pyroligneous acid [38]. Pyrolysis methods can be grouped into two large categories, slow and fast (or flash) pyrolysis. Slow pyrolysis consists of slow heating rates of 0.1–1 °C/s, a residence time anywhere from hours to minutes, and a temperature range of 400–600 °C. It has been used for centuries to produce methanol and yields approximately equal quantities of char, gas, and liquid [39-40]. Fast pyrolysis is a relatively new, promising technology involving a high liquid yield achieved through rapid heating rates of 10 to >1000 °C/s, short residence times of less than 2 s and temperatures of 400–650 °C, and rapid quenching of the vapors. For a more extensive review of reactors, processes, and their corresponding liquid products see *Bridgwateret et. al.*[41]. As studied by *Islam et. al.* [36] pyrolysis basically involves the thermal decomposition of the tyre rubber at high temperatures (300-900°C) in an inert atmosphere. The pyrolysis of solid tyre 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 transported to where it can be most efficiently utilized. As reported in [28], a flow diagram of tyre pyrolysis process, including the proposed thermal decomposition model, is presented in Figure 3.1. The three types of arrow in the flow diagram indicate three decomposition reactions. The higher weight or color deepness of the arrows indicates the decomposition of the corresponding tyre materials in the higher temperature regions.

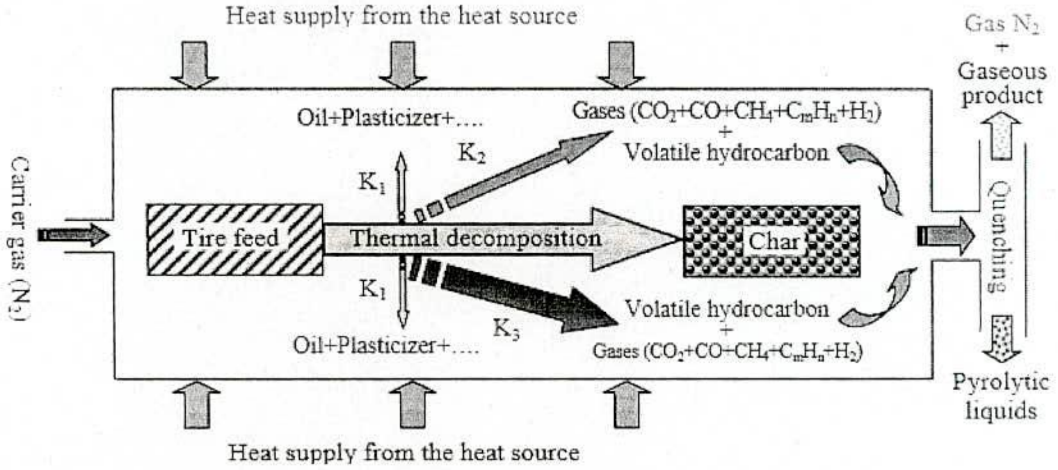


Figure 3.1: Flow diagram of tyre pyrolysis process .

3.2.2 Effect of Pyrolysis

The pyrolysis process has been established for many years but is currently receiving renewed attention. The process produces liquid, char and gas product, all of which have the potential for use. The recovery of liquid oil known as pyrolysis oil or pyrolytic oil can be as high as 58 % (by weight) for tyre rubber and has a higher calorific value of the order of 42 MJ/kg. It can be used as a fuel, chemical feedstock or can be added to petroleum refinery feedstock. The char can be used as a solid fuel, or can be upgraded for use as activated carbon or carbon black. The yield of char from the process is of the order of 35-38 % (by weight) for tyre rubber. The derived gas has a sufficiently high calorific value to provide the energy requirements for the pyrolysis process. In addition the steel reinforcement can be easily separated from the friable char and recycled back into the steel industry [42]. In a previous study thermal cracking of model seven components mixed plastics (HDPE, LDPE, LLDPE, PP, PVC, PET, PS) into oils/waxes, woody material and pyrolysis of plastics and biomass were decomposed to find out the effect of the experimental conditions on products yields and composition [43].

Pakdel et al. developed the vacuum pyrolysis process for used tyres and got 45% of oil from which 27% was naphtha and showed that the mass spectrometry provides superior quantitative capabilities, although infrared spectroscopy is an excellent complementary technique for simultaneous qualitative analysis of pyrolytic oil [44]. During the pyrolysis of car tyre it was observed that there was no significant influence of temperature and characteristics of pyrolysis products over 500°C. The oils obtained were 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 pyrolysis gases obtained composed of hydrocarbons of which C_1 and C_4 are predominant, together with some CO, CO_2 and H_2S and they have very high gross calorific values (68–84 MJ/ kg). Authors have also showed that at 500°C, 600°C and 700°C and at longer reaction time do not decrease solid yields in tyre pyrolysis. Therefore, it can be concluded that tyre decomposition at 500°C, 600°C and 700°C is complete and that 3–4% of char or carbonaceous material is produced. *Chang* [45], studied that pyrolysis of waste tyre at different degradation rate and product yields 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. No difference in conversion and yields was found when nitrogen was used.

In the present study, scrap tyres will be thermally converted with the aim of studying the effect of experimental conditions that would maximize liquid yields.When the temperature will increased, the amount of the aromatic content of the oil will increase, at the same time aliphatic content will decrease.

3.2.3 General Cracking

Cracking is the name given to breaking up of large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are revaporised before cracking.

There is no single unique reaction occuring in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds. One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:

$$C_{15}H_{32} \longrightarrow \underset{\text{Ethane}}{2C_2H_4} + \underset{\text{Propane}}{C_3H_6} + \underset{\text{Octane}}{C_8H_{18}}$$

3.2.4 Catalytic Cracking

Modern cracking uses zeolites as the catalyst. These are complex aluminosilicates and are large lattices of aluminum, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. One may have come across a zeolite if someone knows about the ion exchange resins used in water softeners. The alkane is brought into contact with the catalyst at a temperature of about 500°C and moderately low pressures.

The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 to10 carbon atoms particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

3.2.5 Catalyst Uses in Tyre Pyrolysis

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts. The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been absorbed by the material. Based on this, he called the material zeolite, from the Greek word ζέω (zéō), meaning "to boil" and λίθος (líthos), meaning "stone". Zeolites occur naturally but are also produced industrially on a large scale. As of July 2015, 229 unique zeolite frameworks have been identified and over 40 naturally occurring zeolite frameworks are known.

Zeolites have a porous structure that can accommodate a wide variety of cat-ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. An example mineral formula is: $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, the formula for natrolite.

Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

As mentioned before zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves." The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8-ring" refers to a closed loop that is built from eight tetrahedrally coordinated silicon (or aluminum) atoms and 8 oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cat ions within the structure. Therefore, the pores in many zeolites are not cylindrical.

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydrocracking. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) are powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. The specific activation modality of most zeolitic catalysts used in petrochemical applications involves quantum-chemical Lewis acid site reactions [46].

Ultrastable Y (USY) is a kind of zeolite with lower Si/Al ratios and larger pore size. The structure of USY is characterized by large, essentially spherical, internal cavities (super cages) linked tetrahedral through pore openings, defined by rings of 12 oxygen atoms (12-rings). The protons existed in the zeolite are associated with aluminum atoms that, along with silicon atoms (occupy sites at the centers of apex-linked tetrahedral of oxygen atoms), form the three-dimensional framework of the zeolite. Though USY was commonly used in hydrocracking and fluid catalytic cracking (FCC) catalysts [47-48], few studies about USY applying in tyre pyrolysis were reported. The application of USY in tyre pyrolysis may enhance to obtain more chemical feedstocks.

3.2.6 Catalytic Reforming

Catalytic reforming is a chemical process used to convert petroleum refinery naphtha distilled from crude oil (typically having low octane ratings) into high-octane liquid products called reformates, which are premium blending stocks for high-octane gasoline. The process converts low-octane linear hydrocarbons (paraffins) into branched alkanes (isoparaffins) and cyclic naphthenes, which are then partially dehydrogenated to produce high-octane aromatic hydrocarbons. The dehydrogenation also produces significant amounts of byproduct hydrogen gas, which is fed into other refinery processes such as hydrocracking. A side reaction is hydrogenolysis, which produces light hydrocarbons of lower value, such as methane, ethane, propane and butanes.

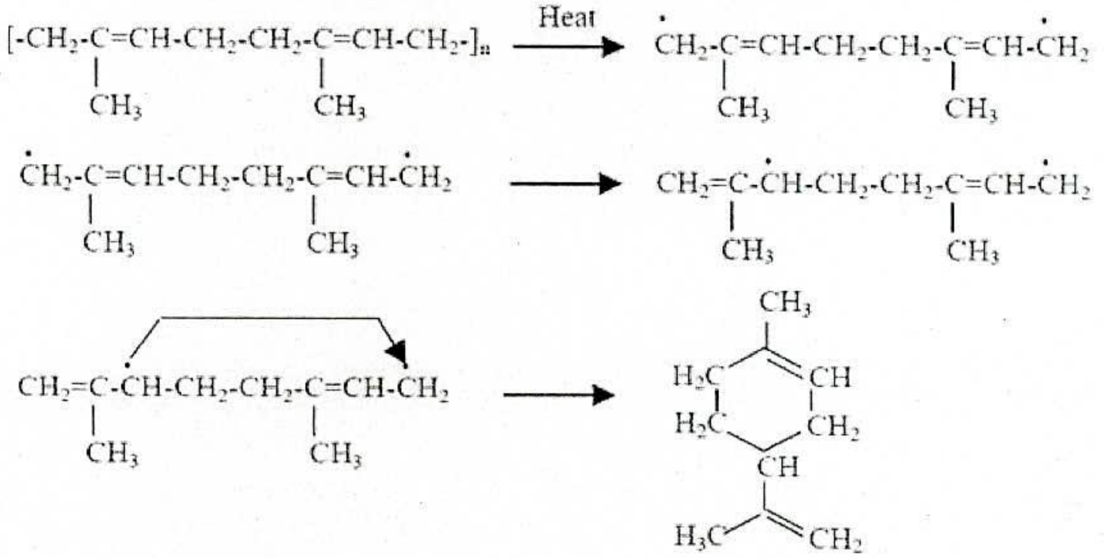
3.2.7 Catalytic Pyrolysis

The derived oils from tyre pyrolysis without catalyst have been shown to be highly aromatic, which are limited to be used as a substitute liquid 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 feedstock's in the chemical industry. So catalysts are used to produce more single ring aromatic compounds during tyre pyrolysis. *Williams and Brindle* [49-50] used USY type catalysts with different Si/Al ratios and pore sizes to study the influence on the yields of products and the composition of derived oils. The Y-zeolite catalyst had a lower silica/alumina (SiO_2/AlO_2) ratio and therefore higher surface acidity and also possessed a larger pore size than the ZSM-5 catalyst. The Y-zeolite catalyst produced significantly higher concentrations of benzene, toluene, xylenes, and naphthalene and alkylated naphthalene's compared to the ZSM-5 catalyst. *Olazar Metal* [51] has used HY and HZSM -5 zeolite catalysts in the pyrolysis of used tyres in a conical spouted bed reactor. The significance of the different shape selectivity of HY and HZSM-5 zeolite is apparent in the transformation reaction of thermal pyrolysis primary products. The capacity of the HZSM-5 zeolite catalyst has major influence for obtaining high yields of olefins (partially ethane and propane) decreasing the molecular weight of the oil fraction and decreasing the yields of tar compared to thermal pyrolysis. Both catalyst increase the yield of the aromatic fraction (with a high concentration of xylenes) compare to thermal pyrolysis.

The conversion of waste tyre rubber into valuable oil hydrocarbons was investigated using catalytic pyrolysis. The mixture of an acidic (SiO_2) and basic (Al_2O_3) catalyst used for pyrolysis, in which the yield of derived gas, oil and solid has been studied in terms of the temperature, time and amount of catalyst. Oil derived with Al_2O_3 containing higher concentration of polar hydrocarbon (40%) and lower concentration of aliphatic hydrocarbons while 40% aliphatic hydrocarbons and 30% polar hydrocarbons were found in oil derived with SiO_2. A mixture of catalyst ($Al_2O_3.SiO_2$) gave equal concentration of aliphatic (35%) and polar (35%) hydrocarbons oil [52]. Evaluation of waste tyre rubber using catalytic pyrolysis is very important from economical 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 [53].

3.3 Reaction Mechanisms during Pyrolysis of Tyre

Pyrolysis of tyre depends on various parameter and reactor type. During the pyrolysis of tyre different types of polymerization reactions are formed inside the reactor [14]. *Tamura et. al.* [54] 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. *Bhowmick et. al.* [55] 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 tyre is by radical generation via polymer chain scission and results in the formation of isoprene, dipentene and other smaller compounds.The thermal decomposition mechanism of waste tyre has been described by *Islam et. al.* [56-57] 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 scheme 2 reaction mechanisms as follows:



Scheme 2 Reaction mechanism during pyrolysis of tyre

The solid char consists of carbon black, some solid hydrocarbons, and a small amount of tyre rubber additives such as zinc, sulfur, clays, silica, and metal oxides. Therefore, there is no obvious mechanism for char loss with increasing temperature, excepting only the higher temperature volatilizes some of the solid hydrocarbon contents of the char [58]. 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 [59]. Since solid yields do not decrease in the temperature range of 475-575°C, it may be concluded that tyre 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 [60] and secondary repolimerization and/or carbonization reactions of oil hydrocarbons into char. 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 tyre rubber by pyrolysis technology, since decomposition is complete and the liquid yields become maximized at this temperature. Some of the research groups [60-63] found very similar product distributions *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.* [61] pyrolyzed automobile tyre 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 30 min for their isothermal experiments. The maximum liquid and char yields were 55.6 and 37.6 % (by weight) at 550°C for isothermal run, and 55.4 and 39% (by weight) at heating rate of 15°C/min for non-isothermal run. *Dai et. al.* [60] studied pyrolysis of automotive tyre waste in a circulating fluidized-bed reactor for temperature range of 360-810°C with 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 respectively with liquid yields of 50% (by weight) and char yields of 32% (by weight). *Chang* [62] pyrolyzed tyre 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 [62] reported that the yield of liquid had a maximum level up to 40 % (by weight) at 350°C with char yield of 17 % (by weight). *Islam et. al.* [63] pyrolyzed automotive scrap tyre in an externally heated fixed-bed reactor with N_2 atmosphere for feed sizes of 0.5-1cm, 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* [58] also found similar results that the oil yield decreases from 58.1-53.1 % (by weight) 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 % (by weight). The decreases in oil yields with increasing temperature and corresponding increase in gas yields have also been found by other researchers.

On the other hand *Ucar et al.* [64] pyrolyzed passenger car and truck tyre 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 % (by weight); with char yields of 41.7±2.7 and 33.8±2.4 % (by weight) at 650°C for car and truck tyre feed, respectively. Similar results have been reported by other research groups. *Roy et. al.* [65] studied tyre pyrolysis in the range 350-700°C, and found no influence of temperature on the pyrolysis yields over 500°C. The thermo-chemical conversion of rubber from scrap tyres by pyrolysis and hydropyrolysis was studied by *Mastral et. al.* [66]. 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 % (by weight) respectively.

CHAPTER IV

EXPERIMENTAL SET UP PROCEDURES

4.1 Introduction

Various types of materials, chemicals and equipments were used for the pyrolytic oil production, upgrading and characterization. Description of materials, instrument and equipment used for the work and methodology applied in the whole works are described in details in the following sections.

4.2 Materials and methods

The raw materials used as feedstock for the pyrolysis were the waste tyre of buses/trucks. The tyres were collected from the nearby bus repairing garage at Ferighat, Khulna, Bangladesh. The collected wastes tyre were washed by detergent to remove the mud, sand, and other contaminations with the tyre body. In order to maintain uniformity of the components in the representative samples of tyres same brand were chopped cross-section wise into four different sizes such as 1.00 × 1.00 × 0.75cm; 1.00 × 1.75 × 0.75cm; 2.00 ×1.00 × 0.75cm and 2.00 × 1.50 × 0.75cm. The cross-sectional pieces, which were representative of the whole tyre, contained no steel cords but the textile fabrics. The sample pieces were sun dried to remove moisture. USY (Manufactured by Xi'an Lvneng Purification Technology Co. Ltd.) was used as the catalyst; it was in the powder form with surface area of 600-630 m^2/g which were purchased from China.

4.3 Experimental Set-up

Batch type fixed-bed pyrolysis reactor was selected for the study. The main reactor chamber was constructed from MS sheet having a length of 56 cm; the outer diameter of the chamber 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 4.1, shows the (2-D) schematic view of the experimental unit, Figure 4.2, shows the (3-D) schematic view of the experimental unit which consists of reactor furnace system for maintaining constant temperature inside and condenser for condensing the pyrolytic vapour to liquid. Schematic arrangement for temperature measurement of reactor and schematic diagram of electric heater are shown in Figure 4.3 and 4.4. The Photograph of the fixed-bed pyrolysis system is shown in Figure 4.5. The major components of the unit are:

(i) A fixed-bed reactor

(ii) A heating system (heater)

(iii) A gravity feed type reactor feeder

(iv) Water-cooled condenser, having a liquid collecting steel bottle

(v) N_2 gas cylinder with connection pipes.

(vi) Temperature indicator

(vii) K-type thermocouples.

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 90 holes of 2.5 mm diameter each. The N_2 gas inlet was below the distributor plate. Four 10 mm diameter tube heater of a total capacity of 2.0 kW were fixed in equal spacing inside the reactor. The reactor was thermally insulated with glass wool and asbestos rope.

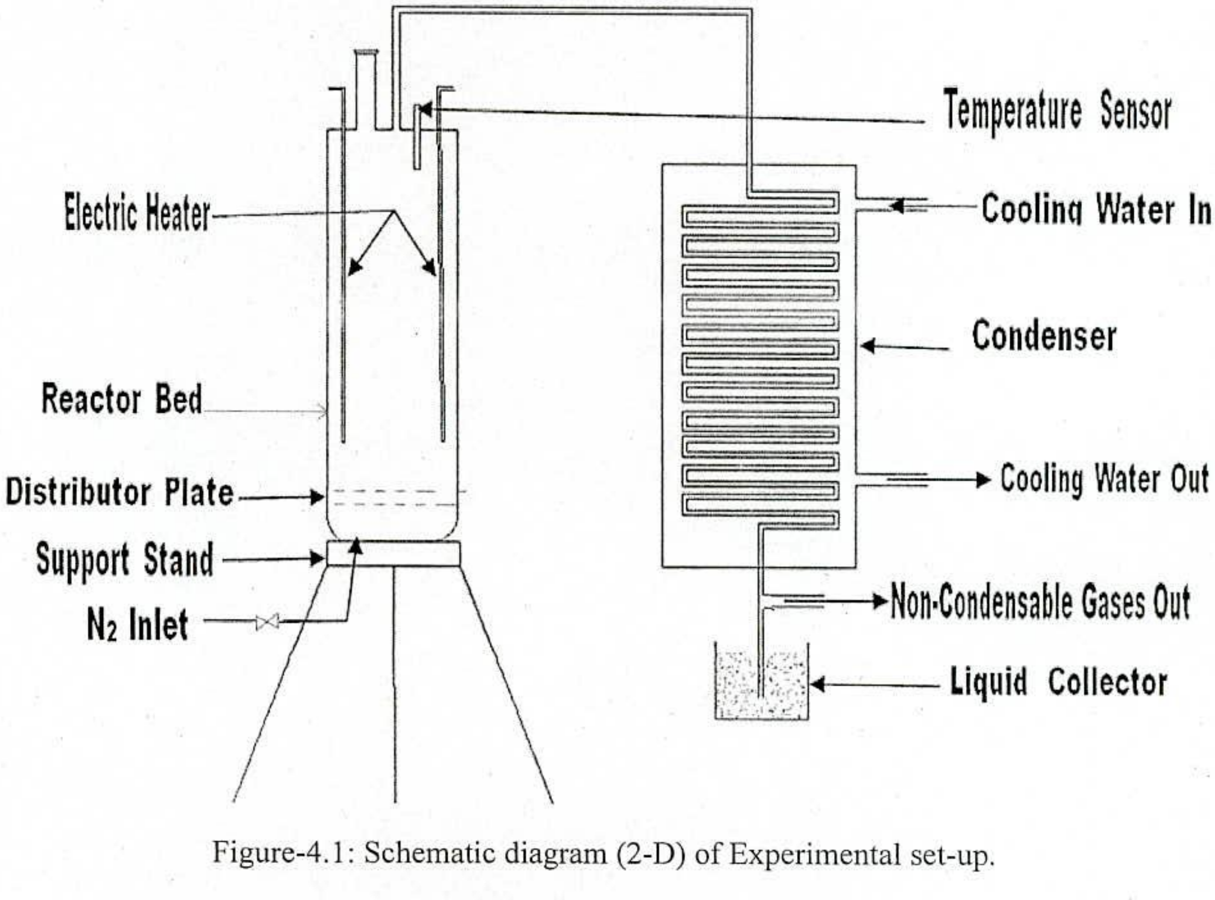


Figure-4.1: Schematic diagram (2-D) of Experimental set-up.

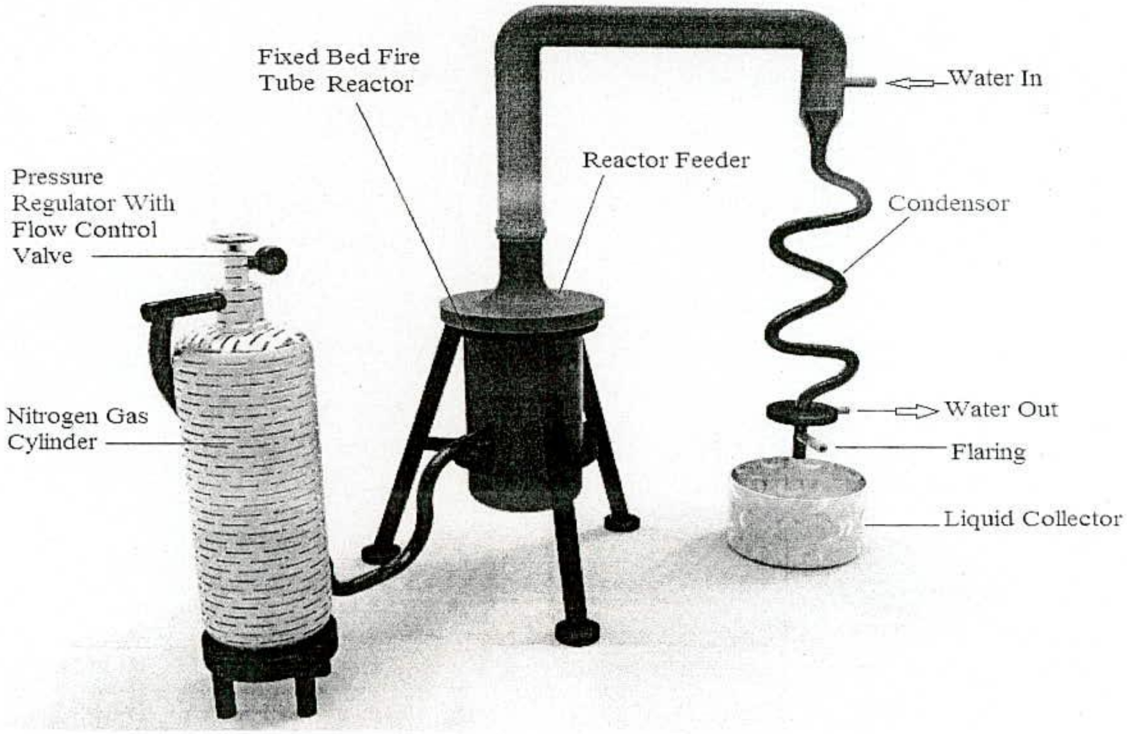


Figure 4.2: Schematic diagram (3-D) of Experimental set-up.

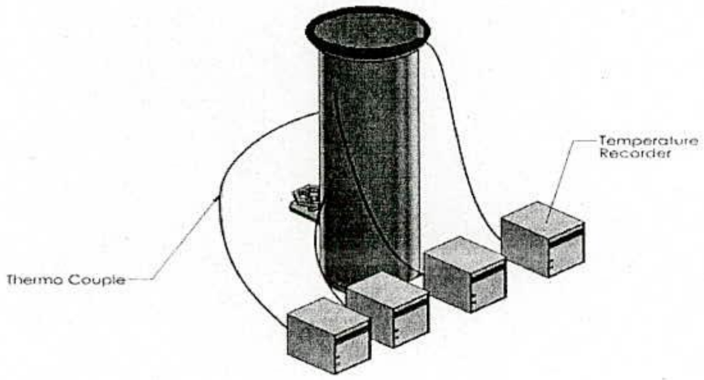


Figure 4.3: Schematic diagram (3-D) of Reactor with temperature display.

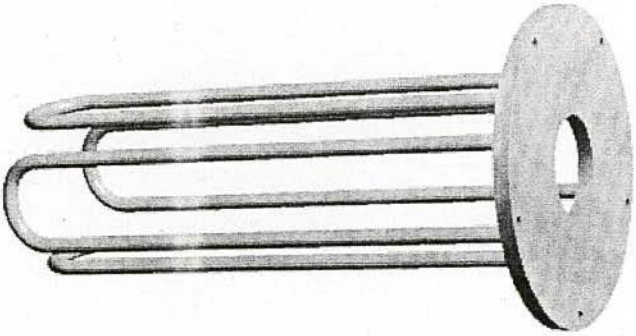


Figure 4.4: Schematic diagram (3-D) of Electric heater.

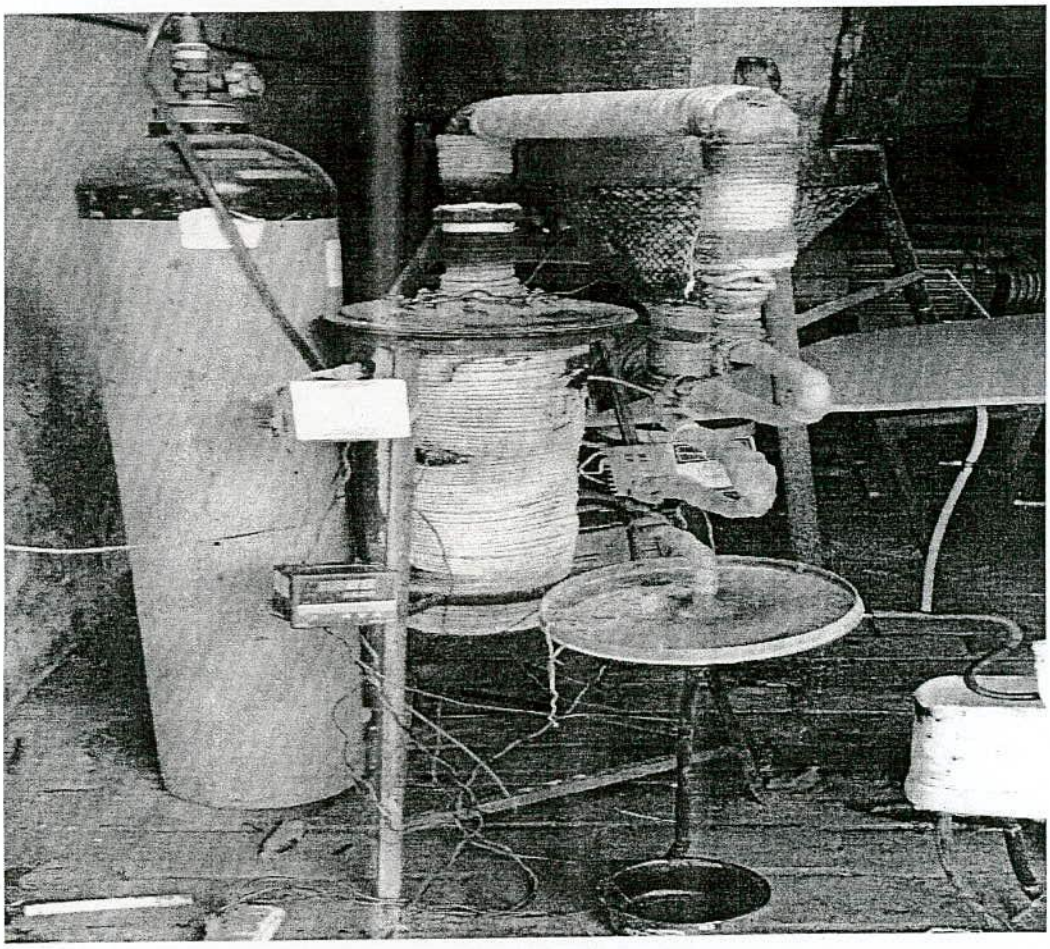


Figure 4.5: Photograph of the Fixed-bed Tube heating pyrolysis system

4.4 Experimental Procedure

The batch type fixed-bed pyrolysis system as described in section 4.3 was constructed and installed in the Heat Engine Laboratory of Department of Mechanical Engineering, Khulna University of Engineering & Technology. The experiments were conducted for different temperatures and feed volumes (size of raw material). The experiments were performed for bus tyres only. The thermocouple sensors were placed in the reactor chamber to record the temperatures inside 1.5 kg tyre sample were taken in the reactor in each run. The loading of raw materials were made by the action of gravity. The catalysts (Zeolite USY) were taken into reactor by the action of gravity after loading feed materials. Before the start of the experiment, the reactor was purged by flowing 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°C indicated by the temperature recorder. The temperatures were noted from the digital recorder during the experiment. During pyrolysis of tyre, a reddish/bright brown visible vapor usually flared into atmosphere. When the decomposition was completed, colorless gas came out from the reactor. The colorless flaring was the indication of the completion of the thermal decomposition of the sample (tyre) inside the reactor. After completion of all runs usually no further visible vapor product came out. Nitrogen gas was supplied in order to maintain an inert atmosphere inside the reactor and also to sweep away the pyrolyzed vapor product to the condensers. Pyrolytic vapor product was passed through the condenser pipes to condense them into liquid and then collected in the glass 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 brought 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 tyre.

4.5 Experimental Data

During the experiments 1.5 kg tyre were charged in the reactor chamber every time. The experiments were conducted for four different sizes of raw materials which were 1.00 × 1.00 × 0.75cm; 1.00 × 1.75 × 0.75cm; 2.00 ×1.00 × 0.75 cm and 2.00 × 1.50 × 0.75 cm respectively. The experiments were performed by varying the temperature within the range of 300-600°C at every 50°C interval for each feed size. The data collected during pyrolytic conversion of tyre are shown in Table 4.1 through 4.10.

Table 4.1: Details of Sample used in various run.

SI. No.	Tyre		Weight of charge
	Sample Size (cm × cm × cm)	Volume (cm^3)	Tyre (kg)
1	1.00 × 1.00 × 0.75	0.75	1.50
2	1.00 × 1.75 × 0.75	1.31	1.50
3	2.00 × 1.00 × 0.75	1.50	1.50
4	2.00 × 1.50 × 0.75	2.25	1.50

Table 4.2: Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 0.75 cm^3 for Various Temperatures ,

Sample-1: (Without catalyst)
Feed Materials: 1.5 kg (size 1 cm × 1 cm × 0.75 cm) Yields: Pyrolytic oil = 0.510 kg; Char product: 0.807 kg; Gas: 0.183 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.35	1.06	0.09	64
2	350	0.42	0.98	0.10	52
3	400	0.55	0.83	0.12	44
4	450	0.63	0.72	0.15	40
5	500	0.59	0.70	0.21	39
6	550	0.54	0.67	0.29	36
7	600	0.49	0.69	0.32	30

Table 4.3: Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 1.31 cm^3 for Various Temperatures.

Sample-2: (Without catalyst)
Feed Materials: 1.5 kg (size 1 cm × 1.75 cm × 0.75 cm) Yields: Pyrolytic oil = 0.500 kg; Char product: 0.810 kg; Gas: 0.190 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.34	1.08	0.08	63
2	350	0.41	0.99	0.10	53
3	400	0.53	0.85	0.12	45
4	450	0.61	0.73	0.16	39
5	500	0.58	0.70	0.22	38
6	550	0.52	0.69	0.29	34
7	600	0.50	0.65	0.35	31

Table 4.4: Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 1.50 cm^3 for Various Temperatures

Sample-3: (Without catalyst)
Feed Materials: 1.5 kg (size 2 cm × 1 cm × 0.75 cm) Yields: Pyrolytic oil = 0.490 kg; Char product: 0.800 kg; Gas: 0.210 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.33	1.07	0.10	62
2	350	0.40	0.99	0.11	50
3	400	0.51	0.83	0.16	45
4	450	0.60	0.73	0.17	40
5	500	0.58	0.68	0.24	38
6	550	0.52	0.67	0.31	31
7	600	0.49	0.66	0.35	29

Table 4.5 Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 2.25 cm^3 for various temperatures.

Sample-4: (Without catalyst)
Feed Materials: 1.5 kg (size 2 cm × 1.5 cm × 0.75 cm) Yields: Pyrolytic oil = 0.500 kg; Char product: 0.800 kg; Gas: 0.200 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.33	1.08	0.09	60
2	350	0.40	0.98	0.12	49
3	400	0.58	0.77	0.15	39
4	450	0.59	0.73	0.18	37
5	500	0.55	0.70	0.25	34
6	550	0.54	0.68	0.28	30
7	600	0.51	0.68	0.31	27

Table 4.6: Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 0.75 cm^3 with Catalyst for Various Temperatures

Sample-5: (CT ratio 0.13)
Feed Materials: 1.5 kg (size 1 cm × 1 cm × 0.75 cm) Yields: Pyrolytic oil = 0.410 kg; Char product: 0.880 kg; Gas: 0.210 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.22	1.17	0.11	62
2	350	0.25	1.12	0.13	52
3	400	0.36	0.98	0.16	45
4	450	0.55	0.75	0.20	39
5	500	0.53	0.72	0.25	38
6	550	0.50	0.72	0.28	35
7	600	0.49	0.68	0.33	29

Table 4.7: Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 0.75 cm^3 with Catalyst for Various Temperatures

Sample-6: (CT ratio 0.20)
Feed Materials: 1.5 kg (size 1 cm × 1 cm × 0.75 cm) Yields: Pyrolytic oil = 0.390 kg; Char product: 0.890 kg; Gas: 0.220 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.21	1.17	0.12	62
2	350	0.24	1.12	0.14	53
3	400	0.35	1.00	0.15	44
4	450	0.51	0.77	0.22	41
5	500	0.49	0.74	0.27	39
6	550	0.48	0.72	0.30	36
7	600	0.43	0.69	0.35	30

Table 4.8: Experimental data for Pyrolysis of 1.50 kg Tyre with Volume 0.75 cm^3 with Catalyst for Various Temperatures

Sample-7: (CT ratio 0.30)
Feed Materials: 1.5 kg (size 1 cm × 1 cm × 0.75 cm) Yields: Pyrolytic oil = 0.370 kg; Char product: 0.890 kg; Gas: 0.230 kg

No. of Observation	Temperature (°C)	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	300	0.20	1.17	0.13	62
2	350	0.23	1.13	0.14	53
3	400	0.33	1.01	0.16	45
4	450	0.50	0.77	0.23	41
5	500	0.47	0.75	0.28	40
6	550	0.47	0.71	0.32	35
7	600	0.42	0.71	0.37	30

Table 4.9: Experimental data for 1.50 kg Tyre for Various Sample size at 450°C

No. of Observation	Feed Size (cm^3)	Product yield, kg			Residence Time (min)
		Oil	Char	Gas	
1	0.5	0.63	0.72	0.15	40
2	1.0	0.61	0.73	0.16	39
3	1.5	0.60	0.73	0.17	40
4	2.0	0.59	0.73	0.18	37

Table 4.10: Experimental data for 1.50 kg Tyre for Various CT ratio at 450°C

No. of Observation	CT ratio	Product yield, kg			Operating Time (min)
		Oil	Char	Gas	
1	0.13	0.55	0.75	0.20	39
2	0.20	0.51	0.77	0.22	41
3	0.30	0.50	0.77	0.23	41

CHAPTER V

RESULT AND DISCUSSION

5.1 General

Pyrolysis, a thermo-chemical conversion process that causes irreversible chemical changes by the action of heat in absence of oxygen, transforms organic or inorganic materials into various compounds that have fuel value. Tyre is composed of 85% carbon, 10-15% fabric material and 0.9-1.25% sulfur. Pyrolysis of tyres yield products like Fuel Oil (40-45%), Carbon black (30-35%), Steel wire (3-5%), Non Condensable Gases (8-10%) and Moisture (3-5%).

The Pyrolytic oil or pyrolysis oil obtained from tyre pyrolysis is a blackish liquid with pungent odor. In an unrefined state it contains small particulate of carbon suspended in the liquid medium. The determination of various properties of pyrolytic oil needs some pre-treatment of the liquid in some cases.

5.2 Presentation of Results

Under the study of pyrolytic conversion of waste tyre in batch type fixed-bed reactor, the experiments were conducted in the temperature range of 300°C to 600°C. The experiments were conducted to examine the effect of temperature on product distribution with catalyst and without catalyst. The experimental data are shown in Table 4.2 to Table 4.10 and the results calculated from these data are shown in Table 5.1 to 5.10, from which Figs 5.1 to 5.12 have been drawn for convenience of analysis. They will be discussed in details in the following sections.

Table 5.1: Effect of Temperature on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 1 × 1 × 0.75 cm; Volume: 0.75 cm^3

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.50	23.33	70.67	6.00
2	350		28.00	65.33	6.67
3	400		36.67	55.33	8.00
4	450		42.00	48.00	10.00
5	500		39.33	46.67	14.00
6	550		36.00	44.67	19.33
7	600		32.67	46.00	21.33

Table 5.2: Effect of Temperature on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 1 × 1.75 × 0.75 cm; Volume: 1.31cm^3

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.50	22.67	72.00	5.33
2	350		27.33	66.00	6.67
3	400		35.33	56.67	8.00
4	450		40.67	48.67	10.67
5	500		38.67	46.67	14.67
6	550		34.67	46.00	19.33
7	600		33.33	43.33	23.33

Table 5.3: Effect of Temperature on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 2 × 1 × 0.75 cm; Volume: 1.50 cm^3

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.50	22.00	71.33	6.67
2	350		26.67	66.00	7.33
3	400		34.00	55.33	10.67
4	450		40.00	48.67	11.33
5	500		38.67	45.33	16.00
6	550		34.67	44.67	20.67
7	600		32.67	44.00	23.33

Table 5.4: Effect of Temperature on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 2 × 1.5 × 0.75 cm; Volume: 2.25cm^3

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.50	22.00	72.00	6.00
2	350		26.67	65.33	8.00
3	400		38.67	51.33	10.00
4	450		39.33	48.67	12.00
5	500		36.67	46.67	16.67
6	550		36.00	45.33	18.67
7	600		34.00	45.33	20.67

Table 5.5: Effect of Catalyst on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 1 × 1 × 0.75 cm; Volume: 0. 75 cm^3; Catalyst: Tyre = 0.13:1

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.50	14.67	78.00	7.33
2	350		16.67	74.67	8.67
3	400		24.00	65.33	10.67
4	450		36.67	50.00	13.33
5	500		35.33	48.00	16.67
6	550		33.33	48.00	18.67
7	600		32.67	45.33	22.00

Table 5.6: Effect of Catalyst on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 1 × 1 × 0.75 cm; Volume: 0. 75 cm^3; Catalyst: Tyre = 0.20:1

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield			Operating time (min)
			Oil	Char	Gas	
1	300	1.50	14.00	78.00	8.00	62
2	350		16.00	74.67	9.33	53
3	400		23.33	66.67	10.00	44
4	450		34.00	51.33	14.67	41
5	500		32.67	49.33	18.00	39
6	550		32.00	48.00	20.00	36
7	600		28.67	46.00	23.33	30

Table 5.7: Effect of Catalyst on Product Distribution for Pyrolysis of Waste Tyres

Sample Size: 1 × 1 × 0.75 cm; Volume: 0. 75 cm^3; Catalyst: Tyre = 0.30:1

No. of Observation	Temperature (°C)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	300	1.50	13.33	78.00	8.67
2	350		15.33	75.33	9.33
3	400		22.00	67.33	10.67
4	450		33.33	51.33	15.33
5	500		31.33	50.00	18.67
6	550		31.33	47.33	21.33
7	600		28.00	47.33	24.67

Table 5.8: Effect of Feedstock size on Product Distribution for Pyrolysis of Waste Tyres at 450°C

No. of Observation	Feed Size (cm^3)	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	0.75	1.50	42.00	48.00	10.00
2	1.31		40.67	48.67	10.67
3	1.50		40.00	48.67	11.33
4	2.25		39.33	48.67	12.00

Table 5.9: Effect of Various CT ratio on Product Distribution for Pyrolysis of Waste Tyres at 450°C

No. of Observation	CT ratio	Weight of tyre (kg)	% of Product yield		
			Oil	Char	Gas
1	0.13	1.50	36.67	50.00	13.33
2	0.20		34.00	51.33	14.67
3	0.30		33.33	51.33	15.33

Table 5.10: Effect of without and with Various CT ratio on Product Distribution for Pyrolysis of Waste Tyres

No. of Observation	Temperature (°C)	Oil Yield %			
		without catalyst	CT ratio 0.13	CT ratio 0.20	CT ratio 0.30
1	300	23.33	14.67	14.00	13.33
2	350	28.00	16.67	16.00	15.33
3	400	36.67	24.00	23.33	22.00
4	450	42.00	36.67	34.00	33.33
5	500	39.33	35.33	32.67	31.33
6	550	36.00	33.33	32.00	31.33
7	600	32.67	32.67	28.67	28.00

5.3. Graphical Presentation of Result.

The tabular values shown in Table 5.1 to 5.10 are plotted on grapes. These are shown in Fig. 5.1 to Fig 5.10 and are discussed below:

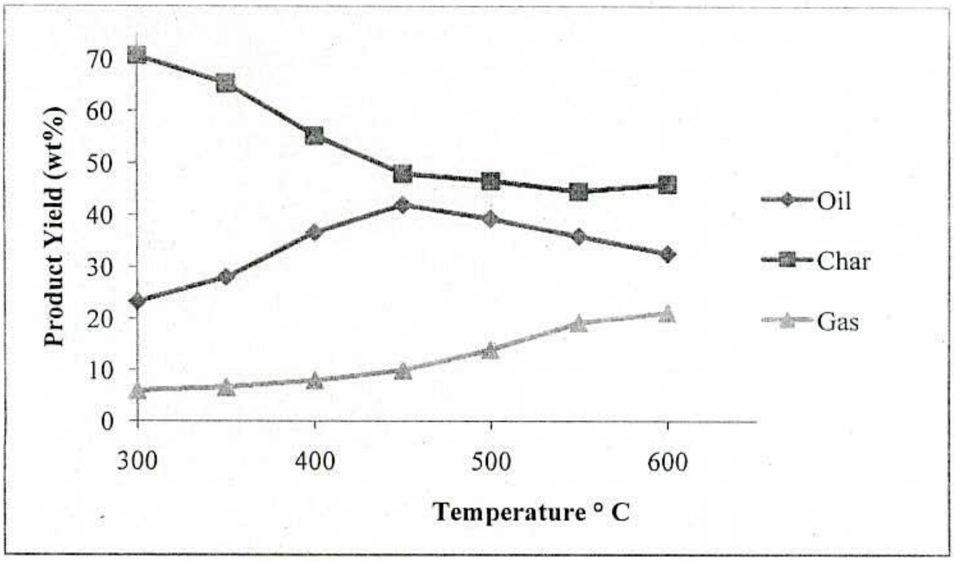


Figure 5.1: Effect of temperature on product yields for tyre pyrolysis with feed size 0.75 cm^3

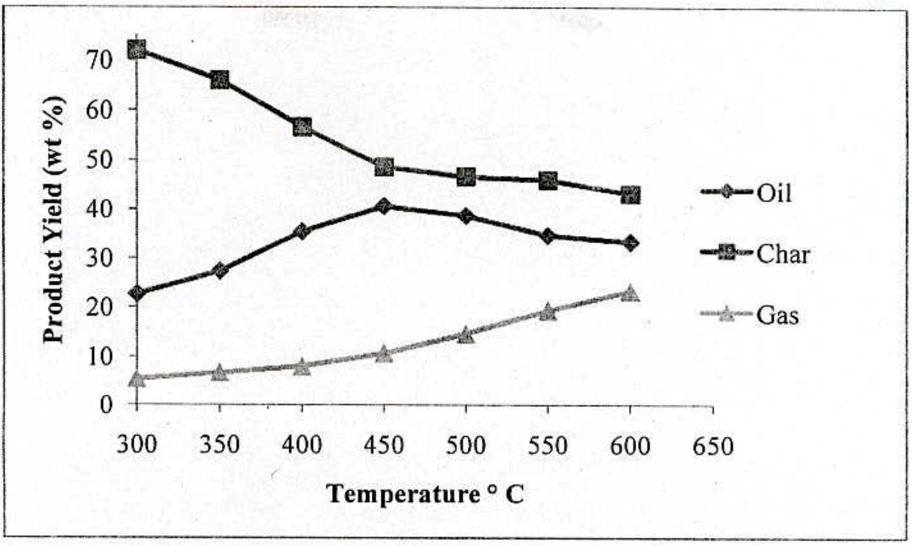


Figure 5.2: Effect of temperature on product yields for tyre pyrolysis with feed size 1.31 cm^3

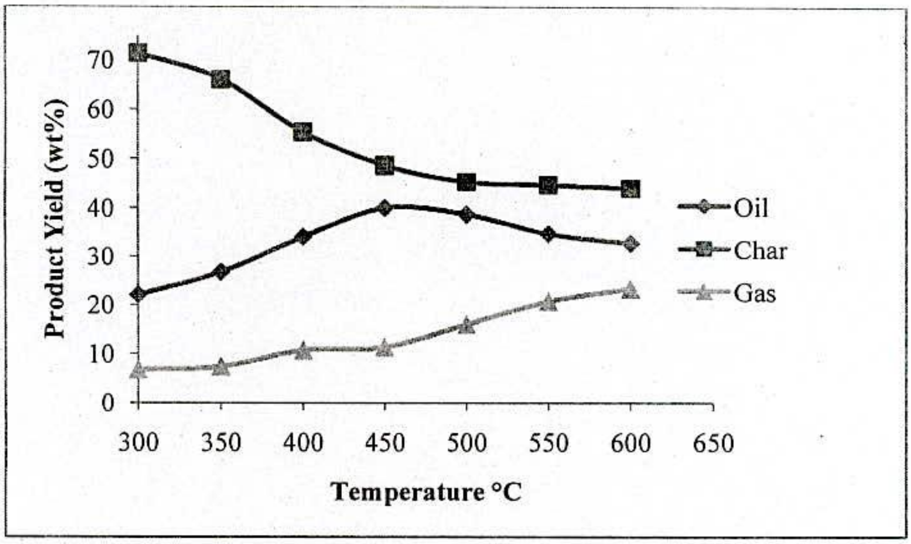


Figure 5.3: Effect of temperature on product yields for tyre pyrolysis with feed size 1.50 cm^3

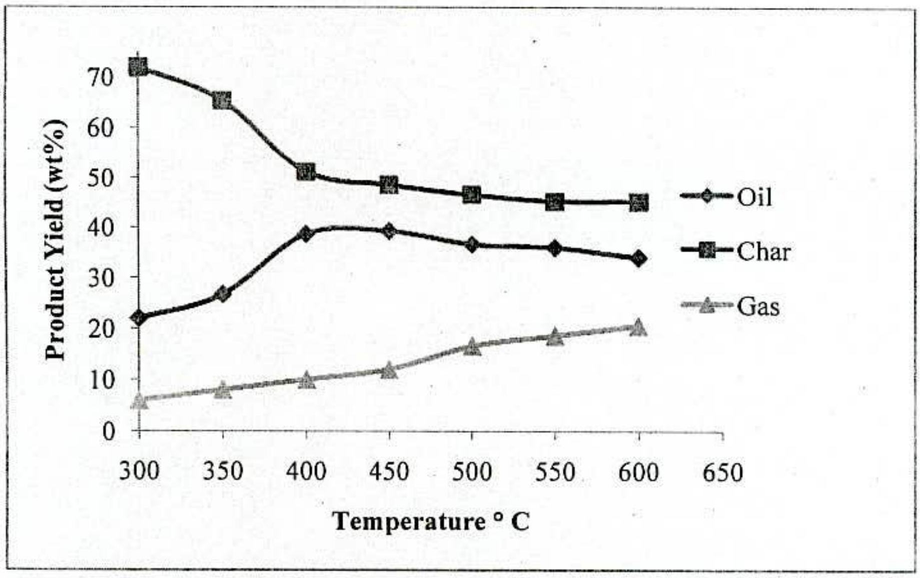


Figure 5.4: Effect of temperature on product yields for tyre pyrolysis with feed size 2.25 cm^3

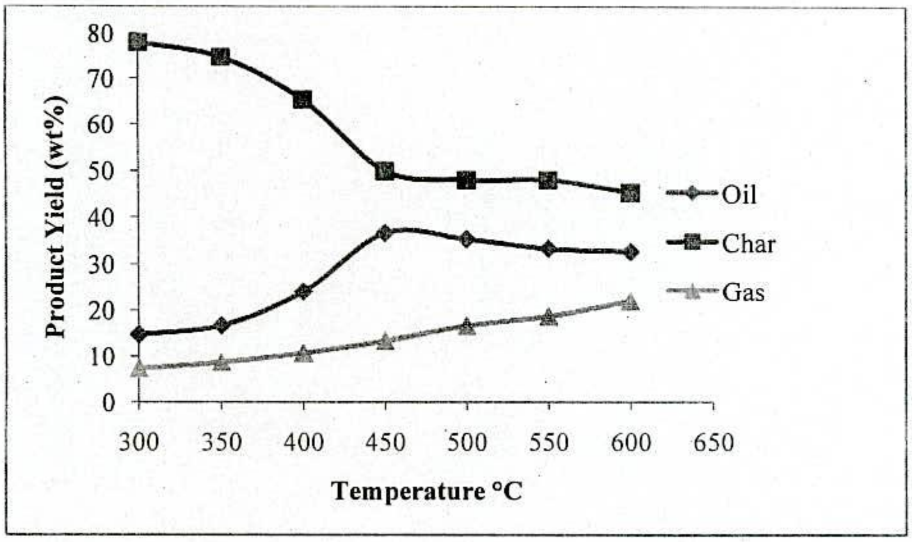


Figure 5.5: Effect of Catalyst on product yields with (CT ratio 0.13) for tyre pyrolysis with feed size 0.75 cm^3

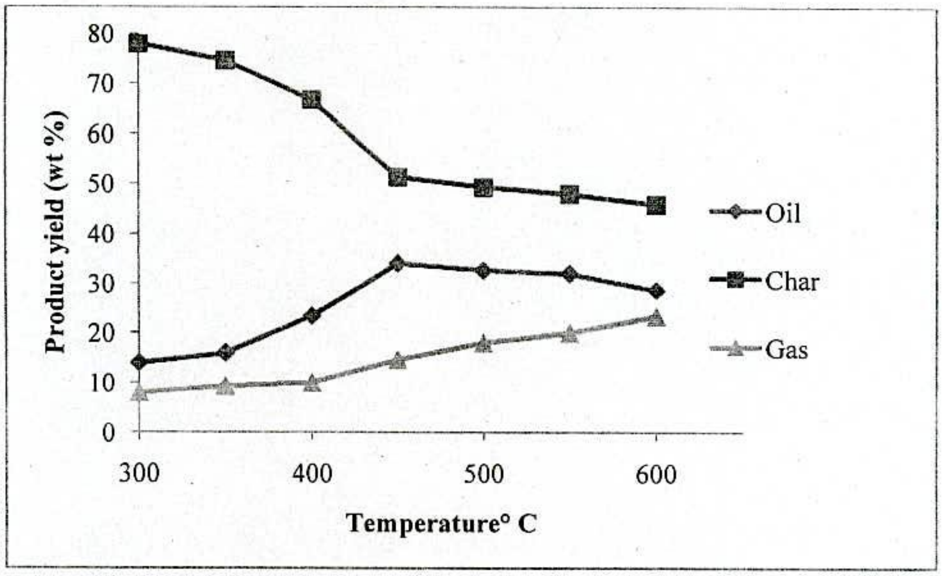


Figure 5.6: Effect of Catalyst on product yields with (CT ratio 0.20) for tyre pyrolysis with feed size 0.75 cm^3

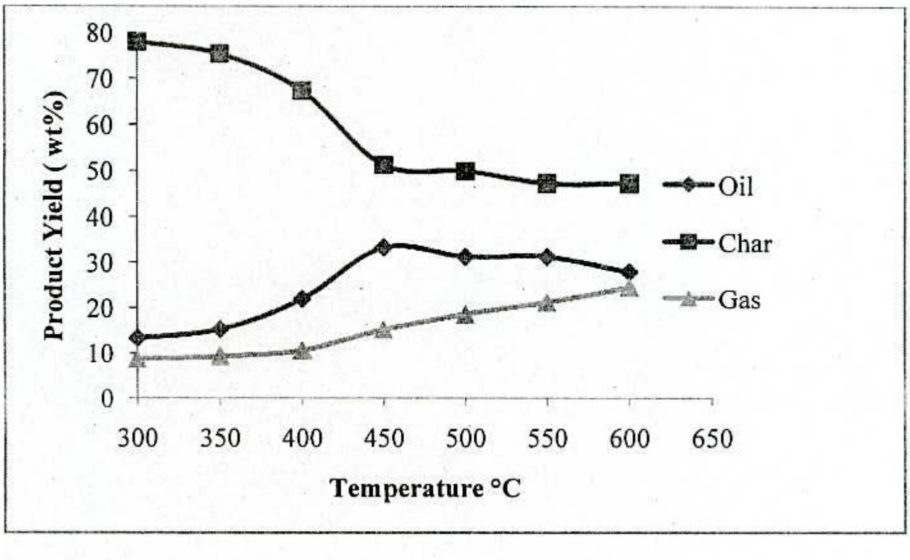


Figure 5.7: Effect of Catalyst on product yields with (CT ratio 0.30) for tyre pyrolysis with feed size 0.75 cm^3

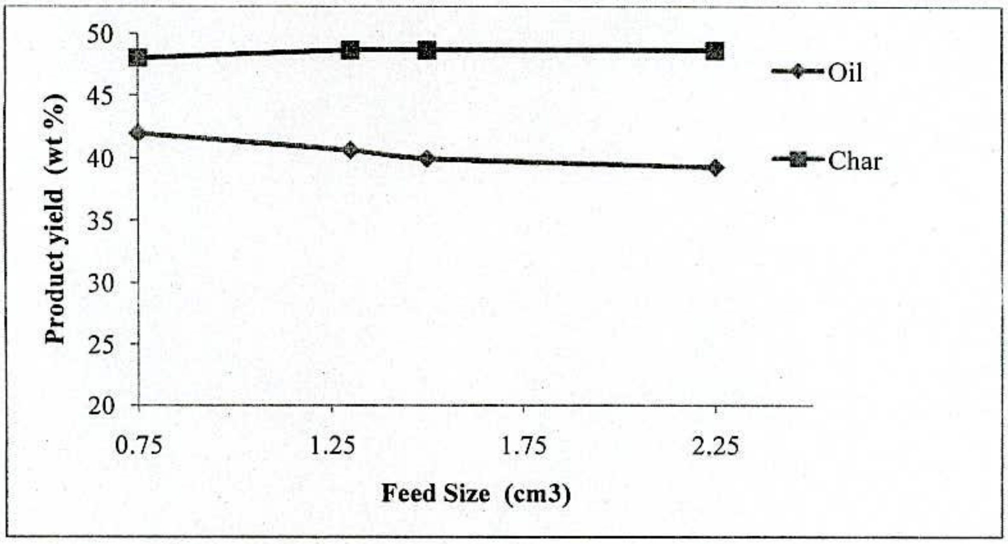


Figure 5.8: Effect of feed size on product yields at 450°C of tyre pyrolysis without catalyst

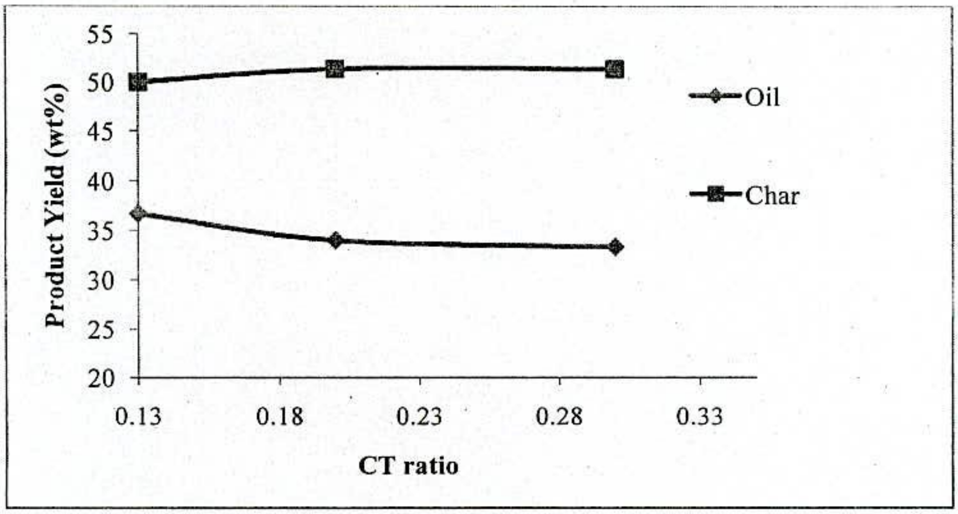


Figure 5.9: Effect of various CT ratio on product yields at 450°C of tyre pyrolysis

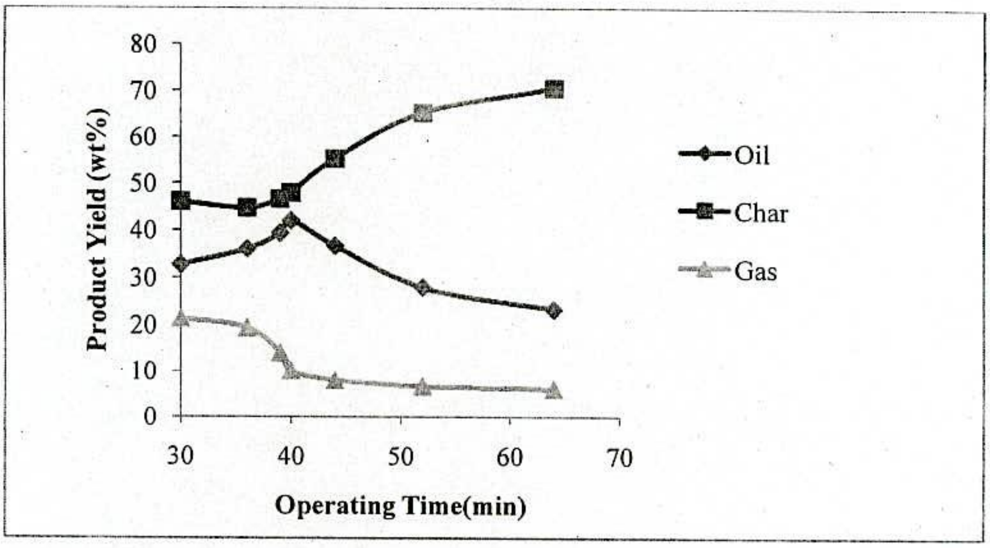


Figure 5.10: Effect of operating time on product yield for tyre pyrolysis with feed size 0.75 cm^3

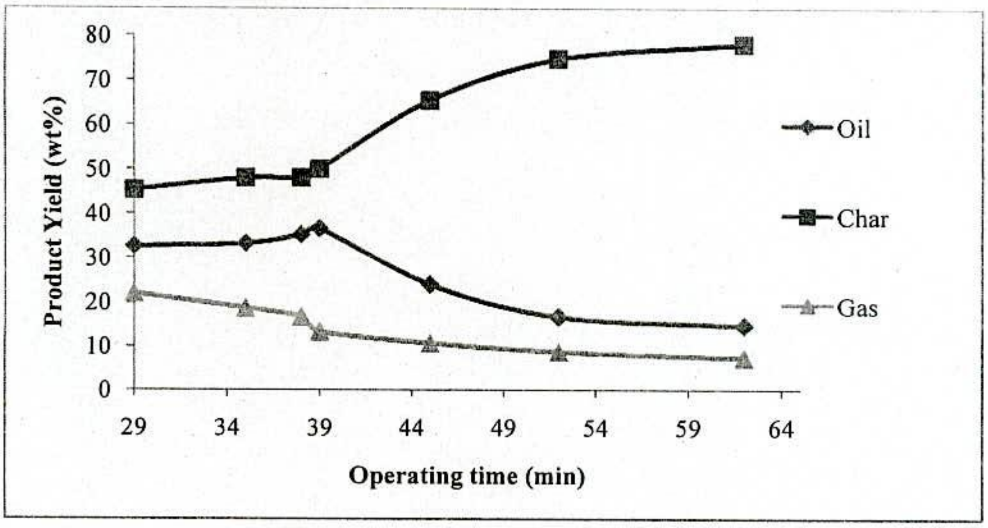


Figure 5.11: Effect of operating time on product yields with (CT ratio 0.13) for tyre pyrolysis with feed size 0.75 cm^3

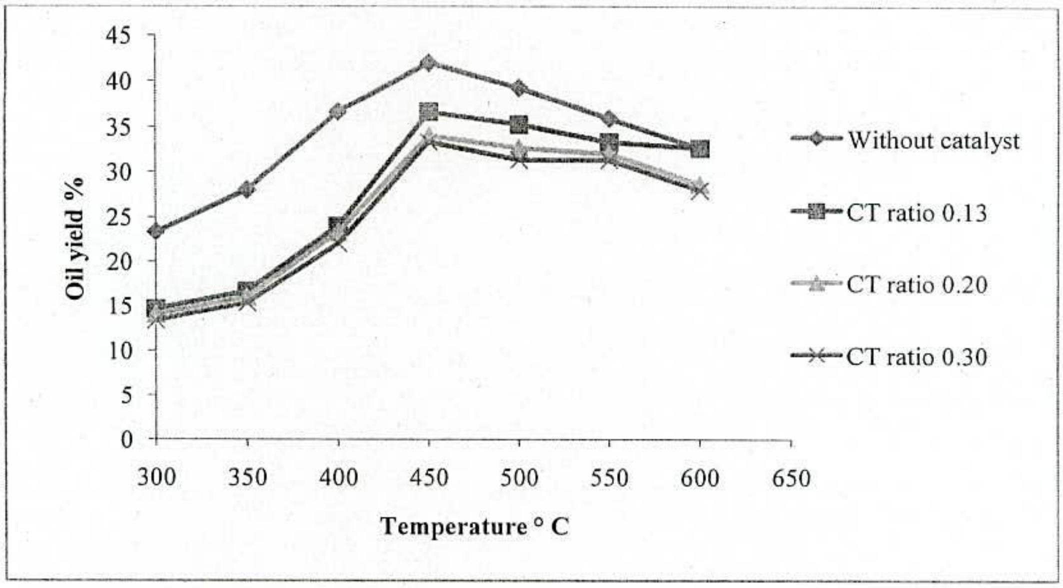


Figure 5.12: Variation of liquid yield at different temperature for various compositions.

5.4 Discussion

5.4.1 Product Analysis

Three types of products were obtained from the pyrolysis of waste tyre of buses / trucks: liquids, solid char, and gases. The product distributions obtained from pyrolysis of waste tyre for temperature range of 300-600°C at every 50°C are presented in Table 4.2 through 4.10 and Table 5.1 through 5.10.

5.4.2 Effect of Temperature and Catalyst on Product Yield of Tyre Pyrolysis

The effect of temperature on pyrolytic products obtained from waste tyre are shown in Tables 5.1 to 5.4. The tests were performed at temperature of 300°C to 600°C and data were collected at every 50°C interval. Four different sizes [0.75 cm^3; 1.31 cm^3; 1.50 cm^3 and 2.25 cm^3] of samples were tested. The results of these are plotted in Figs. 5.1 to 5.4. The same tests were carried out in the presence of catalyst and feed size of only 0.75 cm^3. The results are shown in Tables 5.5 to 5.7. In both the cases three types of products which are liquid oil, solid and gas were obtained.

It is observed that with the increase in temperature the liquid production rate increases until it reaches a maximum and then decreases. All the curves from Figs. 5.1 to 5.4 show the similar nature. Among the four samples the best result was obtained for feed size of 0.75 cm^3 (Size 1 cm × 1 cm × 0.75 cm). The result of which is shown in Fig. 5.1. The maximum oil yield of about 42.0% (by weight) can be obtained from the pyrolysis of waste tyre without catalyst. The yield then decreases to 32.67 % (by weight) at a temperature of 600°C. It is apparent that a fairly sharp optimum exists in temperature at which maximum yield of liquid was achieved probably due to strong cracking at this temperature. It can be postulated that the decreasing of liquid yield at higher temperatures was due to the rapid increase of gas yield; the char yields at these temperatures was also decreased. Since the char consists mainly of carbon with a solid hydrocarbon fraction and metal oxides and there is no obvious mechanism for carbon loss with increasing temperature, such a result suggests that higher temperature volatilizes some of the solid hydrocarbon content of char and decomposes some oil vapors to permanent gases [67].

The gas yield increases over the whole temperature range to a maximum value of 21.33% 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 tyre at this temperature and rubber of the tyre is not completely decomposed (pyrolysis is not complete) at a temperature less than 450°C. Further it was observed that solid yield decreases, liquid and gas yields increases. This is probably due to complete thermal decomposition of rubber of the tyre. It was apparent that at lower temperature the tyre was partially pyrolysed to give less oil and volatiles with maximum retention of material in solid form as char [13].

In presence of catalyst, the thermal pyrolysis of tyre yields three different products, viz. oil, char and gas. After using catalyst, the yield of oil is known as catalytic liquid or catalytic oil. The effect of catalytic cracking on product yield is shown in Figs. 5.5 to 5.7. It was observed from Fig. 5.5 in presence of catalyst in tyre (CT ratio 0.13) as temperature increases from 300 to 600°C, the yield of liquid increases first to a maximum value of 36.67 % (by weight) at 450°C, and then decreases to a minimum value of 32.67 % (by weight) at 600°C for various tyre feedstock.

It was observed from Figure 5.6 when amount of catalyst is increased (CT ratio 0.20) in feedstock and temperature increases from 300 to 600, the yield of liquid increases first to maximum 34 % (by weight) at 450°C and then decreases to a minimum 28.67 % (by weight) at 600°C for same sizes of tyre feedstock which is slightly lower compared to CT ratio is 0.13.

From Figure 5.7 when catalyst is further increased (CT ratio 0.30) in feedstock and temperature increases from 300 to 600, the yield of liquid increases first to maximum 33.33 % (by weight) at 450°C and then decreases to a minimum 28.0% (by weight) at 600°C for same sizes of waste tyre. From these three Figs. it could be concluded as CT ratio increases, the liquid yield decreases.

When CT ratio is 0.30, the yield of gas increased markedly at the expense of oil yield with the increasing of catalytic temperature. For example, the gas yield increased from 15.33 to 24.67% (by weight) when the catalytic temperature increased from 450 to 600°C. It indicated that the yield of oil decreased with the increasing catalytic temperature. For example, oil yield decreased from 33.33 to 28.0% (by weight) when the catalytic temperature increased from 450 to 500 C. After catalytic pyrolysis, the incondensable gases go out to flaring.

It is also envisaged that the liquid product yield in catalytic pyrolysis is always lower than of non- catalytic pyrolysis when the catalyst was used in the pyrolysis of waste tyres. The reason might be large molecular materials were cracked into un-condensed gaseous products with the effect of catalyst resulted in increasing gas production. *Venuto and Habib* [68] reported that catalytic cracking had been shown to yield large amounts of gaseous products and *Williams and Brindle* [13] also found that the oil yield was decreased with the catalyst cracking of tyre pyrolysis. It is known that the catalytic activity improved with the increase of catalyst. This phenomena is happening in the present work. Thus verifying the previous work.

5.4.3 Effect of Sample Size and CT ratio on Product Yield of Tyre

The effect of sample size on product yield of tyre under optimum reactor temperature (450°) is presented in Table 4.9 and Table 5.8 and also in Figure 5.8. The weight fractions of liquid oil, char and gas produced were plotted together with sample size in the Figure 5.8. It shows that liquid yield from tyre first slightly increases up to a maximum value of 42.0% (by weight) for sample size of 0.75cm^3 and then decreases for larger sample while the char yield increases and gas yield decreases through all the sample sizes from 1.31 to

$2.25cm^3$. Smaller sample size provides more reaction surface causing high heating rate and too quick decomposition of the rubber sample. From Figure 5.8 it is observed that liquid yield is a maximum for sample size of 0.75 cm^3

The oil vapor comparatively get enough time for secondary reaction in the reactor and consequently increase gas yields and decrease the 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. This coincides with the result that mention in [13].

The effect of various CT ratio on product yields of tyre under optimum reactor temperature (450°C) is presented in Table 4.10 and Table 5.9 The weight fractions of liquid oil, char and gas produced were plotted together with sample size in Fig. 5.9. This shows that liquid yield from tyre first slightly increases up to a maximum value of 36.67% (by weight) when CT ratio 0.13 for sample size of 0.75 cm^3 and then liquid production slowly decreases for increasing CT ratio while the char yield increases first then nearly little bit decreases and gas yield slightly increases through the same sample sizes.

5.4.4 Effect of Operating Time on Product Yield of Tyre

The effect of operating time on the product yield is shown in Figure 5.10 for without catalyst and in Figure 5.11 for with catalyst in tyre pyrolysis. From Figure 5.10, it is evident that more operating time was required to complete the conversion which results in incomplete deploymerisation of the sample that leads more production of char and less amount of oil. At less operating time was required to complete the conversion, which leads to more oil and less char. There is no obvious mechanism for gas loss with operating time. It was also observed that low temperature with longer operating time contributes to secondary reaction of primary products, which leads to less oil and more char products This agree with the result that mention in [14]. In Figure 5.11, it is observed that the effect of catalyst and operating time with yield follow the similar trend but the gas production is slightly more than that in absence of catalyst. In Figure 5.12, it is observed that the effect of catalyst with the yield follows the similar trend but the oil production is little bit decrease due to increase CT ratio as well as the gas production is slightly more than that in absence of catalyst. However, the oil production is slightly more than for without catalyst compare to CT ratio.

5.5 Analysis of Properties of Pyrolytic Oil:

The analyses of the properties of pyrolytic oil as mention in section 2.7 are briefly explained below:

5.5.1 Physical Properties

The physical composition of the liquid sample obtained from waste tyre pyrolysis is presented in Table: 5.11. The most important property obtained is the energy content of the liquid and it is 37.98 MJ/kg without catalyst and 39.01MJ/kg when CT ratio of 0.30, reflecting high potential utilization of the oil as raw fuel. The test was carried in the laboratory of Petromax Refinery Ltd, Mongla, Bagerhat. The result of pyrolytic oil's is presented in Table 5.11 and the result of various pyrolytic oil's Fractionation distillation range are presented in Table 5.12

5.5.2 Chemical Properties

The chemical properties of pyrolytic oil can be determined by the following the test such as Gross calorific value (GCV), FTIR. These are briefly described below:

Gross Calorific Value (GCV)

The test was conducted in the Heat Engine laboratory of the Department of Mechanical Engineering, KUET, Khulna. The higher heating values of pyrolytic oil result are presented in Table 5.11.

Table:-5.11: Properties of Raw Pyrolytic Oil, Catalytic Oil with Conventional Diesel and Furnace Oil.

Physical Properties	Without catalyst	Pyrolytic oil with CT ratio 0.13	Pyrolytic oil with CT ratio 0.20	Pyrolytic oil with CT ratio 0.30	Reference with	
					Diesel	Furnace oil
Density (kg/m^3), 30°C	935.1	909.2	898.5	895.3	820 to 860	890 to 960
Kinematic Viscosity at@40°cSt(centistokes)	6.59	2.5	2.12	2.01	3 to 5	45
Flash Point °C	37	35	32	32	≥ 55	70
Pour Point °C	-7	-12	-14	-16	-40 to -1	10 to 33
Gross Calorific Value (MJ/Kg)	37.98	38.1	38.95	39.01	42 to 44	42 to 43

Table:-5.12: Fractionation Distillation of Pyrolytic and Catalytic Oil from Waste Tyres Compared to Naphtha, Kerosene and Diesel

Distillation ASTM D86							
Tests	without catalyst	CT ratio 0.13	CT ratio 0.20	CT ratio 0.30	Naphtha	Kerosene	Diesel
IBP^{0}C	88	82	80	77	87	172	200
10%	115	97	96	97	110	176	214
20%	152	130	128	120	114	178	222
30%	170	144	135	130	118	180	228
40%	192	172	165	162	122	182	234
50%	220	212	200	200	125	184	242
60%	254	263	250	248	130	186	252
70%	306	290	280	276	138	195	262
80%	362	330	315	314	150	205	274
90%	373	360	354	351	160	230	295
95%	--	365	355	350	165	265	315
EBP^{0}C	382	368	356	351	180	300	343
Recovery	93%	95%	96%	97%	99	99	99
Residue	6%	5%	4%	3%	0.55%	1%	1%
Loss	1%	0%	0%	0%	0.50%	0%	0%

Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy

The test carried out at CARS, University of Dhaka. The FTIR results are shown in Table: 5.13

Chemical Composition Group Analysis

The absorption frequency spectra representing the functional group composition analysis of the waste tyre pyrolysis oil are presented in Figure 5.13 for without catalyst, Figure 5.14 for CT ratio 0.13 and Figure 5.15 for CT ratio 0.20 are summarized in Table 5.13.

The strong absorbance peaks of C-H vibrations for without catalyst is between 3000-2800 cm^{-1} and 1300-1450 cm^{-1} which indicate the presence of alkanes. Also when CT ratio 0.13, it shows the absorbance peak between 2900-2800 cm^{-1} and 1300-1400 which is alkanes group.

The absorbance peaks for without catalyst is between 1030-1370 cm^{-1} represent the C-O stretching vibration, indicates the presence of primary, secondary and tertiary alcohols, phenol, esters and ethers. On the other hand, for with catalyst the absorbance peaks are 1200-1300 cm^{-1} represent C-O stretching vibration indicating similar result.

The possible presence of aromatics are indicated by the absorbance peaks between (1450-1600 cm^{-1}) and (1600-2000 cm^{-1}) presenting Csp^2=Csp^2 stretching vibration for without catalyst which is almost similar when CT ratio 0.13 and 0.20.

The strong absorbance peaks between 3600-3400 cm^{-1} represent the O-H stretching vibration; indicate the presence of alcohol, phenol, carboxylic acid. The absorbance peaks between 2800-3000 cm-1 and 3000-3400 cm^{-1} symbolize the N-H vibration which specifies the alkynes and amines. Similar, The absorbance peaks for without catalyst is between 2900-3300 cm^{-1} which designates the possible presence of alkynes group.

From the FTIR analysis it is revealed that the oil obtained from wastes tyre mostly the hydrocarbon compounds but in catalytic cracking the aromatic content in the liquid fuel is increased. The effect of aromatic compound in liquid fuel which is increased the cyclic group as well as octane number is also increased.

Table:-5.13: The FTIR Functional Groups and the Indicated Compound of Pyrolysis

Absorbance Range (cm-1)	Functional Group	Class of Compound	Without catalyst	CT ratio 0.13	CT ratio 0.20
3200-3650	O-H	Alcohol, phenol, Carboxylic acid	3300-3700	3300-3700	3400-3600
3300-3500	N-H	Amines			3000-3400
2850-2960	C-H	Alkanes and Alkyl group	2800-3000	2800-2900	2850-2960
1660-2000	C=C	Aromatic	1600-1700	1600-1800	1600-1900
1450-1600	C-H	Alkanes	1450-1600	1400-1600	1450-1600
1325-1425			1300-1450	1300-1400	1300-1450
1175-1300	C-O	Primary, secondary and tertiary alcohols, phenol, esters and ethers	1030-1370	1200-1300	1100-1300
1000-1150	C-H	Alkanes	966-1030	1000-1200	950-1100
875-950	HC≡CH	Alkynes	812-966		850-950
600-950		Aromatic compound	752-812	750-850	700-850

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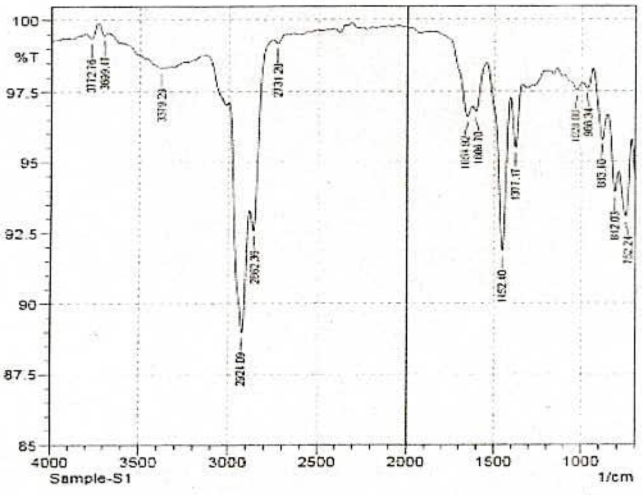
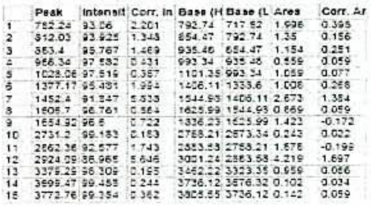


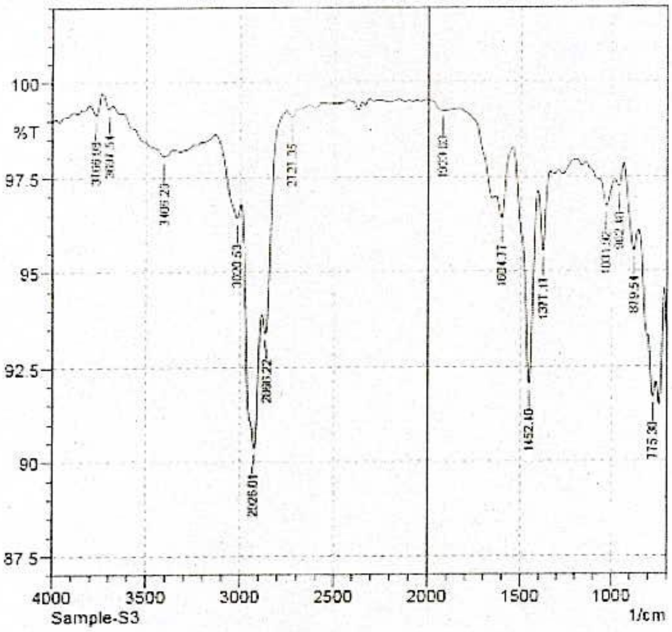


	Peak	Intensit	Corr. In	Base (H	Base (L	Area	Corr. Ar
1	752.24	93.06	2.201	792.74	717.52	1.996	0.395
2	812.03	93.925	1.345	854.47	792.74	1.35	0.156
3	863.4	95.767	1.469	935.46	854.47	1.154	0.251
4	966.34	97.582	0.431	993.34	935.46	0.559	0.059
5	1028.06	97.519	0.357	1101.35	993.34	1.059	0.077
6	1377.17	95.431	1.954	1406.11	1333.6	1.008	0.266
7	1452.4	91.347	5.533	1544.95	1406.11	2.673	1.354
8	1606.7	96.761	0.564	1625.99	1544.95	0.669	0.059
9	1654.92	96.5	0.722	1836.23	1625.99	1.423	-0.172
10	2731.2	99.183	0.183	2788.21	2873.34	0.243	0.022
11	2862.36	92.577	1.743	2883.58	2788.21	1.676	-0.199
12	2924.09	88.965	5.646	3001.24	2883.58	4.219	1.697
13	3375.25	98.309	0.155	3462.22	3323.35	0.959	0.056
14	3699.47	99.455	0.244	3736.12	3676.32	0.102	0.034
15	3772.76	99.354	0.362	3805.55	3736.12	0.142	0.059

Sample: Without Catalyst

Fig.5.13: FTIR spectra of pyrolysis liquid derived from waste tyre for without catalyst at operation temperature at 450°C

CARS, DU



	Peak	Intensit	Corr. In	Base (H	Base (L	Area	Corr. Ar
1	775.33	91.701	0.316	805.26	759.56	1.602	0.052
2	879.54	96.541	1.065	935.46	856.39	1.265	0.233
3	962.43	97.22	0.369	993.7	935.46	0.547	0.041
4	1031.92	96.714	0.696	1066.64	993.7	1.063	0.116
5	1377.17	95.535	1.797	1406.11	1334.74	1.061	0.236
6	1452.4	92.054	5.457	1544.93	1406.11	2.806	1.402
7	1604.77	96.4	1.024	1635.64	1544.93	1.059	0.144
8	1923.03	99.248	0.036	2011.76	1911.45	0.265	0.002
9	2727.35	99.063	0.196	2756.28	2666.64	0.246	0.025
10	2866.22	93.392	1.303	2855.51	2756.28	1.771	-0.213
11	2926.01	90.374	4.578	2997.38	2855.51	3.747	1.43
12	3020.53	96.421	0.685	3138.18	2997.38	1.593	0.179
13	3405.29	98.051	0.301	3566.35	3360	1.508	0.155
14	3697.54	99.319	0.219	3732.26	3578.25	0.126	0.029
15	3766.96	99.143	0.449	3803.63	3732.26	0.199	0.071

Sample: Catalyst: Tyre = 0.13: 1

Fig.5.14: FTIR spectra of pyrolysis liquid derived from waste tyre with CT ratio 0.13 at operating temperature of 450°C

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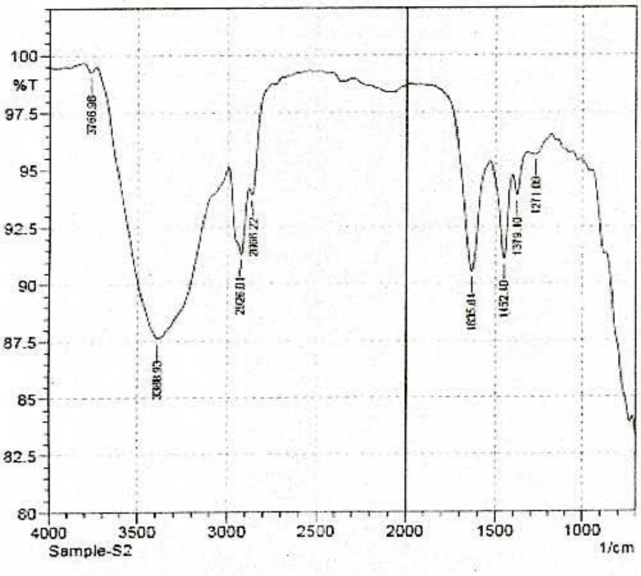
CARS, DU



	Peak	Intensit	Corr. In	Base (H	Base (L	Area	Corr. Ar
1	1271.09	95.653	0.377	1319.31	1182.36	2.448	0.11
2	1379.1	93.875	1.19	1406.11	1319.31	1.995	0.161
3	1452.4	91.1	3.868	1531.43	1406.11	3.596	0.926
4	1635.64	90.555	5.521	1866.17	1531.43	6.703	2.273
5	2866.22	93.505	0.895	2883.58	2750.49	1.563	-0.223
6	2926.01	91.325	3.232	2997.38	2883.58	3.577	0.966
7	3388.93	87.642	9.799	3736.05	2997.38	27.167	16.332
8	3766.96	99.269	0.307	3809.41	3736.05	0.173	0.046

Sample: Catalyst: Tyre = 0.20: 1

Fig.5.15: FTIR spectra of pyrolysis liquid derived from waste tyre with CT ratio 0.20 at operating temperature of 450°C

5.5.3 Investigation of Product oil

The liquid obtained from pyrolysis of tyre 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 which are difficult to remove by detergent and an acrid smell for a few days. 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 oil obtained under the different liquid yield conditions were well mixed and homogenized prior to analysis being made. Physical properties such as, density, Kinematic viscosity, flash point, pour point, gross calorific values (GCV), distillation oil were determined. The oil obtained after thermal pyrolysis of waste tyre is 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 waste tyre were analyzed and compared with that of furnace oil, diesel which are summarized in Table 5.11 and Table 5.12

The fuel properties of the pyrolytic oil 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 oil was found 935.1 kg/m^3 for tyre without catalyst and 909.2 kg/m^3 for CT ratio of 0.13, 898.5 kg/m^3 for CT ratio of 0.20, 895.3 kg/m^3 for CT ratio of 0.30 which are comparable to commercial furnace oil (890 to 960 kg/m^3) and higher than that of the commercial diesel (820-860 kg/m^3) and petrol (700-800 kg/m^3). This is attributed to the presence of heavier compounds in both the pyrolysis oil. The viscosity of liquid products from the waste tyre (6.59 cSt @40°C) was slightly higher than that of diesel (3 to 5 cSt @ 40°C) but too much lower than that of furnace oil (45 cSt@40°C). But the viscosity of liquid products from the tyre pyrolysis with CT ratio of 0.13 and 0.20, 2.59 cSt @40°C and 2.12 cSt @40°C respectively are lower than that of the diesel (3 to 5 cSt @40°C). When catalyst in the tyre is increases the viscosity of derived oil also is decreasing. 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. The flash point obtained from the pyrolytic oils derived from tyre was less than that of diesel. The flash point of the liquid derived from tyre was 37°C. On the other hand the flash points of the liquid derived from tyre in the presence of catalyst were 35°C, 32°C, and 32°C respectively at various CT ratios. The flash point is low when compared with petroleum-refined fuels; for example, furnace oil has a required minimum flash point of 70°C, diesel fuel of 55°C. The low flash points of the liquids derived from tyre are not surprising since the product obtained is unrefined with a mixture of components having a wide distillation range. The pour point of the waste tyre pyrolysis oils are 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 (GCV) of the pyrolytic oil for without catalyst 37.97MJ/kg and the tyre pyrolysis with CT ratio 0.13, 0.20, and 0.30 are 38.10 MJ/kg, 38.95 MJ/kg and 39.01 MJ/kg respectively is less than that of diesel and gasoline.

5.5.4 Analysis of Char after Pyrolysis of Tyre

The solid char fractions obtained at optimum reactor conditions were of equal size and shape as original tyre pieces, which were easily disintegrable into black powder and steel cords. The gross calorific value of char fraction was 22–25 MJ/kg, which is comparable with that of the good quality coal. This similar with the result that mention in[14].

5.6 Cost Analysis for Present Project:

Capital cost:

Capital costs are fixed, one-time expenses incurred on the purchase of land, buildings, construction, and equipment used in the production of goods or in the rendering of services. Put simply, it is the total cost needed to bring a project to a commercially operable status. Whether a particular cost is capital or not depend on many factors such as accounting, tax laws, and materiality.

The cost analysis is based on the following assumptions:

Equipment expected life = 5 years

4 runs per day and 300 working days per year.

The details of capital cost are shown in Table 5.14:

Table-5.14 Components of Capital Cost

Name of material	Amount taken	Unit Price Tk.	Total Cost (Tk.) (without catalyst)	Total Cost (Tk.) (with catalyst)
Reactor	1 pc	1500	1500	
Heater Coil	4 pcs	650	2600	
N_2 Gas	lump sum	---	500	
Thermocouple weir	5 pcs	180	900	
Temperature Recorder	5 pcs	1350	6750	
Asbestos ropes and blanket	1.5 kg	300	450	
MS angle	4 kg	75	300	
Condenser coil	12 m	40	480	
Fabrication	lump sum	---	500	
Cost of Catalyst	216 kg /yr	1000	---	216000
Total Capital cost for 5 yrs			13980	1080000
Total capital cost per yr = Tk.2796				Cost of Catalyst per yr =216000

Operating cost:

Operating costs are the expenses which are related to the operation of a business, or to the operation of a device, component, and piece of equipment or facility.

The cost analysis for the present project is based on one single run

Waste tyre = 1.5kg @ Tk.10 =Tk.15

Total Electricity required for pyrolysis of 1.5 kg tyre == 1.5 kWh

Cost for electricity = Tk. 4.5 /kWh.

Charge for electricity =4.5×1.5= Tk.6.75

Labour = 2 hr@ Tk. 50 = Tk.100

Miscellaneous = Tk. 20

Total operating cost per batch for without catalyst =Tk.141.75

Total annual operating cost without catalyst = 300×4 ×141.75 =Tk.170100

Cost of catalyst per kg = Tk.1000

Catalyst required for single batch = 0.180 kg

Total Catalyst required =0.180 × 300 × 4 =216 kg/yr

Total annual cost of catalyst =216×1000 =Tk.216000

Total annual operating cost including catalyst = (170100+216000) =Tk.386100

Total Cost for without catalyst = Total Annual capital cost + Total Annual operation cost

= Tk. (1, 70,100 + 2796) = Tk.172896

Total Cost for with catalyst = Total Annual capital cost + Total Annual operation cost

= Tk. (3, 86,100 + 2796) = Tk.388896

Payback Period

Payback period is the time in which the initial cash outflow of an investment is expected to be recovered from the cash inflows generated by the investment. It is one of the simplest investment appraisal techniques.

$$\text{Payback Period} = \frac{\text{Initial Investment}}{\text{Cash Inflow per Period}}$$

Calculation:

Operation time: 2 hrs per batch and 4 batches per day

Yield of oil per batches =0.420 kg (without catalyst)

Yield of oil per batches =0.367 kg (with catalyst)

Annual product yield for without catalyst = 0.420 kg/run × 4 runs /day ×300 days/ yr

=504 kg/yr

Annual product yield for with catalyst = 0.367 kg/run × 4 runs /day ×300 days/ yr

=440 kg/yr

Price of furnace oil = Tk.32/ kg

Total annual value of product (without catalyst) = Tk. (504 × 32) Tk. =Tk.16128

If price of chemical feed stock or Naphtha or diesel =Tk. 50/ kg

Total annual value of product (with catalyst)

.= Tk.(440× 50) = Tk.22,000

Payback period for without catalyst = (1, 72,896) % (16128)

= 10 yrs

Payback period for with catalyst = (3, 88,896) % (22000)

= 17.6yrs

Based on present calculation, the payback period is not feasible because the calculation is for lab scale plant. If the feed materials are in large scale then it could be feasible. On the other hand the important environment issues are the vital factor to consider operating cost. Scrap tyre is increasing day by day and it is dumping on various places in the cities. Dumped scrap tyre in massive stockpiles is one of the possible causes of ideal breeding grounds for disease carrying mosquitoes and other vermin with the aid of rain water, which is deposited in the free space of the tyre wall. So, if the environment issues are considered for operating cost, it could be viable.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Under this study, the recovery of value added products, i.e; pyrolysis oil from waste tyre, were investigated. Thermal pyrolysis and catalytic pyrolysis of waste tyre has been studied. Within the range of experimental limit the following conclusions can be made from the analysis of the results.

i. The maximum yield of pyrolytic oil from the waste tyre was 42.0 % (by weight) at a temperature of 450°C with the tyre size of 0.75 cm^3 with loading size of 1.5 kg.

ii. The maximum yield of pyrolytic oil from the waste tyre in presence of catalyst (CT ratio 0.13) was 36.67% (by weight) at a temperature of 450°C when the tyre size was 0.75 cm^3 with same loading.

iii. Physical properties of pyrolytic oil derived from wastes tyre are comparable with that of kerosene, naphtha and diesel fuel.

iv. Pyrolysing of waste tyre in presence of catalyst using zeolite USY catalyst have been investigated and the results showed that the influence of the presence of catalyst was to reduce the yield of oil with a consequent increase in the gas yield.

v. The FTIR four groups: alkane, alkenes, alkynes and aromatic compound were investigation showed that the more aromatic hydrocarbons were found in derived oil from the pyrolysis of the waste tyres with catalyst. Since it can obtain higher concentrations of certain aromatic compound in the derived oil, which was used as chemical feedstock rather than a fuel.

Considering all these results, it can be concluded that the oil obtained from pyrolysis of wastes tyre can be used as alternative fuel or chemical feedstock after some treatment. This also reduces the environmental hazards of resulting from the unmanaged disposal of waste tyres.

6.2 Recommendations for Future work,

Better experimental model can be made to improve the quality and quantity of products.

- Different catalysts can be used to obtain more yields of oil products.
- More efficient fractionating columns can be used for separation of pyrolysis oil fuel into different fractionates.
- 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.
- Pyrolysis reactor can be designed in such a way that lower cost catalytic cracking can occur for production of petrol and LPG like liquid fuel.
- The catalytic oil could be analyzed for desulfurization and decolonization which would be solvent, alternative fuel etc.

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