

Pyrolysis of Organic Waste: A Way to Solid Waste Management and Extraction of Fuel

by

Farzana Yeasmin Nipa

A project report submitted in partial fulfillment of the requirements for the degree of
Master of Science in Engineering in the Department of Energy Science and Engineering



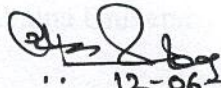
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY

KHULNA-9203, BANGLADESH

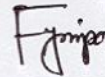
JUNE, 2019

Declaration

This is to certify that the project work entitled "Pyrolysis of Organic Waste: A Way to Solid Waste Management and Extraction of Fuel" has been carried out by Farzana Yeasmin Nipa in the Department of Energy Science and Engineering, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above project work or any part of this work has not been submitted anywhere for the award of any degree or diploma.


12-06-19

Signature of Supervisor

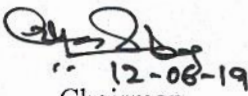
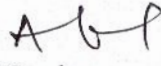



 12.06.19

Signature of Candidate

Approval

This is to certify that the project work submitted by Farzana Yeasmin Nipa entitled "Pyrolysis of Organic Waste: A Way to Solid Waste Management and Extraction of Fuel" has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of Master of Science in Engineering in the Department of Energy Science and Engineering, Khulna University of Engineering & Technology, Khulna, Bangladesh in June, 2019.

BOARD OF EXAMINERS

1. Prof. Dr. A. N. M Mizanur Rahman
Department of Mechanical Engineering
Khulna University of Engineering & Technology

12-08-19
Chairman
(Supervisor)
2. Prof. Dr. Mohammad Ariful Islam
Head, Department of Energy Science and Engineering
Khulna University of Engineering & Technology

Member
3. Md. Shameem Hossain
Assistant Professor, Department of Energy Science and Engineering
Khulna University of Engineering & Technology

Member
4. Dr. Md. Abul Hashem
Assistant Professor, Department of Leather Engineering
Khulna University of Engineering & Technology

Member
5. Prof. Dr. Mohammad Rofiqul Islam
Department of Mechanical Engineering
Rajshahi University of Engineering & Technology

Member
(External)

Acknowledgement

At first, I would like to express my praise and gratitude to the Merciful and Almighty Allah, who makes me capable to successfully complete this work.

I would like to express my heartiest gratitude to my supervisor, Prof. Dr. A. N. M. Mizanur Rahman, Department of Mechanical Engineering, KUET, for his proper guidance, supervision, suggestions, inspiration and all kinds of supports to create adequate facilities in performing and completing this work and also to write this report in time. I am really honored for the opportunity to work under his supervision.

I would like to express my heartfelt gratitude to Prof. Dr. Mohammad Ariful Islam, Head, Department of Energy Science and Engineering, KUET, for allowing me to conduct the project work. I would also like to express my heartfelt gratitude to Prof. Dr. Sobahan Mia, Head, Department of Mechanical Engineering, KUET, for allowing me to use the facilities and supports to carry out the experimental part of the project in the Heat Engine Lab.

My sincere gratitude and thanks are extended to Prof. Dr. Quazi Sazzad Hossain, the honorable Vice-Chancellor of KUET, for the financial support given to this project without which this work could not be completed.

Warmest and sincere thanks are extended to Mr. Pollob Jodder, Senior Technician, Heat Engine Lab, for his expertise help in precise fabrication work and assistance during the experiments. He also provided necessary helps for other laboratory analysis.

Special gratitude to my beloved parents for their blessings and support during my study period. Also, the patience, understanding, moral support and cooperation of my beloved husband is deeply acknowledged and thanks for always being there for me. May Allah bless and reward all of them.

June, 2019

Farzana Yeasmin Nipa

Abstract

Bangladesh is a developing country and is one of the most densely populated countries in the world. Her per capital energy consumption is also low compared to others. At present, the energy demands are becoming more acute day by day. Environmental issues and energy scarcity led the government of the developing countries to think about new and alternative energy resources. Renewable energy resources may be one kind of alternative energy. Various waste materials derived from agriculture or industrial sectors can contribute to these issues. Tyre wastes, mixture of organic and inorganic materials, already become potential source to derive liquid fuel as well as solid fuels by pyrolysis.

Shoe/sandal soles have similar compositions like tyres and also create environmental pollution problems. Rubber containing wastes such as shoe/sandal soles are solid waste which is non-biodegradable and with increased production of shoe/sandal, the volume of waste soles will also be increased. Some typical problems are created to the environment as well as to our surroundings by the disposal of such wastes. The dumping of waste (shoe/sandal soles) in the drain is one of the main environmental issues in the municipal/city areas of Bangladesh. Blockage of drain and generation of mosquitoes or other bacteria are favored by the disposal of such wastes in unplanned manner. So, deliberately this matters to the authority and researchers to manage these non-biodegradable waste materials (soles of shoe/sandal). So, a way to manage waste as well as extraction of fuel may be a good solution to this problem.

Under the circumstances, extraction of fuel from shoe/sandal sole waste materials that manages the environment, pyrolysis is the best way. It will indirectly help to manage such non-biodegradable wastes, also low grade liquid fuels may be obtained. When waste materials were pyrolyzed, they generate oil, char and gas, which are valuable. The oil has sufficient calorific value and may be used to provide process energy and char may be used as activated carbon or carbon black. So, they may be considered as a new raw material for pyrolysis. In the present study, waste shoe/sandal soles were collected from the nearby

local area of Jashore and Khulna city of Bangladesh were pyrolysed in a batch type reactor.

Experiments on pyrolysis of shoe/sandal soles were conducted by varying the temperature within the range of 200-250°C at every 25°C. The batch type fixed-bed pyrolysis system was constructed and installed in the Heat Engine Laboratory of Department of Mechanical Engineering, Khulna University of Engineering & Technology. The maximum yield of pyrolytic oil and pyrolytic solid from waste shoe/sandal soles was 36.0 % (by weight) and 53.0 % (by weight) with the feed size of 0.75 × 0.50 cm and 1.25 × 1.0 cm respectively with loading size of 1.7 kg.

The properties of pyrolytic oil obtained from waste soles of shoe/sandal such as density, flash point, boiling point and pour point were measured and the respective values are in the range of 0.877 – 0.934 g/cm³, 96 - 108°C, 153 – 158°C and -11 to -12.5°C respectively and the gross calorific value (GCV) is around 35 - 38 MJ/kg. The gross calorific value (GCV) of pyrolytic solid is around 11 - 16 MJ/kg which is comparable to same of peat (12 to 16 MJ/kg) and lignite coal (13 to 16 MJ/kg). The concentrations of elemental compositions of pyrolytic liquid obtained from shoe/sandal sole pyrolysis were found to be almost 71.7% for carbon, 10.9% for hydrogen, 1.12% for nitrogen, 0.50% for sulphur and 15.78% for others at 200°C. The derived oil from pyrolysis of waste shoe/sandal soles were investigated for FTIR four groups: alkane, alkenes, alkynes and aromatic compounds. The results showed more aromatic hydrocarbons. The TGA analysis of the same shows that the experimental curve is higher from 200 to 400°C, when the rate of weight loss of shoe/sandal sole pyrolysis is higher. The oil obtained from pyrolysis of shoe/sandal sole wastes can be used as alternative fuel or chemical feedstock after some treatment. The results show that these properties are similar to that of the low grade liquid fuels and thus pyrolysis of such waste soles of shoe/sandal will reduce environmental pollution to some extent as well as be an alternative source of energy.

Contents

| | PAGE |
|--|-------------|
| Title Page | i |
| Declaration | ii |
| Approval | iii |
| Acknowledgement | iv |
| Abstract | v |
| Contents | vii |
| List of Tables and Appendix | x |
| List of Figures | xiii |
| Nomenclature | xv |
| | |
| CHAPTER I | |
| Introduction | 1 |
| 1.1 General | 1 |
| 1.2 Objectives of the Present Research Work | 5 |
| 1.3 Scope of Present Investigation | 5 |
| | |
| CHAPTER II | |
| Theoretical Aspects | 7 |
| 2.1 Shoe/sandal Sole Fundamentals | 7 |
| 2.2 History of Shoe/sandal Sole Invention | 10 |
| 2.3 Materials Used in Shoe/sandal Production | 12 |
| 2.3.1 Materials of Shoe/sandal | 12 |
| 2.3.2 Materials of Shoe/sandal Soles | 17 |
| 2.3.3 Comparison of Tyre and Shoe/sandal Sole Compositions | 19 |
| 2.4 Waste Products and Their Classification | 19 |
| 2.5 Waste Generation of Shoe/sandal Soles | 21 |
| 2.6 Difficulties with the Shoe/sandal Wastes | 23 |
| 2.7 Effects of Shoe/sandal Waste on Environment | 24 |
| 2.8 Analysis of Properties of Feed Materials and Pyrolytic Products | 26 |

| | |
|--|-----------|
| 2.8.1 Physical Properties | 27 |
| 2.8.2 Chemical Properties | 28 |
| 2.9 Cost Analysis | 31 |
| 2.9.1 Cost Analysis of Pilot Plant | 32 |
| 2.9.2 Capital Costs | 32 |
| 2.9.3 Operating Costs | 32 |
| CHAPTER III Literature Review | 34 |
| 3.1 Managing Technology of Shoe/sandal Sole Waste | 34 |
| 3.2 Various Recycling Process to Reduce Wastes Soles | 36 |
| 3.2.1 Pyrolysis Process | 37 |
| 3.2.2 General Cracking | 37 |
| 3.2.3 Catalytic Cracking | 38 |
| 3.2.4 Catalytic Reforming | 38 |
| 3.2.5 Catalytic Pyrolysis | 39 |
| 3.3 Technique to Remove Sole Wastes with Energy Recovery | 39 |
| 3.3.1 Pyrolytic Conversion | 39 |
| 3.3.2 Effect of Pyrolysis | 41 |
| 3.3.3 Parameters of Pyrolysis | 42 |
| 3.3.4 Reaction Mechanisms for Pyrolysis of Sole Wastes | 45 |
| CHAPTER IV Experimental Set-up and Methodology | 47 |
| 4.1 Introduction | 47 |
| 4.2 Materials and Methods | 47 |
| 4.3 Selection of Reactor | 48 |
| 4.4 Experimental Set-up | 52 |
| 4.5 Methodology | 54 |
| CHAPTER V Results and Discussions | 56 |
| 5.1 General | 56 |
| 5.2 Production of Pyrolytic Products | 56 |

| | |
|---|----|
| 5.3. Analysis of Pyrolytic Products | 59 |
| 5.4 Effect of Pyrolytic Conditions on Pyrolytic Product | 59 |
| 5.4.1 Effect of Temperature on Product Yield | 60 |
| 5.4.2 Effect of Feed Size on Product Yield | 61 |
| 5.4.3 Effect of Operating Time on Product Yield | 63 |
| 5.5 Analysis of Properties of Feed Materials and Pyrolytic Products | 65 |
| 5.5.1 Physical Properties | 65 |
| 5.5.2 Chemical Properties | 66 |
| 5.6 Comparison of Sole Waste Pyrolysis Products with Petroleum Products | 80 |
| 5.7 Management of Shoe/sandal Sole Wastes | 83 |
| 5.8 Cost Analysis for Present Project | 84 |
| 5.8.1 Capital Costs | 84 |
| 5.8.2 Operating Costs | 85 |
| 5.8.3 Payback Period | 86 |
| CHAPTER VI Conclusions and Recommendations | 87 |
| 6.1 Conclusions | 87 |
| 6.2 Recommendations for Future Work | 88 |
| References | 89 |
| Appendix | 97 |

LIST OF TABLES AND APPENDIX

LIST OF TABLES

| Table No | Description | Page |
|----------|--|------|
| 2.1 | Material Composition of a Shoe/sandal | 12 |
| 2.2 | Comparison of Tyre and Sole Compositions | 19 |
| 2.3 | Waste Inventory from a Footwear Factory | 21 |
| 2.4 | Parameters used in Annual Cost Estimation of a Shoe/sandal Sole Pyrolysis Plant | 32 |
| 3.1 | Advantages and Disadvantage of Shoe/sandal Soles Managing Technology | 35 |
| 5.1 | Percentage of Product Yield of Shoe/sandal Sole Pyrolysis for loading of 1.7 kg | 59 |
| 5.2 | Properties of Pyrolytic Oil from Sole Pyrolysis with Feed Size 1.25×1.0 cm at Different Temperatures | 65 |
| 5.3 | Calorific Value of Pyrolytic Oil from Sole Pyrolysis with Feed Size 1.25×1.0 cm at Different Temperatures | 67 |
| 5.4 | Calorific Value of Pyrolytic Solid (Char) from Sole Pyrolysis with Different Feed Size at Different Temperatures | 67 |
| 5.5 | CHNS Analysis of Pyrolytic Liquid Product from Sole Pyrolysis | 68 |
| 5.6 | FTIR Functional Groups and Indicated Compound of Pyrolytic Liquid Derived from Sole Pyrolysis at 200°C | 69 |
| 5.7 | FTIR Functional Groups and Indicated Compound of Pyrolytic Liquid Derived from Sole Pyrolysis at 225°C | 71 |
| 5.8 | FTIR Functional Groups and Indicated Compound of Pyrolytic Liquid Derived from Sole Pyrolysis at 250°C | 73 |
| 5.9 | FTIR Functional Groups and Indicated Compound of Pyrolytic Solid Derived from Sole Pyrolysis at 250°C | 75 |
| 5.10 | TGA of Pyrolytic Liquid Derived from Waste Soles at 250°C | 77 |

| | | |
|------|---|----|
| 5.11 | TGA of Pyrolytic Solid Derived from Waste Soles at 250°C | 79 |
| 5.12 | Comparison of Pyrolytic Sole Oil with Pyrolytic Tyre & Tube Oil, Diesel and Furnace Oil | 81 |
| 5.13 | Comparison of Pyrolytic Solid with Peat and Other Coals | 83 |
| 5.14 | Components of Capital Costs | 84 |

LIST OF TABLE IN APPENDIX

| Appendix No | Description | Page |
|-------------|---|------|
| A-1 | Details of Sample used in Various Run | 97 |
| A-2 | Pyrolysis Data of Waste Soles with Sample Size 1.25×1.0 cm at 200°C | 97 |
| A-3 | Pyrolysis Data of Waste Soles with Sample Size 1.25×1.0 cm at 225°C | 97 |
| A-4 | Pyrolysis Data of Waste Soles with Sample Size 1.25×1.0 cm at 250°C | 97 |
| A-5 | Pyrolysis Data of Waste Soles with Sample Size 1.0×0.75 cm at 200°C | 98 |
| A-6 | Pyrolysis Data of Waste Soles with Sample Size 1.0×0.75 cm at 225°C | 98 |
| A-7 | Pyrolysis Data of Waste Soles with Sample Size 1.0×0.75 cm at 250°C | 98 |
| A-8 | Pyrolysis data of Waste Soles with Sample Size 0.75×0.50 cm at 200°C | 98 |
| A-9 | Pyrolysis data of Waste Soles with Sample Size 0.75×0.50 cm at 225°C | 99 |
| A-10 | Pyrolysis Data of Waste Soles with Sample Size 0.75×0.50 cm at 250°C | 99 |
| A-11 | Effect of Temperature on Product Yield of Shoe/sandal Sole Pyrolysis | 99 |
| A-12 | Effect of Feed Size on Product Yield of Shoe/sandal Sole Pyrolysis | 99 |
| A-13 | Effect of Operating Time on Product Yield of Shoe/sandal Sole Pyrolysis | 100 |

LIST OF FIGURES

| Figure No | Description | Page |
|-----------|--|------|
| 2.1 | Schematic Diagram of a Shoe | 7 |
| 2.2 | Photographic View of Waste Shoe/sandal Soles | 22 |
| 2.3 | Photographic View of Drain Blockage caused by Waste Shoe/sandals | 22 |
| 2.4 | Landfilling of Shoe/sandal | 23 |
| 2.5 | Drainage Problem by Shoe/sandal | 24 |
| 2.6 | Environmental Impacts by Shoe/sandal Waste Landfilling | 25 |
| 2.7 | Environmental Impacts on Drain Blockage by Shoe/sandal Waste | 26 |
| 3.1 | Shoe/sandal Waste | 34 |
| 4.1 | Photographic View of Chopped Soles | 47 |
| 4.2 | Schematic Diagram of the Experimental Set-up | 53 |
| 4.3 | Photographic View of the Experimental Set-up | 54 |
| 5.1 | Pyrolytic Oil after Production from Shoe/sandal Sole Pyrolysis | 57 |
| 5.2 | Pyrolytic Oil Sample after Production from Shoe/sandal Sole Pyrolysis | 57 |
| 5.3 | Pyrolytic Solid after Production from Shoe/sandal Sole Pyrolysis | 58 |
| 5.4 | Pyrolytic Solid Sample after Production from Shoe/sandal Sole Pyrolysis | 58 |
| 5.5 | Effect of Temperature on Yield for Sole Pyrolysis with Feed Size 1.25×1.0 cm | 60 |
| 5.6 | Effect of Temperature on Yield for Sole Pyrolysis with Feed Size 1.0×0.75 cm | 60 |
| 5.7 | Effect of Temperature on Yield for Sole Pyrolysis with Feed Size 0.75×0.50 cm | 61 |
| 5.8 | Effect of Feed Size on Product Yields for Sole Pyrolysis at 200°C | 62 |

| | | |
|------|---|----|
| 5.9 | Effect of Feed Size on Product Yields for Sole Pyrolysis at 225°C | 62 |
| 5.10 | Effect of Feed Size on Product Yields for Sole Pyrolysis at 250°C | 62 |
| 5.11 | Effect of Operating Time on Product Yields for Sole Pyrolysis with Feed Size 1.25 × 1.0 cm | 63 |
| 5.12 | Effect of Operating Time on Product Yields for Sole Pyrolysis with Feed Size 1.0 × 0.75 cm | 63 |
| 5.13 | Effect of Operating Time on Product Yields for Sole Pyrolysis with Feed Size 0.75 × 0.50 cm | 64 |
| 5.14 | Effect of Operating Time on Feed Size and Temperature for Sole Pyrolysis | 64 |
| 5.15 | FTIR Spectra of Pyrolytic Liquid from Sole Pyrolysis at 200°C | 70 |
| 5.16 | FTIR Spectra of Pyrolytic Liquid from Sole Pyrolysis at 225°C | 72 |
| 5.17 | FTIR Spectra of Pyrolytic Liquid from Sole Pyrolysis at 250°C | 74 |
| 5.18 | FTIR Spectra of Pyrolytic Solid from Sole Pyrolysis at 250°C | 76 |
| 5.19 | TGA of Pyrolytic Liquid Derived from Waste Sole at 250°C | 78 |
| 5.20 | Boiling Point Distribution of Pyrolytic Liquids Compared to Petroleum Products | 79 |
| 5.21 | TGA of Pyrolytic Solid Derived from Waste Sole at 250°C | 80 |
| 5.22 | Properties of Pyrolytic Oil with Pyrolytic Tyre & Tube Oil, Diesel and Furnace Oil | 81 |
| 5.23 | Waste Sole of Shoe/sandal is converted to Pyrolysis Oil and Char | 84 |

Nomenclature

| | |
|-------------------|--|
| Wt % (w/w) | Weight Percent |
| MJ/kg | Mega Joule per kilogram |
| kg/m ³ | kilogram per cubic meter |
| kgOE | kilogram of Oil Equivalent |
| SBR | Styrene Butadiene Rubber |
| BR | Butadiene Rubber |
| IR | Isoprene Rubber |
| HDPE | High Density Poly Ethylene |
| LDPE | Low Density Poly Ethylene |
| PVC | Poly Vinyl Chloride |
| PET | Poly Ethelene Terapthalate |
| PS | Poly Styrene |
| EPT | Ethylene Propylene Terpolymer |
| IIR | Isobutylene Iso-prene Rubber |
| NR | Natural Rubber |
| PBR | Polybutadiene Rubber |
| EPA | European Pollution Authority |
| MJ | Mega Joule |
| kW | kilowatt |
| ASTM | American Society for Testing Materials |
| CARS | Centre for Advanced Research in Sciences |
| 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) |

CHAPTER I

Introduction

1.1 General

The living standard and quality of life of a nation depends upon 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 168.07 million in 2019. Her per capita energy consumption is far below the world average. In 2013, energy consumption mix of Bangladesh 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 population lives in rural areas and meet most of their energy needs from traditional biomass fuels. About 32% people have access to electricity, while in rural areas only 22% have availability of electricity. Only 3-4% of the households have connection to natural gas network for cooking. About 2-3% households use kerosene for the same purpose and the rest depend upon biomass for energy need [1]. At present, more than 62% of the population lives in rural areas and meet most of their energy needs from traditional biomass fuels. About 90% people have access to electricity [2]. Thus, it is a crucial need to find alternative and sustainable resources to mitigate this problem.

Energy security and environmental issues have emerged as public and political concern recently that led to the government and researchers to find alternative energy resources and a way of thinking for sustainable development. As energy crisis is becoming acute day by day, scientists are giving effort on potential of utilizing appropriate technologies to recover energy and useful by-products from domestic as well as industrial solid wastes [3]. Research has already been carried out on both biodegradable and non-biodegradable waste materials. Among non-biodegradable materials rubber and plastic are most important one. Several researchers have already worked with biodegradable and non-biodegradable waste in the country to extract liquid fuel and substitute for petro-chemicals [4-5].

From 1990 to 2004, worldwide footwear production increased by a staggering of 70% to more than 17 billion pairs of shoes per year [6]. In fact, world-wide footwear production

and consumption are being doubled every 20 years, from 2.5 billion pairs in 1950 to an expected 20 billion pairs of shoes in 2010 [7]. In developing countries like Bangladesh, waste sandal soles are creating environmental pollution. In one hand, these sole wastes create the landfills polluted by decreasing its fertility which indirectly pollute the underground drinking water. On the other hand, these wastes create drain blockage in urban areas where mosquitoes or other bacterias breed. It becomes the cause of various harmful diseases specially malarial fever to human being [3, 8]. Various processes of recycling like reclaiming, grinding, retreading etc. are being used but these processes have some disadvantages. When these wastes are directly burned, particularly in brick manufacturing industry or parboiling of rice, they produce harmful gases like CO₂, CO, SO_x, and NO_x etc. At present some industries in the country are commercially extracting liquid oil from tyre waste [9].

Now days, use of rubbers and plastics have been drastically increased in the footwear industries. They are mostly used as soles of shoes/sandals. After use of this foot wears, they are thrown away in a scattered manner. These waste shoe/sandal soles, as they are from non-biodegradable material, created problems and pollution to the environment. On the one hand, when these wastes are thrown to the land, they degraded the soil quality and also cause breeding place for mosquitoes and other harmful bacteria and insects, thereby pollute the environment. Also, in urban areas, footwear along with its solid waste are disposed into the prescribed landfills which creates a source of environmental pollution. These landfill waste materials when mixed with underground water, they pollute drinking water. The waste footwear materials are composed of different types of rubber, plastic and other wastes elements that are unhygienic to our body. People are suffering from various diseases because of drinking this contaminated water. On the other hand, when they are thrown to the drains, particularly in the urban areas, this waste creates the drain blockage. Therefore, disposal of such solid wastes from human activity is a growing environmental issue, especially in the developing countries like Bangladesh.

Constantly increasing production of rubber products such as tyres, conveyor belts, cables, gaskets or footwear made of rubber and the associated subsequent accumulation of rubber waste results in an increasing trend for energy recovery using rubber waste as an alternative fuel source. However, there are many difficulties associated with the recycling

of this waste [10-11]. Many authors come with various methods of recycling or degradation of discarded tyres and other rubber waste [12]. Utilization of waste tyres in a coal combustion plant can reduce NO emissions and recover energy from waste tyres by pyrolysis efficiently and help solve a major environmental pollution problem [13]. The problem of tyres management strongly affects not only the environmental protection but even the resources maintenance, since problems related to the depletion of resources, energy demand and waste management by pyrolysis [14]. Rubber is also used to produce certain types of footwear. The paper entitled “Shoe Manufacturing Wastes Characterization of Properties and Recovery Options” [15], presents characterization of the chemical and physical properties of shoe manufacturing wastes which created an environmental unrest problem [16].

Pyrolysis is an endothermic reaction process which can be used for the treatment of waste materials in an oxygen free environment. It is 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 [4]. Shoe/sandal soles compositions are very similar to tyre. As the tyre wastes pyrolysis has increased to produce high energy density liquids, char and gases [17], so, shoe/sandal soles could be converted to usable products by pyrolysis. Since the derived oil contain concentrations of valuable chemicals such as benzene, toluene, xylene etc. [18]. Pyrolytic oil from pyrolysis of sandal soles may be used as furnace oil in industry. Pyrolytic solid product may be used as a solid fuel or as activated carbon [19-22]. Thus, it is crucial to develop an upgrading technology for the sandal soles derived pyrolysis liquid. Recently environmental issues and energy security have been emerged as the public and political concern which led to alternative way of thinking. Rubber containing wastes such as tyre, tube and soles of shoes/sandals are causing a big environmental problem because it is an artificial polymer and are not biodegradable [23]. Rubber is 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 soles used in different types of shoe/sandal. Shoe/sandal soles are made of leather (25 wt %), polyurethane (17 wt %), thermoplastic rubber (16 wt %), ethylene vinyl acetate (14 wt %), poly vinyl chloride (8 wt %), other rubbers (7 wt %), adhesives & metals (7 wt %), textiles and fabrics (6 wt %) [24].

There are various experimental methods that can produce liquid products 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 vary in their characteristics and quality depend on type and size of feedstock, size and system configuration of reactor, efficiency of heat transfer, vapor residence time etc. The influences of pyrolysis temperature, heating rate and the yield and fraction of the derived oils were investigated by different researchers. A detailed characterization of the whole pyrolysis liquids obtained at optimum operating conditions has been carried out including physical properties, elemental analyses, GCV etc.

After thermal decomposition solid char, liquid oil (known as pyrolytic oil or pyrolysis liquid) and gas will be evolved. The pyrolytic oil obtained from tyre pyrolysis has been found to have a gross calorific value of around 41- 44 MJ/kg which would encourage its use as replacement for conventional low grade liquid fuels [1]. Tyre pyrolysis conducted by Hossain and Rahman, (2015) showed liquid yield of 42% (w/w) with density of liquid as 0.935 gm/cm^3 and GCV of 37.98 MJ/kg [5]. As mentioned before, shoe/sandal soles have very similar compositions to that of the tyres. So, disposal of used shoe/sandal soles may produce similar products by pyrolysis. Hashem et. al., (2017) conducted experiment on pyrolysis of waste thermoplastic rubber (TPR) and polyvinylchloride (PVC) soles [25]. The maximum production of pyrolytic oil and char from waste thermoplastic rubber (TPR) soles was 0.30 kg and 1.14 kg respectively at 450°C and 250°C with loading size of 1.3 kg, where the maximum production of pyrolytic oil and char from waste polyvinylchloride (PVC) soles was 0.14 kg and 1.18 kg respectively at 450°C and 250°C with same loading size. This would cause an effective means to pollution control caused by shoe/sandal soles, at the same time it will help to get liquid and solid fuels from these wastes.

The pyrolytic oil from pyrolysis of shoe/sandal soles could also be used as furnace oil in the industry. So far no literature is available for pyrolysis with shoe/sandal soles. In the present work, an attempt has been made to extract liquid fuel from shoe/sandal soles. A batch type pyrolysis reactor will be designed and constructed for charging approximately 1.7 kg of sample and experiments would be conducted to find the optimum temperature for pyrolysis product and also to analyze the various properties of the pyrolysis products.

1.2 Objectives of the Present Research Work

The aim of the present project is to effectively handle the non-biodegradable organic waste (soles of shoe/sandal) and also to extract solid and liquid fuels by pyrolysis of such material in small scale at KUET.

The main objectives of this research are:

1. Selection and erection of a pilot scale batch type pyrolysis reactor for solid waste material.
2. To pyrolyze organic waste (soles of shoe/sandal) in the reactor under different pyrolysis conditions.
3. To determine the quantity of solid, liquid and gaseous yield at various pyrolysis temperatures.
4. To investigate the effect of material size, pyrolysis temperature and vapor residence time on product yield and their compositions.
5. To determine the physical and chemical properties of the solid and liquid products and contrast them with the commercial fuels.

1.3 Scope of Present Investigation

Bangladesh is one of the developing and most densely populated countries with a total population of about 166 million. The demand for energy is growing due to increasing industrialization of the country and concomitantly increasing the growth of population [26]. The energy crisis and environmental degradation are the main problems that 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. On the other hand, the soles (TPR, PVC, EVA, VR, leather, etc.) are used for the production of footwear after a certain period users indiscriminately discard it as waste. Disposal of organic wastes e.g. sole, tyre, etc. from the anthropogenic activity is a growing environmental issue for the modern society, especially in the developing country due to its

non-biodegradability. 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 resources from non-conventional sources, like municipal and industrial organic waste, refused plastic, used soles, etc.

Searching for the alternative fuel to meet the increasing fuel demand the present investigation will put emphasis in the followings:

- Study of the wastes shoe/sandal soles as feed materials for the availability in this country at cheap price.
- Proper disposal of ever increasing shoe/sandal sole wastes with potential material recovery.
- Emphasis on the production of the liquid fuel.
- Study for the high quality oil production.
- Emphasis on the production of the solid fuel.

CHAPTER II

Theoretical Aspects

2.1 Shoe/sandal Sole Fundamentals

The footwear industry is a diverse manufacturing sector which employs a wide variety of materials to make products ranging from different types and styles of footwear to more specialized shoes. Leather, synthetic materials, rubber and textile materials are amongst the basic materials most commonly used in shoe manufacturing. Materials significantly influence, not only the life of the footwear but also the end-of-life treatment of the product.

A shoe/sandal is composed of several parts. Some parts that all shoes have such as the sole, while others may only apply to certain types or style of shoe. The schematic diagram of a shoe is shown in Figure 2.1. The important components of shoe/sandal [27] are briefly discussed below:

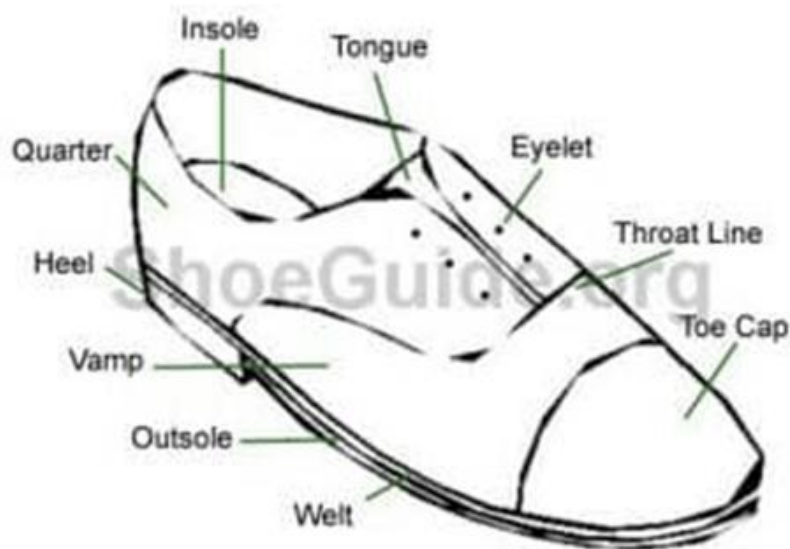


Figure 2.1: Schematic Diagram of a Shoe

Breast: The forward facing part of the heel, under the arch of the sole.

Counter: A stiff piece of material at the heel of a shoe positioned between the lining and upper that helps maintain the shape of the shoe. The counter helps strengthen the rear of the shoe.

Feather: The part of the shoe where the upper's edge meets the sole.

Heel: The heel is the part of the sole that raises the rear of the shoe in relation to the front. The heel seat is the top of the heel that touches the upper, this is typically shaped to match the form of the upper. The part of the heel that comes in contact with the ground is known as the top piece.

Insole: A layer of material that sits inside the shoe that creates a layer between the sole and the wearer's foot. The insole adds comfort for the wearer, while hiding the join between the upper.

Linings: Most shoes include a lining on the inside of the shoe, around the vamp and quarter. These linings improve comfort, and can help increase the lifespan of the shoe.

Outsole: The exposed part of the sole that is contact with the ground. As with all parts of the shoe, outsoles are made from a variety of materials. The properties of the outsole need are: grip, durability and water resistance.

Quarter: The rear and sides of the upper that covers the heel those are behind the vamp. The heel section of the quarter is often strengthened with a stiffener, which helps support the rear of the foot. Some shoe designs use a continuous piece of leather for the vamp and quarter.

Seat: Where the heel of the fit sits in the shoe. It normally matches the shape of the heel for comfort and support.

Shank: A piece of metal inserted between the sole and the insole lying against the arch of the foot.

Throat: The front of the vamp next to the toe cap.

Toe cap: Shoes may have a toe cap in the front upper of the shoe. Toe caps can take various forms, but the distinct types are: complete replacements for the front upper of the shoe; stitched over toecaps that add an extra layer to the upper; solid toe caps for protection, such as steel toe caps.

Top Piece: The part of the heel that comes in contact with the ground.

Topline: The top edge of the upper.

Upper: The entire part of the shoe that covers the foot.

Vamp: The section of upper that covers the front of the foot as far as the back as join to the quarter.

Welt: A strip of material that joins the upper to the sole.

Sole: The entire part of the shoe that sits below the wearer's foot. The upper and sole make up the whole of the shoe. It is usually constructed of several layers:

- i. Insole:** The insole is the part of the sole that sits directly beneath the wearer's foot. Its purpose is to provide a comfortable layer above the joining of the upper to the sole.
- ii. Mid-sole:** A mid-sole can be found on some shoes, and is a layer between the in-sole and out-sole.
- iii. Outsole:** The outsole is the layer of sole that is exposed to the ground. Due to the amount of wear and stress this part of the shoe receives it is usually made of a very durable material. It is also important that it provides enough friction with the floor to prevent the wearer from slipping.

The sole is a critical component of any item of footwear. It protects the foot from the ground, and contributes substantially to the structural integrity of the shoe. The user must ensure that footwear chosen protects against the risks involved in the work place.

Soling Thickness:

The thickness of a sole must be sufficient to provide an acceptable level of ground insulation, and an acceptable wear life. A minimum of 2 mm in any type of sole is needed to give a stable base for the tread.

Properties of an ideal soling material:

The properties of an ideal soling material on processing needs are low cost raw materials, cheap to process, easy to mould with good definition, form strong bonds with conventional adhesives and recycled.

The properties of an ideal soling material on wearing needs are low density (light weight for comfort), high elasticity (soles must not spread especially in hot conditions), high resilience (for energy return), high flexibility, good wet and dry slip resistance (for safety), good abrasion (wear) resistance, good water resistance (for comfort), good shock absorption (to protect wearer from injury), good ageing resistance and good appearance.

Soling's selection:

Soling's are supplied in several forms, depending on the type of footwear being manufactured. They may also vary according to the manufacturing process, such as rubber vulcanization, and the nature of the soling material, for example its thermo plasticity. The common forms are: sheet, caster shapes, built units, molded units and molded-on.

2.2 History of Shoe/sandal Sole Invention

There is much evidence that [28] a foot covering was one of the first things made by our primitive ancestors. Necessity compelled them to invent some method of protecting their feet from the jagged rocks, burning sands, and rugged terrain over which they ranged in pursuit of food and shelter.

The history of human development shows that the importance of protecting the foot was early recognized. In its first form the shoes was just a simple piece of plaited grass or rawhide which was strapped to the feet. The sandal still is the most generally worn type of footwear in many warm countries. In form and ornamentation it reflects the environment in which it was worn, together with the artistic tastes of the peoples. The Japanese, a long sandal wearing people indicated the social status of the wearer by making distinctive sandals for the Imperial Household, merchants and actors, in fact, for the whole range of vocations and professions.

Through all this development, comparatively little attention was devoted to fitting qualities or comfort. When the medieval guilds controlled craftsmanship in Europe, perfection in workmanship and extravagance in style seems to have been sought in shoes rather than foot comfort and protection.

As late as 1850 most shoes were made on absolutely straight lasts, there being no difference between the right and the left shoe. Breaking in a new pair of shoes was not easy. Up to 1850 all shoes were made with practically the same hand tools that were used in Egypt as early as the 14th century B.C. as a part of a sandal maker's equipment. They had all failed and it remained for the shoemakers of the United States to create the first successful machinery for making shoes.

In 1845 the first machine to find a permanent place in the shoe industry came into use. It was the Rolling Machine, which replaced the lap stone and hammer previously used by hand shoemakers for pounding sole leather, a method of increasing wear by compacting the fiber's. This was followed in 1846 by Elias Howe's invention of the sewing machine. The success of this major invention seems to have set up a chain reaction of research and development that has gone on ever since. In 1858, Lyman R. Blake, a shoemaker, invented a machine for sewing the soles of shoes to the uppers. His patents were purchased by Gordon McKay, who improved upon Blake's invention.

This unique service was used in the shoe industry long before it spread to other industries. McKay quickly found that in order to ensure payment for the use of the machines it was necessary to keep them in operation. A machine which wasn't working did not earn any money for McKay. In 1875 a machine for making a different type of shoe was developed. Later known as the Goodyear Welt Sewing Machine, it was used for making both Welt and Turn shoes.

For centuries it was the hand shoemaker's only tool for shaping the shoe around the form on which it is made aided only by thumbs and tacks. The lasting pincer is a good tool and is still occasionally useful; with it a century ago a man with great effort might form or last a few pair in a long day. Today's automatic toe laster for Goodyear Welt shoes can last 1.200 pairs in an 8-hour day.

The first shoes were made out of natural materials, so the outsoles were very thin. American Indians made soft-soled moccasins out of animal hides. During the middle ages shoes began to feature soles with hardier materials such as leather and jute. In the 1600s shoe soles were almost always made out of leather, which is still the standard in fine leather dress shoes to this day.

Up until the Industrial Revolution shoemaking was done entirely by hand. It was an extremely time-consuming process because the leather soles had to be meticulously hand-stitched onto shoes. Leather is a very sturdy material, which is good for durability, but its stiffness makes it very difficult material to work with. The invention of the machine

revolutionized the shoemaking process. By the turn of the century, shoemaking had become almost completely mechanized.

2.3 Materials Used in Shoe/sandal Production

Shoe/sandal is created by different types of material which are briefly described below:

2.3.1 Materials of Shoe/sandal

Approximately 40 different materials can be used in the manufacturing of shoe [29]. However, the common material composition of a typical shoe/sandal is presented in Table 2.1 [24].

Table 2.1: Material Composition of a Shoe/sandal

| Footwear Materials | Percentage (% wt) |
|---------------------------------|----------------------|
| Leather | 25 |
| Polyurethane (PU) | 17 |
| Thermoplastic Rubber (TPR) | 16 |
| Ethylene Vinyl Acetate (EVA) | 14 |
| Poly Vinyl Chloride (PVC) | 8 |
| Rubber | 7 |
| Other (Adhesives, Metals, etc.) | 7 |
| Textiles and Fabrics | 6 |

This shoe/sandal's material briefly describes which were found to be relevant in shoe production during the initial research.

Leather

Since the raw material used in leather production is animal hides, animal production and slaughtering initiates the life cycle of leather [30]. Transportation of animals and hides is also required in this phase [31]. After the initial treatment, a tanning process is used to remove proteins and turn the hides into stable leather.

The whole leather production process generates waste water containing chemicals and biological material as well as solid waste such as contaminated sludge [32]. Despite the issues regarding water and toxicity, leather can be seen as a renewable alternative to materials made from fossil resources if raw hides are classified as a by-product from the meat and milk industry [33]. Leather produced as a by-product is an example of a sustainability demand from shoe companies [34]. The insoles are cut from the bellies and the outsoles from the skin cut along the backbone where the leather has the greatest abrasion resistance.

Polyurethane (PU)

Polyurethane (PU) can be blended to be solid, cellular, flexible or rigid. Normally for shoe the blend is a flexible cellular structure. PU is a very hard wearing polymer resistant to most chemicals. It is used frequently as a two-part sole material with a thin solid PU-polymer and a blown PU-material for most of the sole making. It is frequently used for safety footwear.

Thermoplastic Rubber (TPR)

Thermoplastic Rubber (TPR) is directly injected to the upper. TPR can be injection molded. It was originally developed for soling to simulate crepe and soft vulcanized rubbers.

Ethylene Vinyl Acetate (EVA)

Ethylene Vinyl Acetate (EVA) is used in an expanded form. Normally used in expanded form either on its own or blended with SBR. It is used for outsole in lightweight footwear and midsoles in trainers.

Poly Vinyl Chloride (PVC)

Polyvinyl chloride (PVC) is cement lasted as a molded unit or directly injected to the upper. PVC is the main synthetic used for shoe soling. The PVC polymer is hard, but when used for soling it is softened by the addition of plasticizers. It can be either used as 'direct injection' to the upper or as a stuck-on unit, 'Cement lasted'.

Rubber

The rubber category involves several different types, including natural and synthetic [35]. The raw material, latex, is extracted from trees and can be treated with chemicals before use [35]. According to Albers et al. (2008), another way to get rubber is to synthesize it artificially by using polymerization. Mostly used in shoe soles and for different kind of boots, rubber is suitable since it is a lasting and often waterproof material [36]. However, rubber production generates emissions to air in the form of volatile organic compounds (VOC) and CO₂ which also contribute to the environmental impact from shoes [35]. The rubber components are briefly described in the following sub-section:

- i. 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. 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. 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 % [37].

- ii. 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. The rest goes into products such as footwear, sponge and foamed products, waterproof materials and adhesives.

SBR 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. 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. Polymerization of pure monomers can be better controlled to give a desired proportion of cis and trans double bonds [38].

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 [39].

- iii. 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. The reclaimed rubber is of less tensile strength, lower in elasticity and possesses lesser wear resistance than natural rubber.

- iv. 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. 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.

- v. 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.

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 structural formulas of rubber compounds can be distinguished from one another, but the main

structures are similar. 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 [19].

Adhesives

Natural, renewable materials in form of wood and cork can be used in shoe production, for example in soles and heels. Cork is extracted from cork oak trees by removing the bark, while the type of trees used for wood may vary [35].

Metals

In general, metals are non-renewable resources extracted from metal ores. The production process depends on the metal in question, since the ore might include several metals which must be separated before further processing steps [40]. According to Norgate et al. (2007), the extraction methods usually result in not only emissions to air, land and water, but also a remaining mixture of toxic metals and chemicals. Therefore, it is suitable to use the high recyclability of metals to avoid the environmental impacts caused during the production phase [40].

Textiles

In shoes, textiles can be used for lining and upper parts. Among the textiles used, cotton is an old and well-known material which is cultivated and made into yarn [35]. According to Albers et al. (2008), cotton blends might also exist in form of cotton thread mixed with nylon, a synthetic fiber made from non-renewable resources which is related to impacts in form of emissions and use of toxic chemicals. Another example of a synthetic fiber made from non-renewable resources is polyester, based on PET [35]. As described by Albers (2008), it is common to extract fibers from plastics such as PET, PU and PVC for shoe production.

Fabrics

A wide range of fabrics is used for shoe uppers, both outers and linings. Fabrics outers are necessarily heavier in weight and are usually of woven (canvas) or knit construction in natural or synthetic yarns, usually combined with another textile for uppers. Linings also

include woven and knitted fabrics as well as non-woven textiles which can be impregnated with plastic to increase their durability. Fabrics include a wide variety of natural and man-made fibers.

2.3.2 Materials of Shoe/sandal Soles

There are different types of soling, materials. They are:

Leather (Vegetable Tanned): It has an unmistakable smell and a fairly hard material. Soles often labeled leather with the hide mark. It may be lightly embossed but no tread. Usually has smooth, slick lightly glossed surface finish. Magnification reveals tiny pin-prick like hair shaft openings. Light grey leather, often with a suede surface, is probably chrome tanned and used in dance and 10 pin bowling shoes.

Vulcanized Rubber (VR) (Solid): It's rubbery smell familiar to most people and has rubbery feel (grippy). It has very good appearance with excellent definition of edges and fine detail. All colors of this are possible including natural translucent. It's very soft versions sometimes labeled 'Latex' and often found as an outsole combined with a softer PU or EVA midsole. Soles which are VR only are relatively heavy. On industrial footwear may be marked 'heat resistant'.

Thermoplastic Rubber (TPR): Superficially similar to vulcanized rubber. It carries a distinctive synthetic smell which is quite different from VR. It is very rubbery feel (grippy) and quite soft as judged by easy indentation, but surprisingly stiff. It has sheened surface finish and available in all colors. It has less even quality of appearance than VR with some hairline molding. It is not found with midsoles in other materials but sometimes two color moldings can mimic an outsole/midsole assembly.

Polyurethane (PU) (Reaction-Molded): It is a polyester type material with no particular smell. There are three types of polymer such as distinctive, quite strong and non-rubbery smell. It is not a heavy material – lighter than solid rubber or PVC. It may feel rubbery but often quite slick with sheen to the surface and has an expanded or microcellular structure, but this may not be evident as molding produces a thin solid skin and usually there are no

cut edges. Soles may be molded with or without a tread pattern. Softeners used in thicker soled footwear where it may be molded to resemble cork or wood.

Natural Crepe Rubber: A translucent pale or honey coloured sheet material with a raw appearance. It has a wrinkled, textured or corrugated surface but no molded sole profile or treads cleats. It is quite soft and very rubbery with a distinctive slightly sweet smell unlike vulcanized or thermoplastic rubber. Sometimes found in black or dark brown and sometimes pale crepe may have blacked or browned edges. It is mostly used on comfort casuals.

Resin Rubber: It is a firm material, superficially leather-like, generally found as a thin sole on women's court shoes and fashion boots and no tread but winter boots may have a serrated forepart wear area. It usually has a glossy low friction (slick) surface finish but worn areas feel rubbery and color mainly black or tan to simulate leather, not translucent. It has good visual quality.

Polyvinyl Chloride (PVC): This is a plastic that has chemical formula: $\text{CH}_2=\text{CHCl}$. PVC is a thermoplastic material. They can be melted again and again. These materials can be heated to a certain temperature and will harden again as they cool. PVC can be clear or colored, rigid or flexible, depending on the added compounds and final application that needs to be achieved. It has plastic vinyl smell familiar to most people. It is a relatively heavy material in solid form and soft grades can feel rubbery, harder grades not, fairly glossy, shiny surface. It tends to wear very smooth, not found with midsoles in other materials but sometimes combined with a leather forepart in dress shoes.

Ethylene Vinyl Acetate (EVA): It has characteristics of non-rubbery smell when new but this fades an extremely lightweight material. It is usually soft enough to be impressionable with a finger. It may have a slick (molded) surface- with sheen or else a matt velvety surface which is a split through the microcellular structure and may have cut or molded edge.

Thermoplastic Polyurethane (TPU): TPU is a fully thermoplastic elastomer. It is elastic, melt able process and can be processed on extrusion, blow, injection and compression

molding equipment. It is difficult to distinguish from PVC, but has no particular smell. They are solid material feels smooth and it not rubbery.

2.3.3 Comparison of Tyre and Shoe/sandal Sole Compositions

The compositions of shoe/sandal sole [41] were compared with that of tyre [42] which is summarized in Table 2.2.

Table 2.2: Comparison of Tyre and Sole Compositions

| Materials of Tyre | Composition of Tyre (wt %) | Materials of Soles | | Composition of Soles (wt %) |
|-------------------|----------------------------|----------------------|------------------------|-----------------------------|
| Rubber | 48 | Leather | | 25 |
| Carbon Black | 22 | Rubber | Polyurethane | 17 |
| Metal | 15 | | Thermoplastic rubber | 16 |
| Textile | 5 | | Ethylene vinyl acetate | 14 |
| Zinc Oxide | 1 | | Poly vinyl chloride | 8 |
| Sulphur | 1 | | Others | 7 |
| Additives | 8 | Adhesives & Metals | | 7 |
| | | Textiles and Fabrics | | 6 |

From the above table, shoe/sandal soles have similar compositions like tyres and also create environmental pollution problems.

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 [43], such as:

1. General Solid Waste
2. Liquid Waste

3. Special Waste
4. Hazardous Waste

General Solid Waste

General solid wastes again can be grouped into two:

- 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 waste: These are wastes which either cannot be broken down by microbes or it takes a long duration for them to do so, Ex: Plastic, Polyethelene etc.

Liquid Waste

For a waste to be classified as a liquid waste it must have the following characteristics: an angle of repose less than 5° above horizontal, becomes free flowing at below 60° or when it is transported and generally not capable of being picked up by a spade or shovel.

Special Waste

‘Special Waste’ is a category of waste that has 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:

- (i) Container: that previously contained goods that are deemed dangerous for transportation, from which residues have not been washed or evacuated;
- (ii) Coal tar or pitch waste;

- (iii) Lead acid or nickel cadmium batteries;
- (iv) Lead plant waste from residential and educational and
- (v) Nuclear waste.

2.5 Waste Generation by Shoe/sandal Soles

To keep pace with worldwide, footwear production is gradually increasing, therewith waste inventory from a footwear factory also increasing. The waste inventory from a footwear factory [44] is shown in Table 2.3.

Table 2.3: Waste Inventory from a Footwear Factory

| Materials | | Waste (%) |
|----------------------|---------|-----------|
| Leather, Natural | | 4.1% |
| Leather, Synthetic | | 3.6% |
| Sole | Outsole | 17.2% |
| | Midsole | 11.8% |
| | Insole | 2.7% |
| Fabric/Textile | | 6.8% |
| Inner Box | | 2.3% |
| Corrugated Outer Box | | 0.4% |

Sole is the backbone of shoe and many other sandals. The footwear industry is a major consumer of the rubber production. However, with increased production of shoe/sandal waste soles generation will also be increased which is proportional to the volume of production of shoe/sandals. As mentioned before worldwide footwear production increased by 70% from 1990 to 2004, so there will be a potential if 31.7% waste generation. These wastes are thrown scattered and sometimes cause drain blockage. The photographic view of waste soles and the blockage caused by them are shown in Figure 2.2 and 2.3.



Figure 2.2: Photographic View of Waste Shoe/sandal Soles



Figure 2.3: Photographic View of Drain Blockage caused by Waste Shoe/sandals

The generation of solid wastes like shoe/sandals is increasing steadily. According to the statistical data with the exponential growth in people, generation of waste shoe/sandals increases. About 100% of people use shoe/sandals. For the demand of using shoe/sandals, this will produce a lot of shoe/sandal sole 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.

2.6 Difficulties with the Shoe/sandal Wastes

Disposing of process residues from the footwear industries, especially production waste of thermoplastic rubber and polyvinyl chloride soles as well as human used soles is a big concern due to its non-biodegradability.

Footwear is the wearing apparel for the foot with two basic parts: i) upper and ii) bottom (sole). In most cases, the bottom (sole) is composed of thermoplastic rubber (TPR), polyvinyl chloride (PVC), ethyl vinyl acetate (EVA), vulcanized rubber (VR), leather, etc. In Bangladesh, most of the footwear industries are using polyvinyl chloride (PVC) and thermoplastic rubber (TPR) as sole for the production of footwear.

The dumping of shoe/sandal wastes is one of the main environmental issues all over the world. One common way of disposal for these shoe/sandal wastes is landfilling as shown in Figure 2.4. Shoe/sandals are bulky and 82% of the space a shoe/sandal occupies is void, so that the landfilling of shoe/sandal has several difficulties. If the shoe/sandal wastes are scattered on land 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 being [3]. Thus, an environmental friendly and economic technology should be developed to manage this and/or recover energy from shoe/sandal wastes.



Figure 2.4: Landfilling of Shoe/sandal

At this moment, the most significant methods and technologies adopted for shoe/sandal wastes recovery and disposal which will remove the landfilling, drain blockage (Figure 2.5) problems etc. are:

- Reusing the original form
- Reconstruction of shoe/sandal wastes
- Thermal treatment to perform material and or energy recovery
- Utilization in building applications
- Other treatments
- Landfilling, heaping and abandonment.



Figure 2.5: Drainage Problem by Shoe/sandal

From the above difficulties created by waste soles, it could be concluded 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. So thermal treatments, aimed at matter and energy recovery, are a promising disposal method as an alternative to landfilling [45].

2.7 Effects of Shoe/sandal Waste on Environment

The most important environmental challenge that the footwear industry is currently facing is the enormous amount of waste generated at the end-of-life phase, with most shoes being

disposed of in landfills. Landfill sites can result in serious environmental pollution of ground water and rivers, caused by landfill leachate (the liquid produced from the decomposition of waste within the landfill). According to Wick's and Bigsten [46], redistribution of second-hand products into developing countries may also lead to net economic damage to the local economies as a result of “dumping” of cheap used footwear.

The manufacturing rubber often creates large quantities of toxic chemical pollutants such as dioxin, hydrochloric acid, and vinyl chloride. This poses a severe health risks to humans during the PVC life cycle. These toxins can produce sever illness like cancer, diabetes, neurological damage, reproductive and birth defects. Due to the quantity and different additives added to PVC and also due to its chlorine contain the final disposal or recycling of PVC is an issue to be closely examined.

Polyurethane polymer is a combustible solid and can be ignited if exposed to an open flame. Decomposition from fire can produce mainly carbon monoxide, and trace nitrogen oxides and hydrogen cyanide. Because of the flammability of the material, it has to be treated with flame retardants (at least in case of furniture), almost all of which are considered harmful. These environmental impacts by shoe/sandal landfilling or thrown to drain create different difficulties as shown in Figure 2.6 and 2.7. Such difficulties are shown as below:



Figure 2.6: Environmental Impacts by Shoe/sandal Waste Landfilling



Figure 2.7: Environmental Impacts on Drain Blockage by Shoe/sandal Waste

Incineration

The incineration of PVC causes the release of dioxins and other toxic chemicals.

Landfill

Landfill of PVC has other environmental and social impacts. This is due to the non-biodegradability of PVC which stays in place indefinitely; besides, attention should be taken to the fact that PVC may leach out toxic chemicals and contaminate the soil and water. There are some “biodegradable” plastics that break down with exposure to sunlight but it still doesn't lead to complete breakdown of the plastic.

Once released to the environment, metal ions associated with a shoe/sandal sole composition are relatively mobile and can migrate to ground and surface waters through soil leaching and runoff. Consequently, the impact of metal on the environment from shoe/sandal leaching is relatively small. Metals and metal oxides covered from the thermal oxidation of shoe/sandal have a higher potential to impact the environment and should be recovered or stabilized.

2.8 Analysis of Properties of Feed Materials and Pyrolytic Products

To study the behavior of any chemical substance its properties are determined. These are two types of properties such as physical and chemical properties. The analyses of the properties of pyrolytic products are briefly explained below:

2.8.1 Physical Properties

The physical properties of pyrolytic products can be determined by following the standard test methods for density, flash point, pour point, boiling point, etc. These are briefly described below:

Density

The density of oil is a measure of its aromaticity in hydrocarbon oils, but not in biomass derived oils, it is a 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 [47]. The pyrolysis liquid having relatively higher density typically has lower water contents. The density of the liquid is measured using methods ASTM D-4052.

Flash point

Flash point of the liquid is defined as the lowest temperature at which the liquid may vaporize and form a mixture in the air that ignites when an external flame is applied [48]. Measuring flash point requires an ignition source. At the flash point, the vapor may cease to burn when the ignition source is removed. 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 is determined according to ASTM-D93 test methods.

Pour Point

Pour point is known as the temperature at which the fluid stops to flow [49]. 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.

Boiling Point

The boiling point of a substance is the temperature at which the vapor pressure of the liquid equals the pressure surrounding the liquid and the liquid changes into a vapor [50]. The boiling point of a liquid varies depending upon the surrounding environmental

pressure. The standard test methods for the determination of the boiling point are ASTM D1120.

2.8.2 Chemical Properties

The chemical properties of pyrolytic products can be determined by the following tests such as gross calorific value (GCV), elemental analysis, compositional group fourier transform infra-red (FTIR) spectroscopy, thermo gravimetric analysis (TGA), etc. but feed materials can be determined by proximate analysis. These are briefly described below:

Proximate Analysis

Proximate analysis is used for calculation of chemical composition of the residue including moisture content, ash content, volatile matter and fixed carbon.

Samples have specific amount of moisture directly affects their heating values. Standard method for moisture determination involves heating of 1 gm sample in a hot air oven at $105 \pm 5^\circ\text{C}$ for 24 hours using the following equation.

$$\text{Moisture (\% M)} = (W_1 - W_2)/W_3 \times 100$$

W_1 = Weight of the crucible & the air dried sample (g),

W_2 = Weight of the crucible & oven dried sample (g),

W_3 = Weight of the air dried sample taken (g)

Ash is defined as the weight of the residue remained after complete burning of 1gm of the sample at $750^\circ\text{C} \pm 25^\circ\text{C}$.

$$\text{Ash (\% A)} = (W_4 - W_5)/W_6 \times 100$$

W_4 = Weight of the crucible & the oven dried sample (g),

W_5 = Weight of the crucible & residue (g),

W_6 = Weight of oven dried sample taken (g)

Volatile matter is termed as the weight loss due to heating of 1gm of sample at $750^\circ\text{C} \pm 5^\circ\text{C}$ in a closed crucible furnace for 7 minutes.

Weight loss due to Volatile Matter (%VM)

$$= \text{Total loss of weight} - \text{Loss due to moisture}$$

The content of fixed carbon (FC) is determined by subtracting the sum of A %, VM & % M from total of 100 % composition.

$$\text{FC} = 100 - (\% \text{ A} + \% \text{ VM} + \% \text{ M})$$

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 [51]. It is the most important fuel property of any fuel. The gross calorific value (GCV) of the pyrolysis liquids are determined by a bomb calorimeter.

Chemical Elemental Analysis

Chemical elementary analysis of raw material gives good idea about the concentration of C, H, S, N, and O. In one hand, C and H concentrations, in addition to the C:H ratio evaluates the valuation of the pyrolysis process. When the C and H are high and the ratio C:H is small; this means that the raw material is very valuable to be pyrolyzed [52].

Elemental analyses of total nitrogen and carbon (and sulfur) is performed to provide carbonate and organic carbon and to get some idea of the composition of the organic matter (i.e., to distinguish between marine and erogenous sources, based on total organic carbon/total nitrogen [C/N] ratios).

On another hand, sulfur (S) presence is undesirable because it diffuses in the three products. This demands complete treatment where ever it is: in the liquid, solid and in the gas product. If the conditions of pyrolysis keep the majority of sulfur in solid or/and gas products; it is better than its transition into liquid product. Oxygen presence in the scrap tyres increases the oxidation process (mainly combustion in addition to other complicated ones), producing more CO₂ and CO at the expenses of other gases. Combustion process reduces the viability of the pyrolysis.

So, high concentration of C and H, small ratio C:H and low concentration of S, N and O give higher energetic valorization to the scrap tyres pyrolysis. Scrap tyres differ from each other in their chemical composition; either at the phase of their manufacturing or because of the way and conditions of using till their being scraps. So, it is necessary to do elementary analysis in order to determine their chemical composition before starting pyrolysis in order to evaluate them energetically. Elemental analysis can be done using FLASH EA 1112 series CHNS-O analyzer with limit of detection 0.2% for each element and sample weight range is 0.5-1.0 mg.

Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy

The functional group compositions of the pyrolysis products 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 products.

FTIR (Fourier Transform Infra-Red) analysis is an analytical method based on the interactions between IR light (i.e. wavelength range from 2.5 to 15 μm) and the matter [53]. Molecules are vibrating at characteristic frequencies. Exposed to IR radiations, a molecule will absorb IR energy only at frequencies matching the molecule's natural frequency of vibration (resonant frequencies). The frequencies of vibration of a molecule (subsequently the frequencies of the radiations absorbed) are directly related to the nature of the atoms and the structure of the molecule.

The absorption intensity is correlated to the change of the dipole moment due to the vibration and to the concentration of molecules. Consequently, qualitative and quantitative results can be extracted. Almost all molecules can be identified by FTIR except for some symmetrical molecules (O_2 , N_2 , H_2 , etc.) and inert gases (Ar, He, etc.) because they do not exhibit any change in their dipole moment.

Thermo Gravimetric Analysis (TGA)

After the elementary analysis step and the decision that the raw material is evaluated to be pyrolyzed, TGA is the intrinsic step to determine the approximated conditions of pyrolysis. TGA helps to determine the range of temperature where the pyrolysis should take place,

the temperature at which it is necessary to heat up the raw material (T_{\max}); the time that the scrap should be stayed at T_{\max} , the effect of heating rate, the effect of inert gas flow rate, and finally the yield of volatile products (gas and liquid) [52]. Volatile yield is the most important information that could be obtained from TGA in addition to T_{\max} .

TGA helps, as well, to calculate the kinetic parameter of degradation process; activation energy E_a , potential factor A, constant factor and order of degradation (pyrolysis) reaction. These kinetic parameters and its importance will be discussed in more details in the next chapter (TGA study). Sample weight range is 50-200 mg, max temperature is 1700°C and inert gas (nitrogen) flow range is 4-200 ml/min. Thermo gravimetric analysis (TGA) is a method that can be used to determine the loss of mass and kinetic parameters. Thermo gravimetric analysis of pyrolysis involves the thermal degradation of the sample in an inert atmosphere obtaining simultaneously the weight loss values of the samples with increasing temperature at a constant heating rate [54-56]. Thus, by measuring the heat flow into the sample during the reaction (using for example the calorimeter DSC method), it is possible to measure the rate of broken bonds occurring in the sample [54].

Thermo gravimetric analysis (TGA) is a well-known experimental technique in which the mass of the sample is recorded while the temperature of the sample, in a controlled atmosphere, is programmed. The sample is no more than a few milligrams to ensure that decomposition is taking place in the kinetic regime. The sample is loaded in an inert crucible (platinum, alumina), placed on (or attached to) a balance. The experiment is usually carried out with a gas flow (inert or reactive).

2.9 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. It is 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:

2.9.1 Cost Analysis of Pilot Plant

Techno-economic assessment showed the production cost for pyrolysis oil and char from solid shoe/sandal sole 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 shoe/sandal sole wastes.

2.9.2 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 [57] by the formula given by Eq. No. (1)

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

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

2.9.3 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 2.4. The analysis of unit production cost of oil is the basis for assumptions.

Table 2.4: Parameters used in Annual Cost Estimation of a Shoe/sandal Sole Pyrolysis Plant

| | |
|--------------------------|-------------------------------------|
| Plant Capacity | 3.4 kg/day, Waste Shoe/sandal Soles |
| Location, Time, Currency | Bangladesh, 2018, Tk |
| Annual Operating Time | 2240 h@ 8 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 | 10 Tk./kg |
| Labor Cost | 300 Tk./day |
| Total Labors | 01 (Working 280 days/yr.) |
| Electricity Price | 6 (Tk./kWh) |
| General Overheads | 40% of total salaries |
| Interest Rate | 10 % |
| Plant Life | 5 years |

CHAPTER III

Literature Review

3.1 Managing Technology of Shoe/sandal Sole Waste

Along with the environmental protection consciousness and management especially in a sustainable developed society today; people are using more fuel resources which are generating more waste materials. Shoe/sandal sole waste must be effectively disposed and recycled, which not only is the requirement of preventing pollution and environment protection, but also is the need of reduction in production cost and improvement in material utilization. There are different managing technologies with advantages and disadvantage of shoe/sandal sole which are given in Table 3.1. Due to its low density and high volume, shoe/sandal sole waste is difficult to treat and dispose of in landfill as shown in Figure 3.1. Incinerations of these wastes also produce poisonous gases.



Figure 3.1: Shoe/sandal Waste

Table 3.1: Advantages and Disadvantage of Shoe/sandal Soles Managing Technology

| Disposal Treatment | Key Technology | Advantages | Disadvantages |
|--------------------|--|---|---|
| Landfill | Leachate guide line system, Anti-seepage | i. Simple operation. ii. Less input. | i. Difficult decomposition. ii. Waste of land resources. |
| Incineration | High temperature burning | i. Recovery of energy. ii. Relatively matured technology. | i. Produce poisonous gases. ii. Serious air pollution and public hazard. |
| Recycling | Degradation reaction | i. Get the pure raw material monomer/small molecule organic matter. ii. Product can be used as raw material for the preparation of new products. | i. High temperature or high pressure. ii. Safety performance of high demand on the equipment. iii. Product needs purification. iv. By-products difficult to control. |

Brief descriptions of these three technologies are given below:

Landfill

A landfill is a facility in which solid wastes are disposed in a manner which limits their impact on the environment. Landfills consist of a complex system of interrelated components and sub-systems that act together to break down and stabilize disposed wastes over time [58]. Landfill is very old but still one of the extensively used technologies for shoe/sandal sole wastes management. Most of the landfill does not have the energy production facilities.

Incineration

Incineration is a thermal waste treatment process where raw or unprocessed waste can be used as feedstock. The incineration process takes place in the presence of sufficient

quantity of air to oxidize the feedstock (fuel). Waste is combusted in the temperature of 850°C and in this stage waste converted to carbon dioxide, water and non-combustible materials with solid residue state called incinerator bottom ash (IBA) that always contains a small amount of residual carbon [59]. It is the process of combustion of solid waste chemical elements (carbon, hydrogen, sulfur) in an oxygen-rich environment, at temperature higher than 850°C and producing combustion gases, especially CO, CO₂, NO_x, H₂O, SO₂, ash, and heat. The inorganic content of the waste is converted to ash.

The object of this thermal treatment method is the reduction of the volume of the treated waste with simultaneous utilization of the contained energy. The recovered energy could be used for: heating, steam production, electric energy production. The method could be applied for the treatment of mixed solid waste as well as for the treatment of pre-selected waste.

Recycling

Integrated waste management options are now been applying in most of the developed countries with resource recycle, recovery and energy generation facilities from the solid waste. Waste-to-energy (WTE) conversion is now considered as one of the optimal methods to solve the waste management problem in a sustainable way.

Landfill will be serious waste of land resources. At the same time shoe/sandal sole wastes are very difficult to decompose in the natural conditions. Incineration will produce poisonous gas, and cause serious air pollution and public hazard. Landfill and incineration will not be recommended except in special circumstances. One can compare the advantages and disadvantages of them from the above table. So, recycling is the most effective treatment method in the future.

3.2 Various Recycling Process to Reduce Wastes Soles

Pyrolysis, gasification, and liquefaction are the thermo-chemical processes that can be used to convert waste shoe/sandal sole as well as other carbonaceous feed stocks such as coal, wood waste, or municipal solid waste into usable products [4].

3.2.1 Pyrolysis Process

Pyrolysis is thermal degradation either in the complete absence of oxidizing agents, or with such a limited supply that gasification does not occur to an appreciable extent or may be described as partial gasification. Relatively, low temperature of 500 to 800°C is employed compared to 800 to 1000°C in gasification [60].

The pyrolysis processes can be categorized into slow and fast pyrolysis. Fast pyrolysis is currently the most widely used pyrolysis system. Slow pyrolysis takes several hours to complete and results in pyrolytic char as the main product. On the other hand, fast pyrolysis yields 60% pyrolytic oil and takes seconds to complete pyrolysis. In addition, it gives 20% pyrolytic char and 20% syngas [61]. Fast or flash pyrolysis is used to maximize either gas or liquid products according to the temperature employed [60].

In the pyrolysis process, the sample is heated in the absence of oxygen and the organic compounds are decomposed generating gaseous and liquid products. On the other hand, the inorganic part of the sample, free from organic matter remains practically unchanged in the solid fraction enabling their separation and recovery for subsequent reuse. Therefore, the pyrolysis is an attractive alternative technique for recycling waste plastics [62-66].

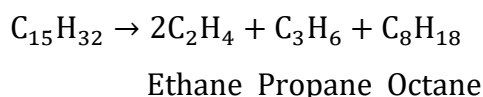
The pyrolysis products can be used as an alternative fuel or as a source of chemicals [66]. The composition of the product also depends on the presence of catalysts (including concentrations and types). Higher temperatures decrease the yield of hydrogen, methane, acetylene and aromatic compounds, whereas lower temperatures favor the generation of gas products [67].

3.2.2 General Cracking

Cracking is the name given to breaking up of large hydrocarbon molecules into smaller and more useful bits [68]. 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 are no single unique reactions that occur during cracking. 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:



3.2.3 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 [68]. 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 to 10 carbon atoms particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

3.2.4 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 [69]. The process converts low-octane linear hydrocarbons (paraffin's) 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.

3.2.5 Catalytic Pyrolysis

Catalytic pyrolysis has been used to enhance the concentration of higher value chemicals in the oil and produce oil which can be used as a chemical feedstock rather than fuel [70] (limonene, benzene, toluene, etc.). NaOH, CaCO₃, MgO. Zeolite is the most famous used catalysts. NaOH, for example, can promote the rapid cracking of organic compounds scrap tyres rubber into small molecular compounds, even at low temperatures [71].

Williams and Brindle [72-73] 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 (SiO₂/AlO₂) 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. The significance of the different shape selectivity of HY and HZSM-5 zeolite is apparent in the transformation reaction of thermal pyrolysis primary products. Both catalyst increase the yield of the aromatic fraction (with a high concentration of xylenes) compare to thermal pyrolysis.

3.3 Technique to Remove Sole Wastes with Energy Recovery

Waste-to-energy (WTE) conversion is now considered as one of the optimal methods to solve the waste management problem in a sustainable way. Different recycling as waste-to-energy technologies are now applying for managing shoe/sandal sole waste. In this study, one recycling technology as pyrolysis is analyzed for managing shoe/sandal sole waste. A brief description of this recycling technology as pyrolysis is given below:

3.3.1 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 hardwoods residues feed,

carefully controlled temperature of around 500°C and rapid cooling of the pyrolysis vapor's to give the bio-oil product [74]. 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 vapors and their quenching influences the composition and quality of the liquid product. High temperatures will continue to crack the vapors and the longer the vapors are at higher temperatures, the greater the extent of cracking. Vapor residence time of a few hundred milliseconds are necessary for optimum yields of chemicals and food additives, while fuels can tolerate vapor residence time of up to around 2s [75]. 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 [76]. 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. 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 [71]. Also, the high char yield at low heating rate has been explained by the vapor-solid, interactions [77].

Advantage of pyrolysis process

- It reduces carbon dioxide emissions
- It reduces landfilling
- It helps to faster commercialization of products

- It helps to extract liquid that could be used to produce electricity and heat
- It is a safer and more environmentally friendly process than incineration and land filling and many other gasification processes.
- It takes trash and converts it into valuable new products, oil, carbon and gas.
- It complements traditional recycling efforts.
- It preserves land for agricultural or other uses that would be taken up by landfills.
- It creates jobs.

3.3.2 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 fuel use. The recovery of liquid oil known as 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 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 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 [78].

Pakdel et al. [79] developed the vacuum pyrolysis process for used tyre's 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. 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 C₅ - C₂₀ organic compounds, with a great proportion of aromatics with high gross calorific values of 42 MJ/kg. Chang [80], 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.

3.3.3 Parameters of Pyrolysis

The yield and composition of each pyrolytic product (char, liquid and gas) is affected by the conditions or parameters of the pyrolysis process. Such parameters of the pyrolysis process are given below:

Temperature

Temperature is one of the most significant operating parameters in pyrolysis since it controls the cracking reaction of the polymer chain. Molecules are attracted together by Vander Waals force and this prevents the molecules from collapsed. When temperature in the system increases, the vibration of molecules inside the system will be greater and molecules tend to evaporate away from the surface of the object. This happens when the energy induced by Vander Waals force along the polymer chains is greater than the enthalpy of the C–C bond in the chain, resulted in the broken of carbon chain [81]. Therefore, the operating temperature required relies strongly on the product preference.

Rofiqul et al. [71], found that the rubber tyre starts to decompose at 375°C that the solid starts to decrease and both gas and liquid start to increase until 475°C, then, above 475°C, the yields of both liquid and gas decreases and increases respectively, it is due to the decompose of some oil vapor into permanent gases. In addition, there is no decrease in the solid yield that means the pyrolysis process is completed.

Particle Size of Feed Stocks

Rofiqul et al. [71], studied the effect of changing particle size on the yield of pyrolytic oil under fixed applied others conditions, temperature at 475°C, residence time 5 second. They found that with increase the particle size from 2 cm³ to 12 cm³, the pyrolytic oil yield increases until the particle size is 4 cm³ with 51%, after that the yield decreases. They concluded that smaller particle size provides more reaction surface causes high heating rate and too quick decomposition of the rubber. On the other hand, the heating rate in large particle size 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.

As pyrolysis is limited by heat and mass transfer within the particle and consequently, as particle size is decreased, the apparent kinetic constant increases. Gartzten et al. [82], found that 1mm particle size is suitable for continuous pyrolysis, bed stability and the removal of adulterer carbon back. On another hand, smaller particle size requires more energy for grinding and the kinetic is not affected when smaller sizes are used.

Design of Reactor

The type of reactors has an important impact in the mixing of the samples and catalysts, residence time, heat transfer and efficiency of the reaction towards achieving the final desired product [52]. Most plastic pyrolysis in the lab scale was performed in batch, semi-batch or continuous-flow reactors such as fluidized bed, fixed-bed reactor and conical spouted bed reactor (CSBR). Different technologies are reported in the literature for pyrolysis. Fixed bed reactors have been commonly used, in which temperature is increased following a ramp until a final temperature is reached.

Furthermore, other authors have operated under isothermal conditions by feeding the sole when the reactor is at reaction conditions. Another successful technology applied in the sole pyrolysis process is that based on the rotary kiln. Fluid bed reactors have been used especially for their high heat transfer and bed isothermicity. The conical spouted bed reactor has been successfully used for both tyre pyrolysis and, previously, in the pyrolysis of other residues, such as biomass and plastics.

Pressure

The effect of pressure to the HDPE pyrolysis product was studied by Murata et al. [83] in a continuous stirred tank reactor in the range of 0.1-0.8 MPa. Based on the studies, they discovered that the gaseous product increased tremendously from around 6 to 13 wt% at 410°C but only a small increase from 4 to 6 wt% at 440°C as the pressure went up from 0.1 to 0.8 MPa. This shows that pressure had high influence to the gaseous product at higher temperature. Pressure also affected the carbon number distribution of the liquid product by shifting to the lower molecular weight side when it was high. Besides, pressure also had a

significant effect on the rate of double bond formation. As reported by Murata et al. [83], the rate of double bond formation decreased when pressure increased and this suggested that pressure directly affected the scission rate of C–C links in polymer.

Residence Time (Reaction time)

It is an important variable in the pyrolysis process; its optimization is a key factor in order to scale up an industrial system. Lower residence times involve lower reactor volumes to process a certain load of tyre and, therefore, lower cost of the system [84]. The variation of the solid residence time involves the variation of the gas residence time. This variation is due to the increment of the free volume inside the reactor. They also discovered that pressure had greater impact on residence time at lower temperature. However, as the temperature increased more than 430°C, the effect of pressure to the residence time became less apparent.

Catalysts

Catalyst speeds up chemical reaction but remains unchanged towards the end of the process. Catalysts are widely used in industries and researches to optimize product distribution and increase the product selectivity. Sermin et al. [85], pyrolysed individual scrap tyres (ST), oily sludge (OS), bilge water oil (BW) and a mix of (OS: BW: ST 1:1:2) in presence/absence of catalysts. The used catalyst were FCC (fluid catalytically cracking used in refinery, commercial catalyst) and RM (Red Mud, disposal catalyst) with ratio 1:5 (catalyst: feedstock) mass rate. The catalysts were laid between two layers of quartz wool in a stainless-steel net basket that was placed in the middle part of the reactor, being in contact with the gaseous products from primary degradation of materials. The result showed that the catalysts didn't have significant effects on the yields of both gas and liquid products for the pyrolysis of scrap tyres.

Type and Rate of Fluidizing Gas

Fluidizing gas is an inert gas (also known as carrier gas) which only engaged in transportation of vaporized products without taking part in the pyrolysis. There are many type of fluidizing gas that can be used for the plastic pyrolysis such as nitrogen, helium, argon, ethylene, propylene and hydrogen. Each type of fluidizing gas has different reactivity based on its molecular weight. Abbas-Abadi et al. [86] reported that the

molecular size of the carrier gas helped in determining the product composition and also dependent on the temperature.

Inert Gas Flow

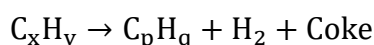
Rofiqul et al. [71], studied the effect of residence time of the vapor in the reactor on gas, char and liquid yields for optimum reactor temperature and for optimum feed size. They arrived to this conclusion: when the flow rate of N₂ is increased, consequently the vapor residence time inversely decreased, increased the rate of removal of pyrolysis vapor products from the hot zone. Then the gas and char yields decrease while the liquid yield increases slightly. But with increase of the residence time, it also help to the decomposition of some oil vapor into secondary permanent gases, which leads to less oil and more gases products. In addition, long contact time between the volatiles and the char leads to another parallel secondary pyrolysis reaction and hence reduces in volatiles yields. The increase of the gas residence time would favor the cracking of the primary pyrolysis products and would promote a change in the gas: liquid ratio.

3.3.4 Reaction Mechanisms for Pyrolysis Sole Wastes

Pyrolysis is the thermal degradation of carbon-based materials through the use of an indirect, external source of heat, typically at temperatures of 450 to 750°C, in the absence or almost complete absence of free oxygen to produce a carbonaceous char, oils and combustible gases. This drives off the volatile portions of the organic materials, resulting in a syngas composed primarily of H₂, CO, CO₂, CH₄ and complex hydrocarbons [87-88]. The reactions taking place initially are decomposition ones, where organic components of low volatility are converted into other more volatile ones [89].



Moreover, at the early stages of pyrolysis process, reactions occurring include condensation, hydrogen removal and ring formation reactions that lead to the formation of solid residue from organic substances of low volatility:



In the case of existence of oxygen, CO and CO₂ are produced or the interaction with water is possible. The produced coke can be vaporized into O₂ and CO₂. The products obtained from the pyrolysis process are solid residues and synthetic gas “syngas”. The majority of

the organic substances in waste are subjected to pyrolysis by 75–90% into volatile substances and by 10–25% to solid residue (coke). The syngas cleanup step is designed to remove carry-over particulate matter from the reactor, sulfur, chlorides/acid gases (such as hydrochloric acid), and trace metals such as mercury [90].

Syngas is used in the power generation plant to produce energy, such as steam and electricity, for use in the process and export energy. The export energy is typically converted into electricity and supplied/sold to the grid. If it is necessary, the cooling part synthetic gas can be collected as condensate to be used as a liquid fuel [91]. The carbon char and metals have use as recyclables in industry. However, the ash from the pyrolysis process is usually disposed of in a landfill [92].

In order to design tyres pyrolysis, it is helpful to know the kinetics of thermal decomposition of tyres. The decomposition of the organic part of tyres can be related to the decomposition of its separate components (extender oil, natural rubber...) [93]. That is reflected in variation in activation energy of pyrolysis process when the tyre's composition is different, in addition to the variation in the parameters (heating range, temperature...) of process itself. Sylvie et al [94], assumed that the reaction rates follow first order kinetics, which is a reasonable assumption for the polymers used in tyres. They used T_{max} method to determine the activation energy E_a and the pre-exponential factor A depending on the following equation:

$$\ln(M/T_{max}^2) = \ln(AR/E) - (E/RT_{max})$$

Where M is heating rate and T_{max} is the temperature at which the rate of volatile evolution is maximum in degrees Kelvin. By plotting the term $\ln(M/T_{max}^2)$ as a function of the inverse temperature ($1/T_{max}$).

These limitations can be resolved by:

- Large number of heating rates.
- Very low heating rates for the improved peak resolution.
- In the case of noisy data, the measurement of T_{max} was made at the mid-point of the peak width in order to minimize the effect of noise on T_{max} .

CHAPTER IV

Experimental Set-up and Methodology

4.1 Introduction

Various types of materials, chemicals and equipment's were used for the conversion of sole waste to pyrolytic oil and char and their 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 soles of shoe/sandal. The waste shoe/sandal soles were collected from the nearby local area of Jashore and Khulna city of Bangladesh.

The soles were detached from the upper part of footwear. The collected shoe/sandal soles were washed by water and detergent to remove the mud, sand, and other contaminations with the soles body. The washed soles were sun-dried and then the sun-dried soles were chopped with a knife into small pieces as desired facilitating to put into the reactor. The photographic view of chopped soles is shown in Figure 4.1.



Figure 4.1: Photographic View of Chopped Soles

In order to maintain uniformity of the components in the representative samples the shoe/sandal soles were chopped cross-section wise into three different sizes such as 1.25×1.0 cm; 1.0×0.75 cm and 0.75×0.50 cm. The chopped pieces were again sun dried to remove any moisture left.

A weighed sample is charged into the batch reactor and is heated in an oxygen free environment. To ensure complete absence of oxygen, inert gas (nitrogen) is purged through the system; even flowing of N_2 may be continued throughout the experiment. By heating, the material decomposes and broken down and converted to gases. The evolved gas is then cooled by passing through a condenser where the condensable gases are condensed and converted to liquid fuel (commonly known as pyrolytic oil or pyrolysis oil). The non-condensable gases are flared into the atmosphere. The heating is continued until all the gases come out. The remaining solid part is char mixed with ash and is collected before next charging by opening the top cover. Even after finishing the experiment, the nitrogen supply was continued for a while so as to restrict the formation of any harmful gas.

4.3 Selection of Reactor

The basic objective in designing a reactor is to produce a specified product at a given rate from known reactants. The principal features of the reactor are the following:

- i. The overall size of the reactor, its general configuration and the more important dimensions of any internal structures.
- ii. The exact composition and physical condition of the products emerging from the reactor. The composition of the products must of course lie within any limits set in the original specification of the process.
- iii. The temperatures prevailing within the reactor and any provision which must be made for heat transfer.
- iv. The operating pressure within the reactor and any pressure drop associated with the flow of the reaction mixture.

The reactor type being used for the pyrolysis of waste has to be given great importance because of the large amount of heat to be transferred across the reactor wall to ensure

material degradation. Reactors used in the pyrolysis of different wastes include fixed bed reactors, batch or semi-batch reactors, rotary kilns, fluidized bed reactors, microwave assisted reactors and some innovative solutions like plasma or solar reactors [95].

Fixed Bed Reactors and Batch Reactors

Fixed bed reactors are the simplest solution available in laboratory-scale studies, because they are easy to design. In this type of reactor, the feedstock is placed in the reactor (often stain-less steel), which is heated externally. The most popular solution is an electric furnace. Before the experiment the reactor is flushed by an inert gas (e.g. N₂, Ar) and the gas flow is maintained during the whole process in order to provide an anaerobic atmosphere. The gases and vapors obtained are discharged from the reactor during the pyrolysis, but char is usually removed after the process. The fixed bed reactor is characterized by a low heating rate. Further-more, the feedstock does not move during the process, thus it is difficult to imagine a uniform heating of a large portion of waste on an industrial scale. This type of reactor could be used on a large-scale provided that the technology used (e.g. heat pipes) enables better heat transfer. Anyway, the fixed bed reactor is a good instrument for providing experimental information on the parameters of pyrolysis and its products.

In general, batch reactors are a closed system with no input or output of reactants or products while the reaction is being carried out resulting in high conversion. On the other hand, semi-batch reactors allow the addition of reactants and the removal of products, while the process is occurring. However, products are not uniform from batch to batch and increasing the scale is problematic. The other disadvantages of this type of reactor are along solid residence time and the difficulty of removing char.

Fluidized Bed Reactors

Typically, fluidized-bed reactors are used to study the behavior of fast pyrolysis and to investigate the secondary cracking of oil at longer residence times. Fluidized-bed reactors are characterized by a high heating rate and a good blending of the feedstock. Therefore, such reactors are widely used in laboratory studies in order to describe the influence of temperature and residence time on pyrolysis behavior and products. This type of reactor seems to be a good solution for waste polymer pyrolysis. For example, polymer pyrolysis

in a fluidized-bed reactor can provide remarkable advantages over the processes in other reactors in which heat is not transferred as efficiently for the cracking of polymers because polymers have a very low thermal conductivity and high viscosity.

On the other hand, there are important difficulties in using fluidized-bed reactors to utilize waste. First, the raw material provided to the reactor must be tiny, so it could float in the fluid. Second, there is a big problem with separating the char from the bed material. Thus, this type of reactor is seldom used in large-scale projects.

Spouted Bed Reactor

This reactor is suitable for handling particles of irregular texture, fine particles, sticky solids and those with a wide size distribution. Furthermore, the system has a great versatility with regard to gas flow, allowing operation with short gas residence times. Additionally, the excellent movement of the solids in this reactor, which leads to high heat transfer rates between phases, makes this reactor suitable for flash pyrolysis. Moreover, the conical spouted bed reactor is appropriate for continuous operation, which is especially relevant for the implementation of biomass pyrolysis at larger scale. In this type of reactor waste plastics melt as they are being fed into the reactor and provide a uniform coating around the sand particles due to their cyclic movement. It also offers high heat transfer between phases and smaller de-fluidization problems with sticky solids from plastics. The solid flow pattern and the action of the spout decrease the formation of agglomerates. However, there is no information about the use of this reactor with mixed waste, because they need very small pieces of feedstock.

Rotary Kiln Reactor

Rotary kiln reactors usually carry out the process in temperatures around 500°C with a residence time of about 1 hour. This is the only type of reactor, which has been successfully implemented as a practical industrial solution at various scales so far. However, even they may need some pre-treatment of waste before pyrolysis. Waste should be sorted in order to remove unwanted materials and then shredded. On the other hand, the preparation of waste as feedstock for the pyrolysis process is quite simple. It is important that solid wastes of various shapes, sizes and heating values can be fed into a rotary kiln either in batches or continuously; this feature allows an extensive use of this type of

reactor. Rotary kilns offer better heat transfer to the feedstock than fixed beds and at the same time they are less complicated in operation than fluidized beds. Also, the flexible adjustment of residence time can make the pyrolysis reaction easy to perform at optimum conditions.

Microwave Assisted Reactors

Microwaves lie between infrared and radio frequencies in the electromagnetic spectrum. The wave lengths of microwaves are between 1 mm and 1 m with corresponding frequencies between 300 GHz and 300 MHz, respectively. The two most widely used microwave frequencies are 915 MHz and 2.45 GHz. They accurately characterized this process, but they concluded that the growth of industrial microwave heating applications is hampered by an apparent lack of the understanding of microwave systems and the technical information for designing commercial equipment for this type of pyrolysis. The combination of microwaves and pyrolysis has attracted much attention due to the nature and many advantages of micro-wave heating. The most important advantages provided by micro-waves are uniform and rapid internal heating of large biomass particles, immediate response for rapid start-up and shut down, high energy efficiency, no need for agitation and controllability.

Plasma Reactors

Plasma is an ionized gas considered by many to be the fourth state of matter, next to solid, liquid and gas. It can be considered as a gaseous mixture of negatively charged electrons and positively charged ions, which is created by heating a gas intensively or by subjecting a gas to a strong electromagnetic field. Thermal plasma generation can be achieved using a direct current or an alternating current electrical discharge or using radio frequency induction or a microwave discharge. Thermal plasma pyrolysis of organic waste produces only two streams: a combustible gas and a solid residue, both of which are useful and easy-to-handle products. Thus it can be used directly as a fuel in various energy applications such as direct firing in boilers, gas turbines or gas engines.

Solar Reactors

It is used for the pyrolysis of beech wood in a laboratory-scale solar reactor. The pyrolysis experiments were carried out in a transparent Pyrex balloon reactor under an argon flow.

The wood pellet was placed in a graphite crucible insulated with black foam and located at the focus of a 1.5 kW vertical-axis solar furnace. This construction allows the system to reach temperatures between 600°C and 2000°C without any additional heating sources. The aim of this study was to check the effect of temperature and heating rate on char composition and structure. The possibility of using renewable energy resources to provide energy to endothermic reactions makes pyrolysis more environmentally friendly. In addition, the energy efficiency increases. This should be the direction of the latest design solutions.

From the above discussions, fixed-bed and batch reactor is the best for shoe/sandal soles pyrolysis, so it is selected.

4.4 Experimental Set-up

Although, various types of reactors were used for the pyrolysis process by different researchers. The methodology is more or less very similar. In the present study shoe/sandal soles will mainly be used as raw materials to recover fuels by pyrolysis with a fixed-bed reactor. In the proposed reactor setup the major components are:

- (i) reactor chamber;
- (ii) heating elements;
- (iii) perforated grate to support the waste materials inside the reactor;
- (iv) facility for charging waste material;
- (v) condenser unit for condensing the vapors;
- (vi) liquid collecting glass bottle;
- (vii) one N₂ gas cylinder with pressure regulator, flow control valve;
- (viii) char collecting bag;
- (ix) K-type thermocouples with temperature indicator and controller.

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 4.2, shows the schematic diagram of the experimental unit.

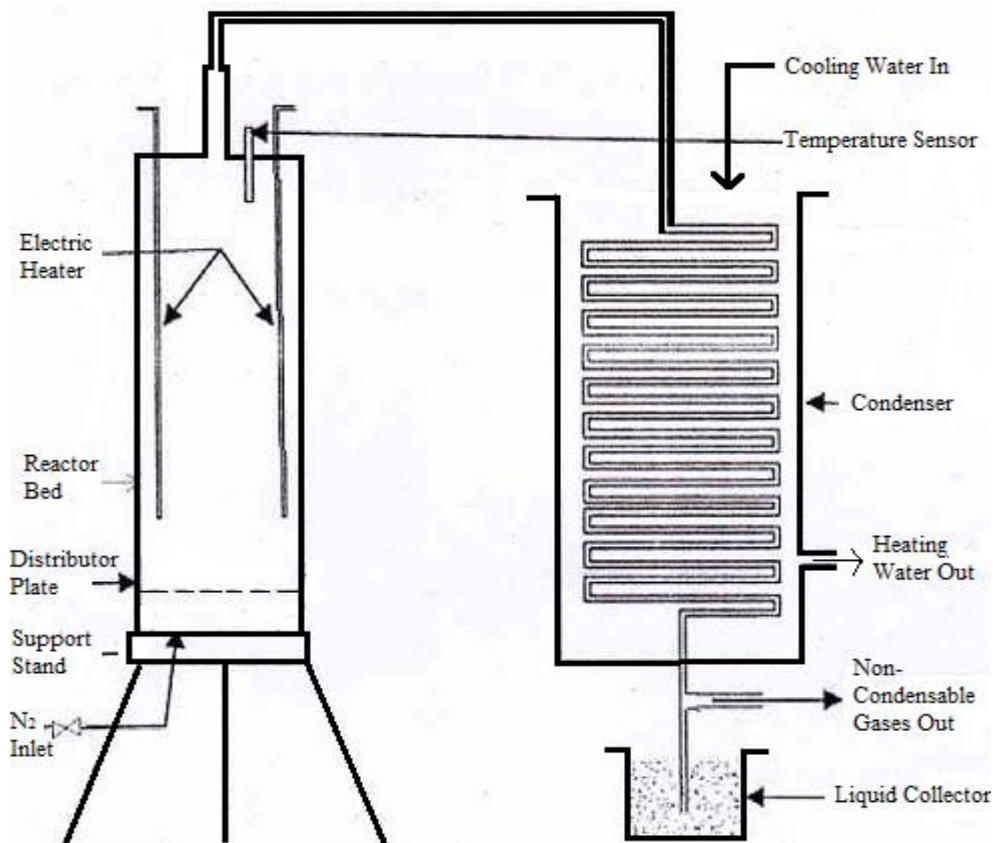


Figure 4.2: Schematic Diagram of the Experimental Set-up

A space is provided at the bottom of the cylinder with a perforated sheet (called distributor plate) to flow N₂ gas under this and also to support the sample in the cylinder. The charging of the reactor is done by opening the top cover plate which is connected to the condenser through a pipe. The condenser is made of copper tube immersed a water bath. Three evenly spaced electrical heaters, with capacity of 1000 watt each, were used for heating the reactor. Care was taken while selecting the length of the heater so that it could heat the whole length of the cylinder.

Thermocouple was used to monitor the inside temperature of the reactor. The thermocouple wire was connected to a temperature controller to maintain the desired temperature within the reactor. The reactor cylinder was insulated at outside with glass wool and asbestos rope to reduce heat loss. Before starting the heater, the whole set up was purged with N₂ gas to remove all oxygen. The photographic view of the experimental set-up is shown in Figure 4.3.



Figure 4.3: Photographic View of the Experimental Set-up

4.5 Methodology

The batch type fixed-bed pyrolysis system was constructed and installed in the Heat Engine Laboratory of the Department of Mechanical Engineering, Khulna University of Engineering & Technology. The experiments were conducted for three different temperatures and feed sizes of 1.25×1.0 cm; 1.0×0.75 cm and 0.75×0.50 cm.

The samples were weighed and 1.7 kg sample was put into the reactor chamber by opening the top cover. The top cover was then closed and the condenser was connected with it. N_2 gas was supplied for 3-5 minutes from a cylinder to maintain oxygen free environment inside the reactor. After completing the experimental set-up, the heater was switched ON and the experiment was started. At temperature about 195°C , pyrolytic products were evolved which were passed through the condenser. The temperature was measured by thermocouple and was maintained at about 200°C . The pyrolytic liquids were collected after condensing the gas in the condenser into the liquid collector (glass bottle) and the non-condensable gases were flared into the atmosphere. After completion of the experiment, the reactor was switched OFF. The solid pyrolytic product (char) was

collected by opening the top cover after the reactor was cooled. Then, the total liquid and solid products were weighed. The weight of gaseous product was determined by subtracting the liquid and char weight from the total weight of feedstock. The assembly is now ready for next experiment.

The experiment was conducted for three different temperatures of 200°C, 225°C and 250°C. Because of heterogeneity in the sample, for each temperature 2-3 samples were used to run the experiment and the average value was taken. The detailed data sheets are presented in Appendix A-1 to A-10. The various properties such as density, flash point, boiling point, pour point and GCV of the pyrolytic products were measured in the laboratory.

CHAPTER V

Results and Discussions

5.1 General

Pyrolysis is a thermo-chemical conversion process where an irreversible chemical change occurs by the action of heat in absence of oxygen, transforms organic or inorganic materials into various compounds that have fuel value [96]. Shoe/sandal soles are made from a variety of different materials, including natural rubber, leather, polyurethane and PVC compounds.

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

5.2 Production of Pyrolytic Products

Under the study of pyrolytic conversion of waste shoe/sandal sole in fixed-bed reactor, the experiments were conducted in the temperature range of 200 to 250°C. Three types of products were obtained: oil, char, and gas. At the same conditions, the weights of the pyrolytic products were varied for the waste soles. The experimental data are shown in Table 4.1 to Table 4.10. They will be discussed in details in the following sections:

Pyrolytic Oil

The liquid obtained from pyrolysis of shoe/sandal sole 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. The yield of pyrolytic oil ranges

from 20% to 36% in various experiments. After production, the pyrolytic oil was stored into the sample bottles as shown in Figure 5.1 and 5.2.



Figure 5.1: Pyrolytic Oil after Production from Shoe/sandal Sole Pyrolysis



Figure 5.2: Pyrolytic Oil Sample after Production from Shoe/sandal Sole Pyrolysis

Pyrolytic Solid/Char

The yield and application of pyrolytic solid depends upon the composition of raw materials and the conditions of pyrolysis process. It is used as a reasonable source of solid fuel or has properties which may be suitable for its use as a low grade activated carbon or carbon black. The yield of pyrolytic solid ranges from 36% to 52% in various experiments. After experiment, the pyrolytic solid was stored into the sample bags as shown in Figure 5.3 and 5.4.



Figure 5.3: Pyrolytic Solid after Production from Shoe/sandal Sole Pyrolysis



Figure 5.4: Pyrolytic Solid Sample after Production from Shoe/sandal Sole Pyrolysis

Pyrolytic Gas

Composed mainly of hydrogen, methane and other hydrocarbons C_1 - C_4 , in addition, it is possible to find some CO and CO_2 , these gases come from the oxygenated polymers of the soles and even come from inorganic matter such as carbonate fillers. Therefore, the pyrolytic gas may be successfully employed as fuel, especially for producing electricity or at least it can provide the energy requirements for the pyrolysis process [58-59, 70].

Pyrolytic gas is calculated by difference between the sample weight and the weight of both char and oil. The pyrolytic products: char, oil and gas vary drastically in composition depending on the composition of raw materials and on the pyrolysis conditions.

5.3 Analysis of Pyrolytic Products

The pyrolysis process was carried out in the temperature range of 200 to 250°C at an interval of 25°C. Products yields of the shoe/sandal sole pyrolysis are showed in Table 5.1.

Table 5.1: Percentage of Product Yield of Shoe/sandal Sole Pyrolysis for loading of 1.7 kg

| Sample No. | Temperature (°C) | Feed Size (cm × cm) | % of Product Yield (w/w) | | |
|------------|------------------|---------------------|--------------------------|-------|-------|
| | | | Oil | Char | Gas |
| 1 | 200 | 1.25 × 1.0 | 21.82 | 51.77 | 26.41 |
| 2 | 200 | | 20.12 | 54.17 | 25.71 |
| 3 | 200 | | 20.47 | 52.94 | 26.59 |
| 4 | 225 | | 27.30 | 45.88 | 26.82 |
| 5 | 225 | | 26.65 | 46.65 | 26.70 |
| 6 | 250 | | 31.41 | 41.59 | 27.00 |
| 7 | 250 | | 32.06 | 41.06 | 26.88 |
| 8 | 200 | 1.0 × 0.75 | 23.00 | 50.53 | 26.47 |
| 9 | 225 | | 29.30 | 43.94 | 26.76 |
| 10 | 250 | | 34.00 | 38.94 | 27.06 |
| 11 | 200 | 0.75 × 0.50 | 24.94 | 48.53 | 26.53 |
| 12 | 225 | | 31.41 | 41.77 | 26.82 |
| 13 | 250 | | 36.00 | 36.88 | 27.12 |

*Note: In the following presentations, the average value of sample 1-3 for 200°C, 4-5 for 225°C and 6-7 for 250°C with sample size 1.25 × 1.0 cm are presented.

5.4 Effect of Pyrolytic Conditions on Pyrolytic Product

The effects of pyrolytic conditions on pyrolytic products such as temperature, feed size and operating time obtained from waste shoe/sandal soles are described as follows:

5.4.1 Effect of Temperature on Product Yield

The effects of temperature on pyrolytic products obtained from waste shoe/sandal soles are shown in Figure 5.5 to 5.7. The tests were performed at temperatures of 200°C, 225°C and 250°C and data were collected. Three different sample sizes 1.25×1.0 cm; 1.0×0.75 cm and 0.75×0.50 cm were tested. In these cases, three types of products which are liquid oil, solid and gas were obtained. The detailed data are presented in Appendix A-11.

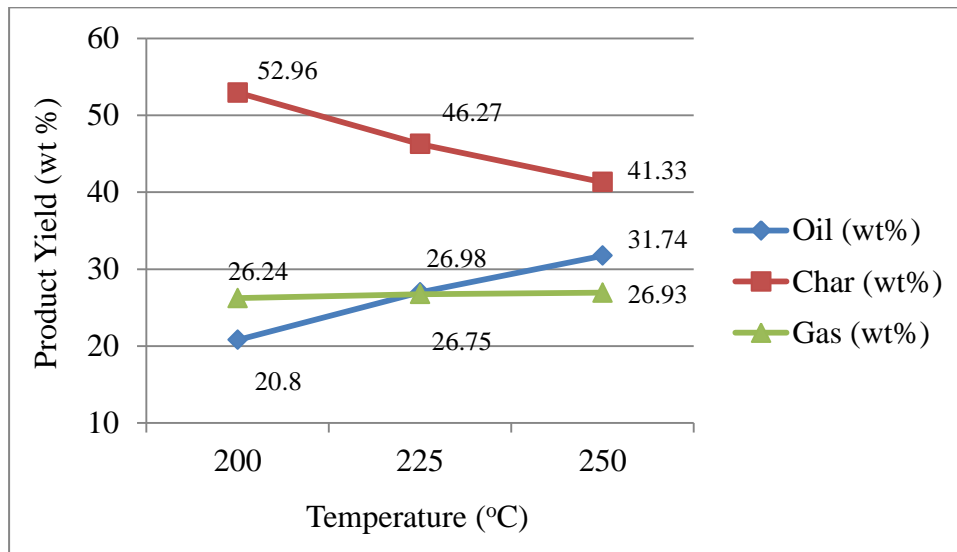


Figure 5.5: Effect of Temperature on Yield for Sole Pyrolysis with Feed Size 1.25×1.0 cm

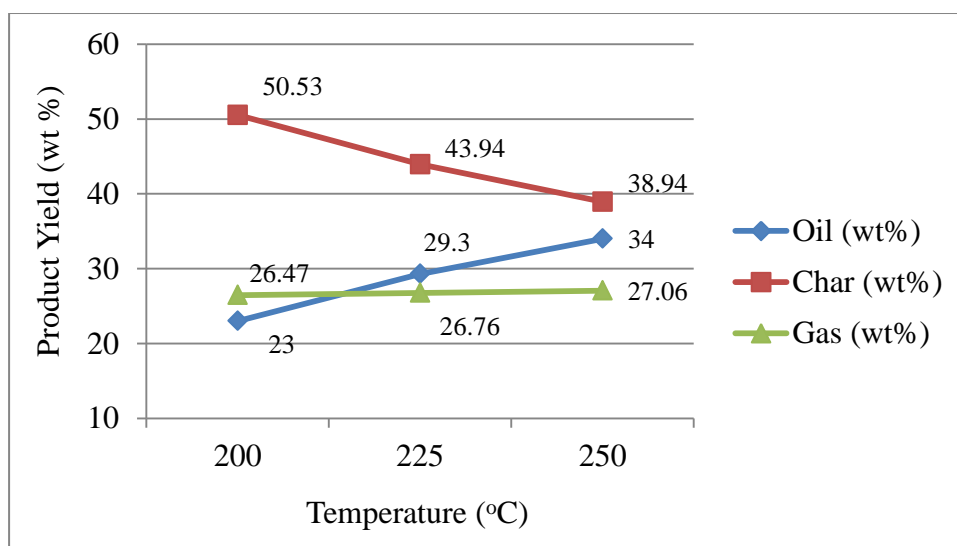


Figure 5.6: Effect of Temperature on Yield for Sole Pyrolysis with Feed Size 1.0×0.75 cm

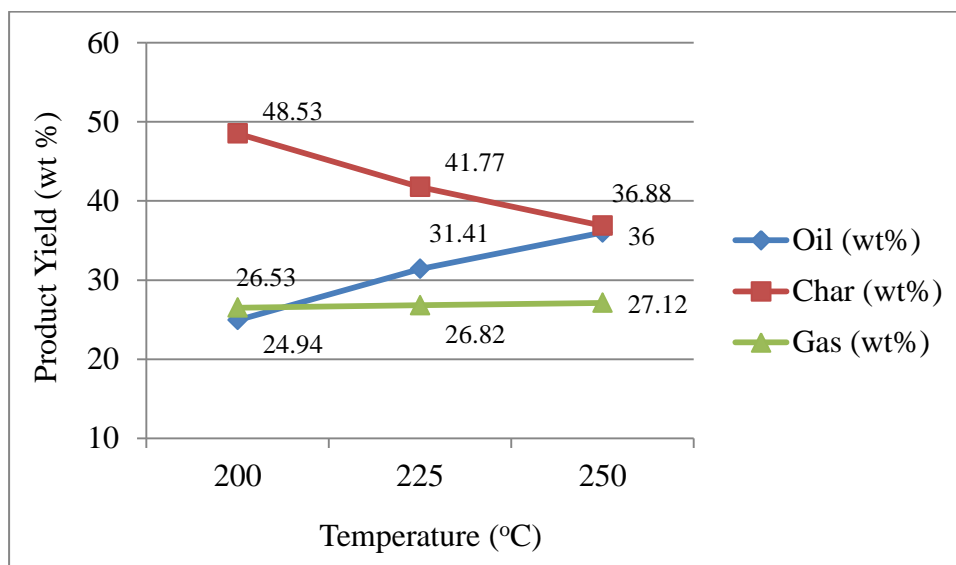


Figure 5.7: Effect of Temperature on Yield for Sole Pyrolysis with Feed Size 0.75×0.50 cm

It is observed from Figure 5.5 to 5.7 that with the increase in temperature the liquid production rate increases; but for solid trend is reverse. All the graphs from Figure 5.5 to 5.7 show the similar pattern. Among the three samples the best result was obtained with feed size 0.75×0.50 cm. The maximum oil yield of about 36.00% (by weight) at 250°C obtained from the pyrolysis of waste shoe/sandal soles. It can be postulated that the liquid yield at higher temperatures was increased whereas the char yields at these temperatures was decreased. The gas yield does not change significantly with temperature. The maximum char yield of about 52.96% (by weight) at 200°C and maximum gas yield of about 27.12% (by weight) at 250°C obtained from the pyrolysis of waste shoe/sandal soles.

So, for liquid production, the pyrolysis process should be carried out at relatively higher temperature at around $225\text{-}250^{\circ}\text{C}$. With temperature, the variation is proportional to higher temperature i.e. as temperature increases, the liquid production increases.

5.4.2 Effect of Feed Size on Product Yield

The effect of feed size on product yield of shoe/sandal soles is presented in Figure 5.8 to 5.10. The detailed data of effect of feed size on product yield are presented in Appendix A-12.

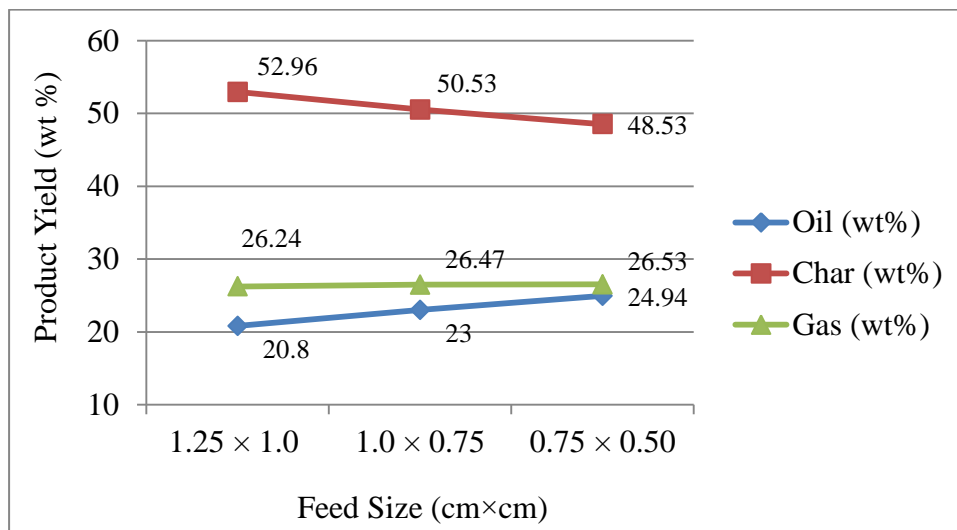


Figure 5.8: Effect of Feed Size on Product Yields for Sole Pyrolysis at 200°C

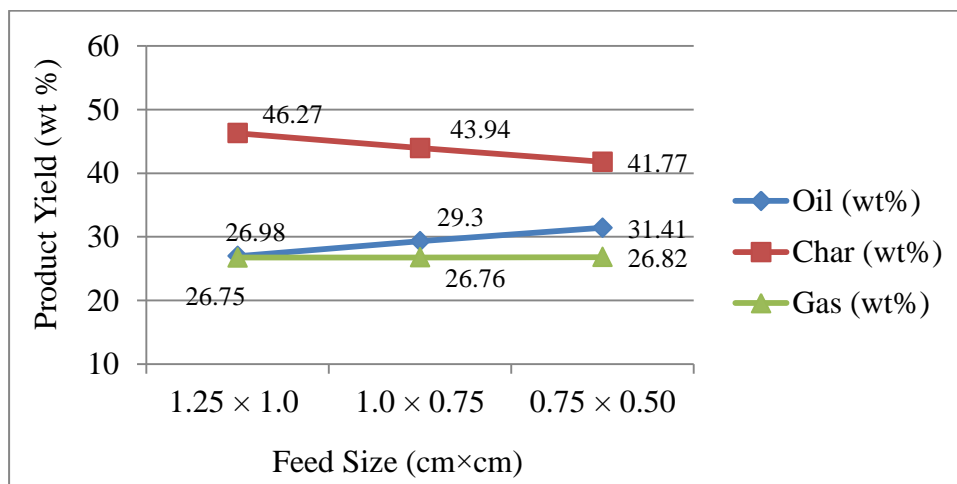


Figure 5.9: Effect of Feed Size on Product Yields for Sole Pyrolysis at 225°C

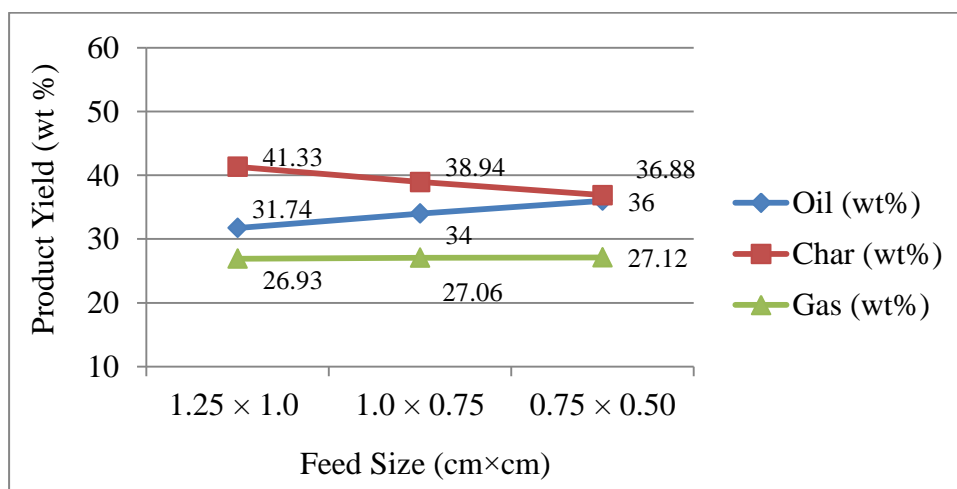


Figure 5.10: Effect of Feed Size on Product Yields for Sole Pyrolysis at 250°C

It is observed from Figures 5.8 to 5.10 that the liquid yield from shoe/sandal soles increases with decrease in sample size. The maximum yield obtained was 36.00% (by weight) with sample size of 0.75×0.50 cm and minimum is 20.80% with feed size of 1.25×1.0 cm. Smaller sample size provides more reaction surface causing high heating rate and too quick decomposition of the sole sample.

5.4.3 Effect of Operating Time on Product Yield

The effect of operating time on the product yield is shown in Figure 5.11 to 5.13 in shoe/sandal sole pyrolysis. The detailed data of effect operating time on the product yield are presented in Appendix A-13.

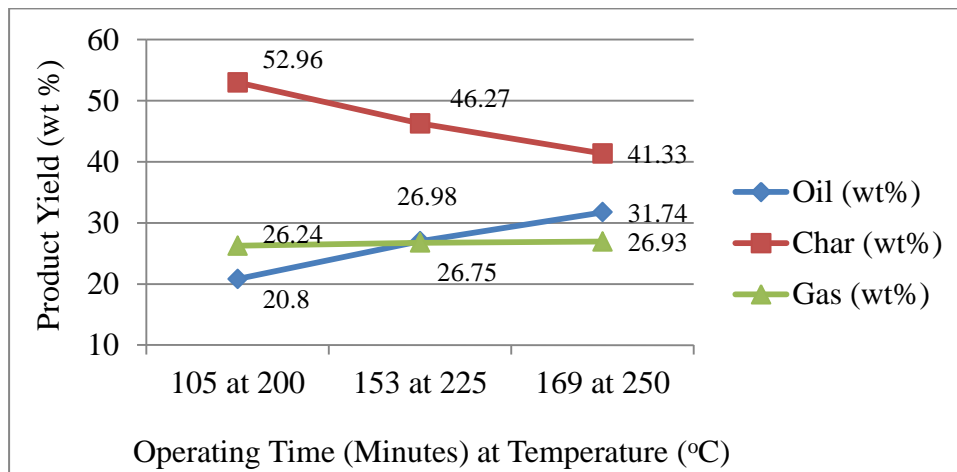


Figure 5.11: Effect of Operating Time on Product Yields for Sole Pyrolysis with Feed Size 1.25×1.0 cm

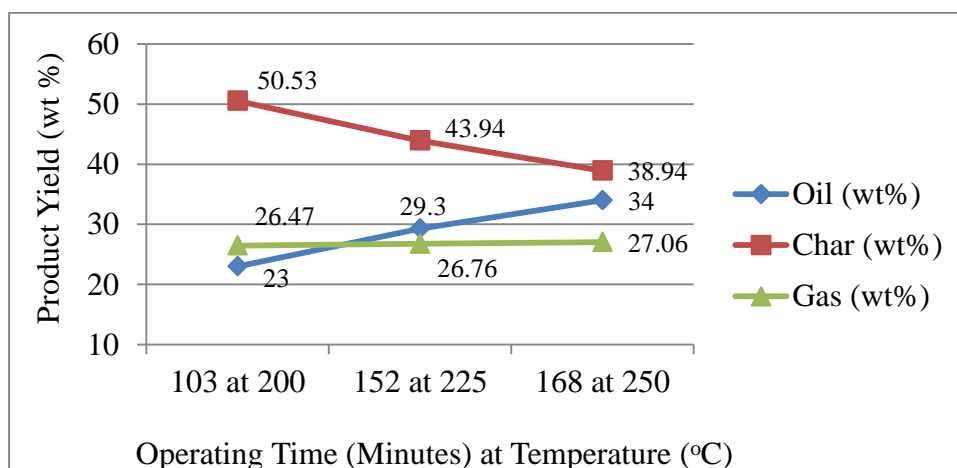


Figure 5.12: Effect of Operating Time on Product Yields for Sole Pyrolysis with Feed Size 1.0×0.75 cm

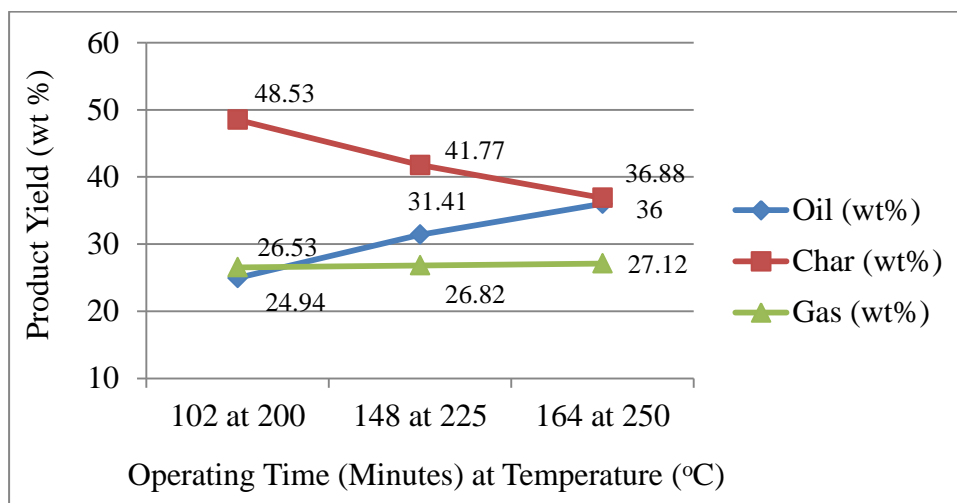


Figure 5.13: Effect of Operating Time on Product Yields for Sole Pyrolysis with Feed Size 0.75×0.50 cm

From Figure 5.11 to 5.13, it is clear that high temperature with more operating time was required to complete the conversion which leads more production of oil and less amount of char. At less operating time with low temperature the conversion of waste soles leads to more char and less oil.

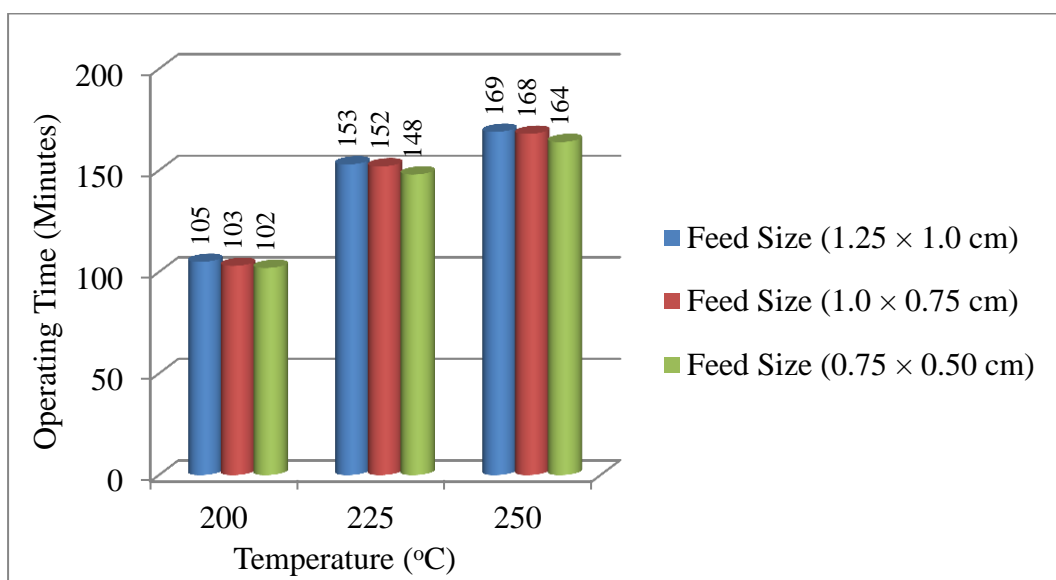


Figure 5.14: Effect of Operating Time on Feed Size and Temperature for Sole Pyrolysis

From Figure 5.14, it could be concluded that higher temperature with more operating time was suitable to convert the long polymer chain to break down into smaller organic compounds with more liquid production.

5.5 Analysis of Properties of Feed Materials and Pyrolytic Products

The analyses of the properties of feed materials (waste soles of shoe/sandal) and pyrolytic products as pyrolytic oil and char are briefly explained below:

5.5.1 Physical Properties

After production of the pyrolytic oil, char and gas, the physical properties of the pyrolytic oil were determined in the laboratory. The physical properties of the pyrolytic oil obtained from shoe/sandal sole pyrolysis are presented in Table 5.2. The tests were carried in the Heat Engine Laboratory of the Department of Mechanical Engineering, KUET, Khulna.

Table 5.2: Properties of Pyrolytic Oil from Sole Pyrolysis with Feed Size 1.25×1.0 cm at Different Temperatures

| Product at Temperature (°C) | Density (gm/cm ³) | Flash Point (°C) | Pour Point (°C) | Boiling Point (°C) |
|-----------------------------|-------------------------------|------------------|-----------------|--------------------|
| 200 | 0.877 | 96 | -11 | 155 |
| 225 | 0.934 | 103 | -11 | 158 |
| 250 | 0.877 | 108 | -12.5 | 153 |

Density

Density is an important property of a fuel oil. If density of fuel is high; fuel consumption will be less. On the other hand, the oil with low density will consume more to supply same amount of heat. Therefore, too low or too high density of fuel oil is not desirable. From the above Table, it is seen that the density of the pyrolytic oil varies with temperature and is within the range of 0.877 - 0.934 gm/cm³. The reason for equal density for 200°C and 250°C temperature of pyrolytic oil might be variations of the composition of the feed material.

Flash Point

Flash point is used to characterize the fire hazards of fuels. A low flash point indicates the presence of highly volatile materials in the fuel that is a serious safety concern in handling and transporting. The flash point of pyrolytic oil is in the range of 96 - 108°C.

Pour Point

Generally, the increase in viscosity may cause the fluid to lose its flow characteristic. Liquid fuel that has a lower pour point has lesser paraffin content but greater aromatic content. The pour point of pyrolytic oil obtained from sole pyrolysis is in the range of -11°C to -12.5°C .

Boiling Point

The boiling point of pyrolytic oil obtained from sole pyrolysis is in the range of $153 - 158^{\circ}\text{C}$.

5.5.2 Chemical Properties

The chemical properties of pyrolytic products i.e., pyrolytic oil and char are determined by the following tests such as gross calorific value (GCV), CHNS analysis, FTIR and TGA; but proximate analysis gives the same for the feed materials. These are briefly described below:

Proximate Analysis

The proximate analysis shows the compositions like moisture content, volatile matter, fixed carbon and ash present in the feed materials. In waste soles of shoe/sandal, these values are 2.25%, 67.95%, 19.42% and 10.38% respectively.

Gross Calorific Value (GCV)

The test was conducted in the Heat Engine Laboratory of the Department of Mechanical Engineering, KUET, Khulna.

The higher calorific value represents the heat of combustion relative to liquid water as the product. For waste soles of shoe/sandal, the gross heating value ranges from 24.17 to 24.38 MJ/kg, so the average calorific value of feed materials is 24.28 MJ/kg.

The average heating values of the pyrolytic oil and solid char obtained from sole pyrolysis at different temperatures and different feed sizes are presented in Table 5.3 and 5.4. The

most important property of any fuel is the calorific value and for the pyrolytic oil it is in the range of 35- 38 MJ/kg with feed size 1.25×1.0 cm at different temperatures.

Table 5.3: Calorific Value of Pyrolytic Oil from Sole Pyrolysis with Feed Size 1.25×1.0 cm at Different Temperatures

| Product at Temperature (°C) | Average Calorific Value (MJ/kg) |
|--------------------------------|------------------------------------|
| 200 | 37 |
| 225 | 35 |
| 250 | 38 |

Table 5.4: Calorific Value of Pyrolytic Solid (Char) from Sole Pyrolysis with Different Feed Size at Different Temperatures

| Temperature (°C) | Feed Size (cm \times cm) | Average Calorific Value (MJ/kg) |
|---------------------|-------------------------------|------------------------------------|
| 200 | 1.25×1.0 | 16.30 |
| 225 | | 12.80 |
| 250 | | 11.10 |
| 200 | 1.0×0.75 | 16.09 |
| 225 | | 12.85 |
| 250 | | 11.16 |
| 200 | 0.75×0.50 | 16.20 |
| 225 | | 12.66 |
| 250 | | 11.04 |

The calorific value of pyrolytic solid is in the range of 11- 16 MJ/kg with different feed size at different temperatures. It is also evident that with same size as temperature increases, the calorific value of pyrolytic solid decreases.

Although, the average calorific value of feed materials is higher than pyrolytic char, yet pyrolysis of waste shoe/sandal sole is effective due to different aspects: (i) production of char along with oil that has also a calorific value; (ii) disposal of waste shoe/sandal soles

involve money to safety discard them. If these costs are considered, then the reduction in calorific value may be waived.

Chemical Elemental Analysis

The main significance of CHNS elemental analysis is to determine the elemental composition of a solid/liquid biomass fuel. The main elements of solid/liquid biomass fuels include carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) in a wide variety of compounds. This test was carried out at the Institute of National Analytical Research & Service, BCSIR, Dhaka. The test results are shown in Table 5.5.

Table 5.5: CHNS Analysis of Pyrolytic Liquid Product from Sole Pyrolysis

| Parameters | Concentration (%) | | |
|--------------|---------------------------|---------------------------|--------------------------|
| | Pyrolytic Liquid at 200°C | Pyrolytic Liquid at 250°C | Pyrolytic Solid at 250°C |
| Carbon (C) | 71.7% | 72.5% | 25.6% |
| Hydrogen (H) | 10.9% | 10.5% | 3.51% |
| Nitrogen (N) | 1.12% | 1.15% | 0.18% |
| Sulphur (S) | 0.50% | 0.31% | 0.51% |
| Others | 15.78% | 15.54% | 70.2% |

From Tables 5.5, variation of concentration of elemental compositions of pyrolytic liquid obtained from shoe/sandal sole pyrolysis between simulation and experimental results were found to be 71.7% to 72.5% for carbon, 10.9% to 10.5% for hydrogen, 1.12% to 1.15% for nitrogen, 0.50% to 0.31% for sulphur and 15.78% to 15.54% for others respectively at 200°C and 250°C. The same for pyrolytic solid were found to be 25.6% for carbon, 3.51% for hydrogen, 0.18% for nitrogen, 0.51% for sulphur and 70.2% for others at 250°C.

Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy

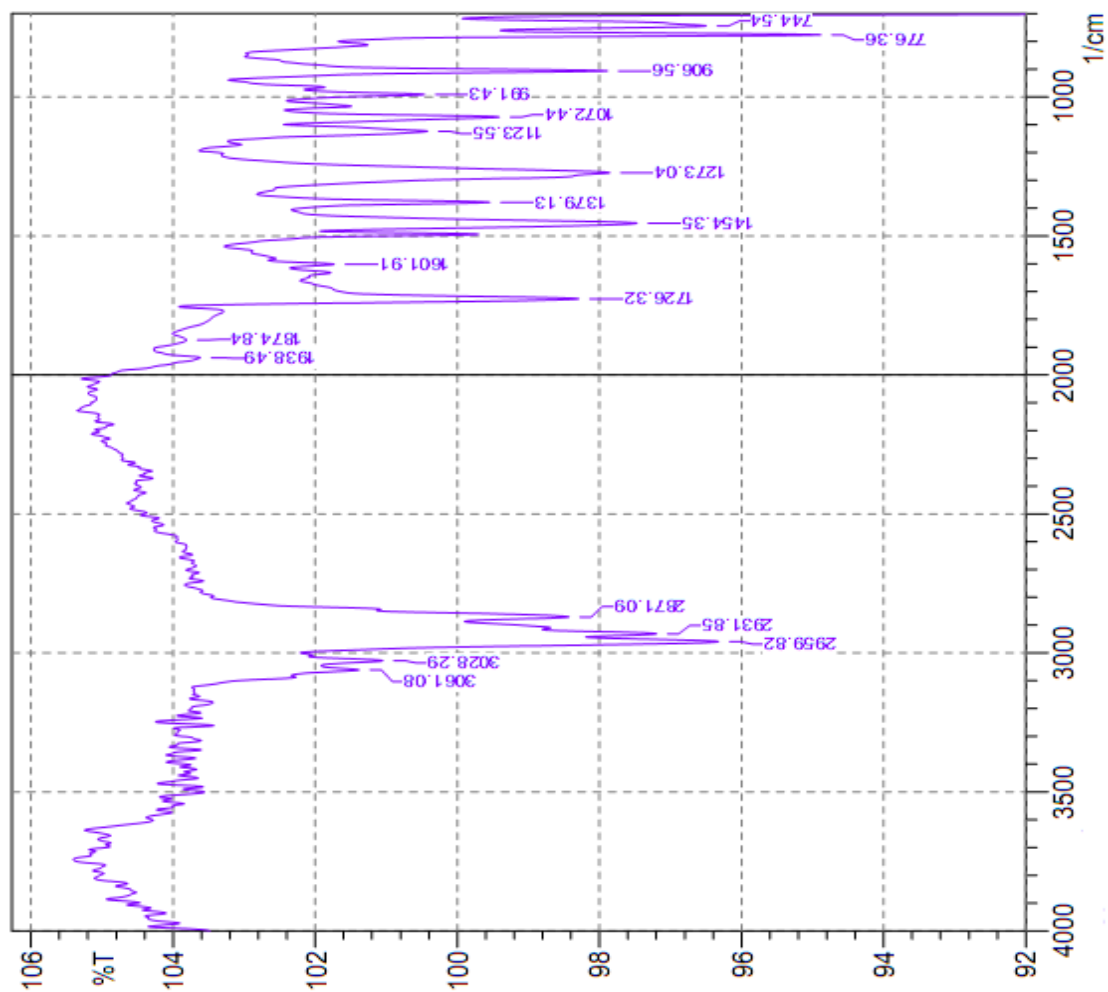
The Fourier Transform Infrared Spectroscopy (FTIR) offers a quantitative and qualitative analysis for organic and inorganic samples. It identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The FTIR is an effective analytical method for

detecting functional groups and characterizing covalent bonding formation. The test was carried out at CARS, University of Dhaka.

The absorption frequency spectra representing the functional group composition analysis of the waste shoe/sandal sole pyrolytic oil is summarized in Table 5.6 and also presented in Figure 5.15 at 200°C.

Table 5.6: FTIR Functional Groups and Indicated Compound of Pyrolytic Liquid Derived from Sole Pyrolysis at 200°C

| Absorbance Range (cm ⁻¹) | Functional Group | Class of Compounds | Pyrolysis Liquid |
|--------------------------------------|------------------|---|------------------|
| 3200-3650 | O-H | Alcohol, Phenol, Carboxylic acid | - |
| 3300-3500 | N-H | Amines | - |
| 2850-2960 | C-H | Alkanes and Alkyl Group | 2871-3061 |
| 1660-2000 | C=C | Aromatic | 1601-1938 |
| 1450-1600 | C-H | Alkanes | 1454-1601 |
| 1325-1425 | | | 1379-1454 |
| 1175-1300 | C-O | Primary, secondary and tertiary alcohols, phenol, esters and ethers | 1273-1379 |
| 1000-1150 | C-H | Alkanes | 1072-1123 |
| 875-950 | HC≡CH | Alkynes | 906-991 |
| 600-950 | | Aromatic compound | 744-776 |



| Peak | Intensit | Corr. In | Base (H | Base (L | Area | Corr. Ar | |
|------|----------|----------|---------|---------|---------|----------|-------|
| 1 | 744.54 | 96.5 | 3.09 | 759.97 | 718.5 | 0.396 | 0.336 |
| 2 | 776.36 | 94.885 | 5.424 | 799.51 | 760.93 | 0.238 | 0.323 |
| 3 | 906.56 | 97.889 | 5.246 | 938.38 | 855.44 | -0.538 | 0.565 |
| 4 | 991.43 | 100.465 | 1.801 | 1013.61 | 974.07 | -0.265 | 0.122 |
| 5 | 1072.44 | 99.41 | 3.031 | 1099.44 | 1047.36 | -0.257 | 0.288 |
| 6 | 1123.55 | 100.42 | 2.343 | 1159.24 | 1099.44 | -0.431 | 0.296 |
| 7 | 1273.04 | 97.858 | 5.068 | 1328.98 | 1212.28 | -0.397 | 1.071 |
| 8 | 1379.13 | 99.546 | 3.021 | 1406.13 | 1349.23 | -0.383 | 0.246 |
| 9 | 1454.35 | 97.472 | 4.614 | 1483.28 | 1406.13 | -0.089 | 0.619 |
| 10 | 1601.91 | 101.735 | 0.776 | 1616.38 | 1587.44 | -0.269 | 0.043 |
| 11 | 1726.32 | 98.293 | 5.098 | 1755.25 | 1661.7 | -0.509 | 0.716 |
| 12 | 1874.84 | 103.817 | 0.304 | 1905.7 | 1851.69 | -0.913 | 0.039 |
| 13 | 1938.49 | 103.618 | 0.833 | 1997.32 | 1912.45 | -1.505 | 0.142 |
| 14 | 2871.09 | 98.431 | 1.981 | 2887.49 | 2847.95 | 0.091 | 0.18 |
| 15 | 2931.85 | 97.198 | 1.24 | 2942.46 | 2916.42 | 0.245 | 0.075 |
| 16 | 2959.82 | 96.326 | 3.045 | 2999.36 | 2943.42 | 0.281 | 0.319 |
| 17 | 3028.29 | 101.051 | 0.962 | 3046.62 | 3012.86 | -0.229 | 0.062 |
| 18 | 3061.08 | 101.384 | 0.709 | 3081.34 | 3046.62 | -0.275 | 0.043 |

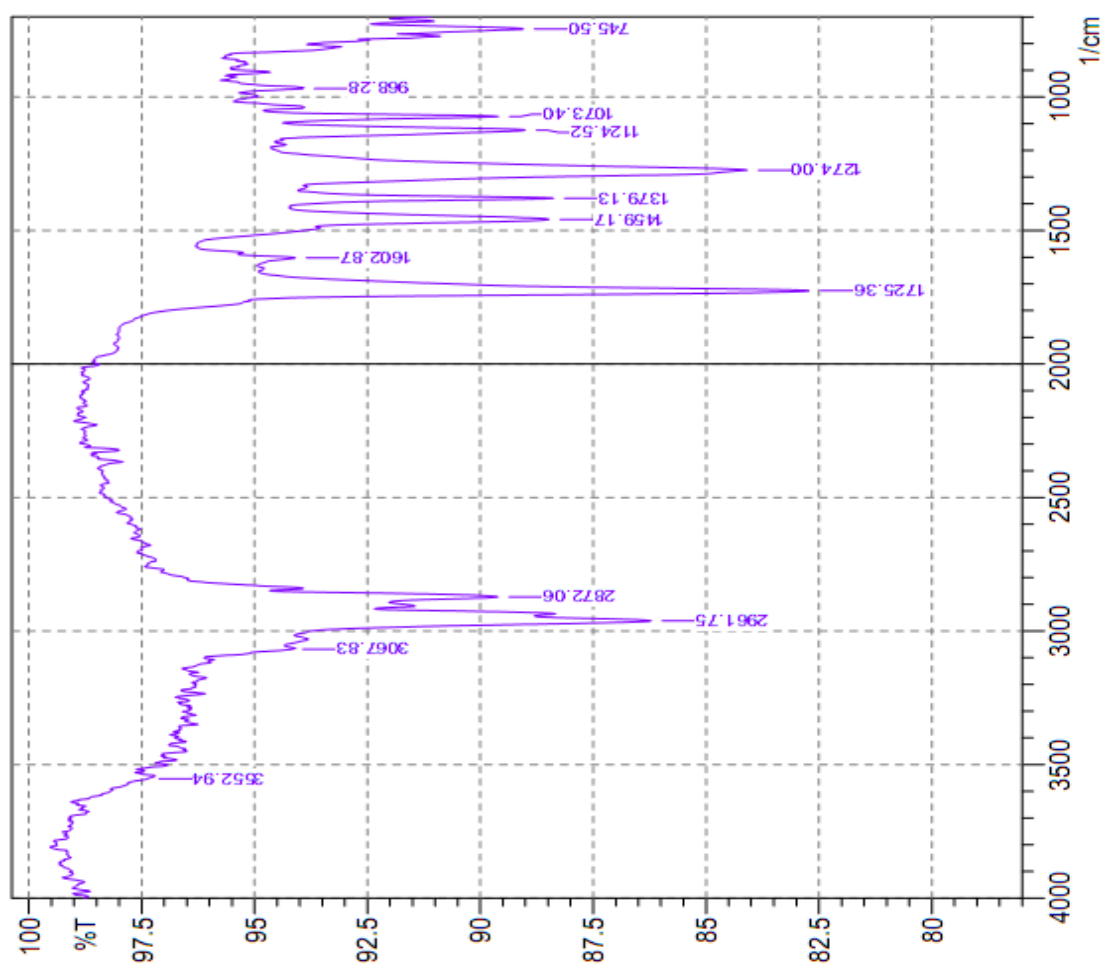
Figure 5.15: FTIR Spectra of Pyrolytic Liquid from Sole Pyrolysis at 200°C

For 200°C, the strong absorbance peak of C-H vibrations is between 2871-3061 cm⁻¹, 1379-1454 cm⁻¹ and 1072-1123 cm⁻¹ which indicate the presence of alkanes. The absorbance peaks for C-O stretching vibration is between 1273-1379 cm⁻¹, indicates the presence of primary, secondary and tertiary alcohols, phenol, esters and ethers. The possible presence of aromatics are indicated by the absorbance peaks between (1454-1601 cm⁻¹), (1601-1938 cm⁻¹) and (744-776 cm⁻¹) presenting Csp² = Csp² stretching vibration. There are no strong absorbance peaks of the O-H and N-H stretching vibration; indicate the presence of alcohol, phenol, carboxylic acid and specifies the alkynes and amines respectively. Similarly, the absorbance peak for HC≡CH is between 906-991 cm⁻¹ which designates the possible presence of alkynes group.

The absorption frequency spectra representing the functional group composition analysis of the waste shoe/sandal sole pyrolysis oil are summarized in Table 5.7 and presented in Figure 5.16 for 225°C.

Table 5.7: FTIR Functional Groups and Indicated Compound of Pyrolytic Liquid Derived from Sole Pyrolysis at 225°C

| Absorbance Range (cm ⁻¹) | Functional Group | Class of Compounds | Pyrolysis Liquid |
|--------------------------------------|------------------|---|------------------|
| 3200-3650 | O-H | Alcohol, Phenol, Carboxylic acid | 3067-3552 |
| 3300-3500 | N-H | Amines | - |
| 2850-2960 | C-H | Alkanes and Alkyl Group | 2872-2961 |
| 1660-2000 | C=C | Aromatic | 1602-1725 |
| 1450-1600 | C-H | Alkanes | 1459-1602 |
| 1325-1425 | | | 1379-1459 |
| 1175-1300 | C-O | Primary, secondary and tertiary alcohols, phenol, esters and ethers | 1274-1379 |
| 1000-1150 | C-H | Alkanes | 1073-1124 |
| 875-950 | HC≡CH | Alkynes | - |
| 600-950 | | Aromatic compound | 745-968 |



| Peak | Intensit | Corr. In | Base (H)Base | (L Area | Corr. Ar | | |
|------|----------|----------|--------------|---------|----------|-------|--------|
| 1 | 745.5 | 89.047 | 3.088 | 763.82 | 727.18 | 1.601 | 0.298 |
| 2 | 968.28 | 93.925 | 0.082 | 984.68 | 967.32 | 0.412 | -0.004 |
| 3 | 1073.4 | 89.599 | 4.997 | 1096.55 | 1051.22 | 1.528 | 0.434 |
| 4 | 1124.52 | 89.005 | 5.397 | 1157.31 | 1096.55 | 2.253 | 0.733 |
| 5 | 1274 | 84.091 | 10.072 | 1331.87 | 1203.6 | 5.956 | 2.621 |
| 6 | 1379.13 | 88.378 | 5.755 | 1409.02 | 1350.19 | 2.092 | 0.548 |
| 7 | 1459.17 | 88.48 | 5.385 | 1486.18 | 1418.67 | 2.625 | 0.786 |
| 8 | 1602.87 | 94.098 | 1.129 | 1631.81 | 1588.41 | 1.029 | 0.093 |
| 9 | 1725.36 | 82.712 | 12.346 | 1762 | 1655.92 | 4.621 | 2.268 |
| 10 | 2872.06 | 89.609 | 3.68 | 2893.27 | 2848.91 | 1.728 | 0.399 |
| 11 | 2961.75 | 86.219 | 3.943 | 3014.79 | 2943.42 | 3.159 | 0.378 |
| 12 | 3067.83 | 94.176 | 0.06 | 3082.3 | 3066.87 | 0.372 | 0.003 |
| 13 | 3552.94 | 97.36 | 0.027 | 3568.37 | 3551.98 | 0.175 | 0 |

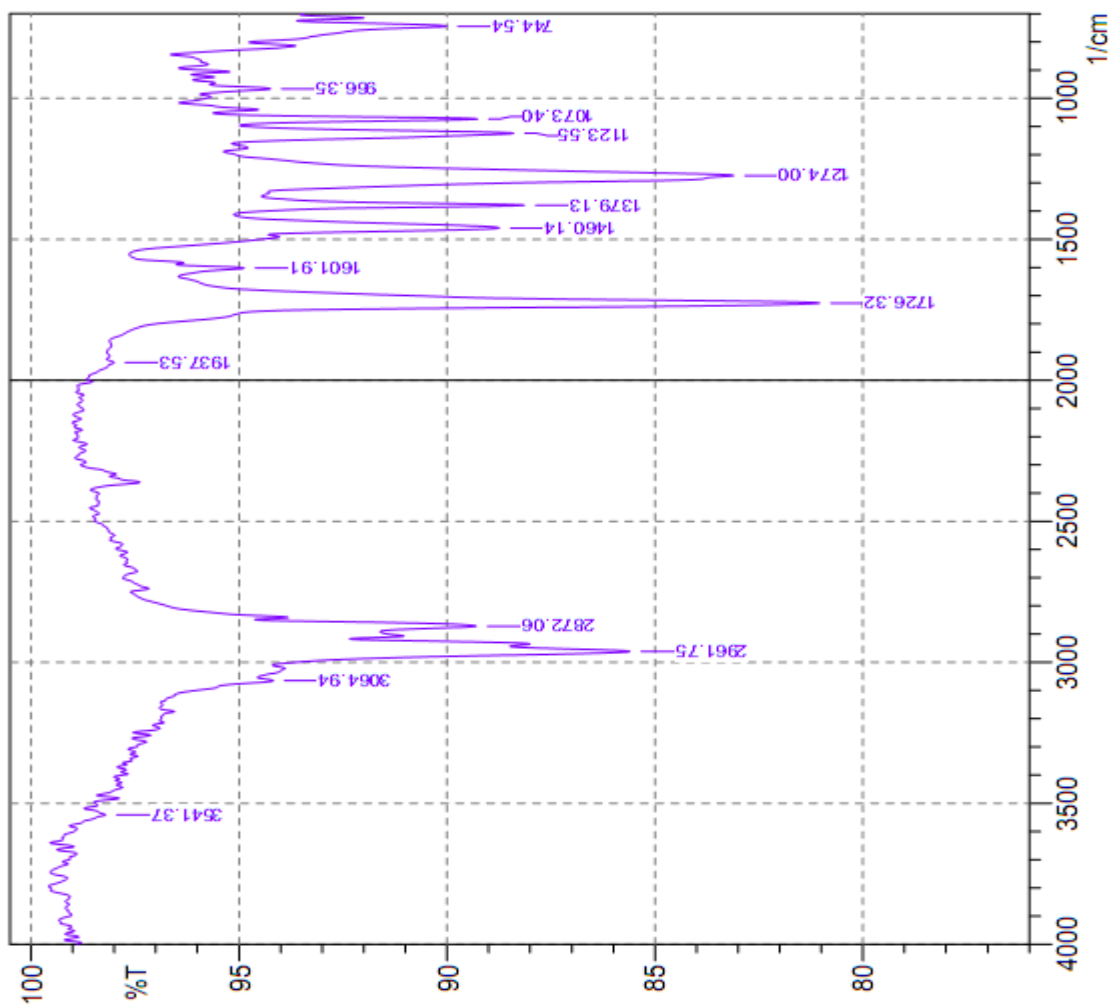
Figure 5.16: FTIR Spectra of Pyrolytic Liquid from Sole Pyrolysis at 225°C

For 225°C, the strong absorbance peak of C-H vibrations is between 2872-2961 cm⁻¹, 1379-1459 cm⁻¹ and 1073-1124 cm⁻¹ which indicate the presence of alkanes. The absorbance peaks for C-O stretching vibration is between 1274-1379 cm⁻¹, indicates the presence of primary, secondary and tertiary alcohols, phenol, esters and ethers. The possible presence of aromatics are indicated by the absorbance peaks between (1459-1602 cm⁻¹), (1602-1725 cm⁻¹) and (745-968 cm⁻¹) representing Csp² = Csp² stretching vibration. The strong absorbance peaks between 3067-3552 cm⁻¹ indicating the O-H stretching vibration; represents the presence of alcohol, phenol, carboxylic acid. There are no strong absorbance peaks of the HC≡CH and N-H stretching vibration; indicate the presence of alkynes group and specifies the amines respectively.

The absorption frequency spectra representing the functional group composition analysis of the waste shoe/sandal sole pyrolysis oil are summarized in Table 5.8 and presented in Figure 5.17 for 250°C.

Table 5.8: FTIR Functional Groups and Indicated Compound of Pyrolytic Liquid Derived from Sole Pyrolysis at 250°C

| Absorbance Range (cm ⁻¹) | Functional Group | Class of Compounds | Pyrolysis Liquid |
|--------------------------------------|------------------|---|------------------|
| 3200-3650 | O-H | Alcohol, Phenol, Carboxylic acid | 3064-3541 |
| 3300-3500 | N-H | Amines | - |
| 2850-2960 | C-H | Alkanes and Alkyl Group | 2872-2961 |
| 1660-2000 | C=C | Aromatic | 1601-1937 |
| 1450-1600 | C-H | Alkanes | 1460-1601 |
| 1325-1425 | | | 1379-1460 |
| 1175-1300 | C-O | Primary, secondary and tertiary alcohols, phenol, esters and ethers | 1274-1379 |
| 1000-1150 | C-H | Alkanes | 1073-1123 |
| 875-950 | HC≡CH | Alkynes | - |
| 600-950 | | Aromatic compound | 744-966 |



| Peak | Intensit | Corr. In | Base (H | Base (L | Area | Corr. Ar | |
|------|----------|----------|---------|---------|---------|----------|-------|
| 1 | 744.54 | 90.008 | 3.898 | 801.44 | 725.25 | 2.599 | 0.618 |
| 2 | 966.35 | 94.245 | 1.561 | 986.61 | 950.92 | 0.78 | 0.118 |
| 3 | 1073.4 | 89.265 | 6.057 | 1096.55 | 1052.19 | 1.43 | 0.504 |
| 4 | 1123.55 | 88.401 | 6.664 | 1160.2 | 1096.55 | 2.299 | 0.904 |
| 5 | 1274 | 83.108 | 11.628 | 1331.87 | 1189.14 | 6.361 | 3.074 |
| 6 | 1379.13 | 88.137 | 6.652 | 1411.92 | 1347.3 | 2.148 | 0.647 |
| 7 | 1460.14 | 88.744 | 5.832 | 1484.25 | 1411.92 | 2.558 | 0.852 |
| 8 | 1601.91 | 94.876 | 1.621 | 1631.81 | 1589.37 | 0.788 | 0.128 |
| 9 | 1726.32 | 81.043 | 16.098 | 1859.41 | 1631.81 | 6.442 | 3.714 |
| 10 | 1937.53 | 98.008 | 0.262 | 1984.79 | 1924.99 | 0.457 | 0.036 |
| 11 | 2872.06 | 89.295 | 3.683 | 2891.34 | 2848.91 | 1.722 | 0.405 |
| 12 | 2961.75 | 85.602 | 4.438 | 3010.93 | 2943.42 | 3.158 | 0.489 |
| 13 | 3064.94 | 94.182 | 0.725 | 3115.09 | 3054.33 | 1.261 | 0.06 |
| 14 | 3541.37 | 98.21 | 0.648 | 3579.94 | 3518.22 | 0.389 | 0.093 |

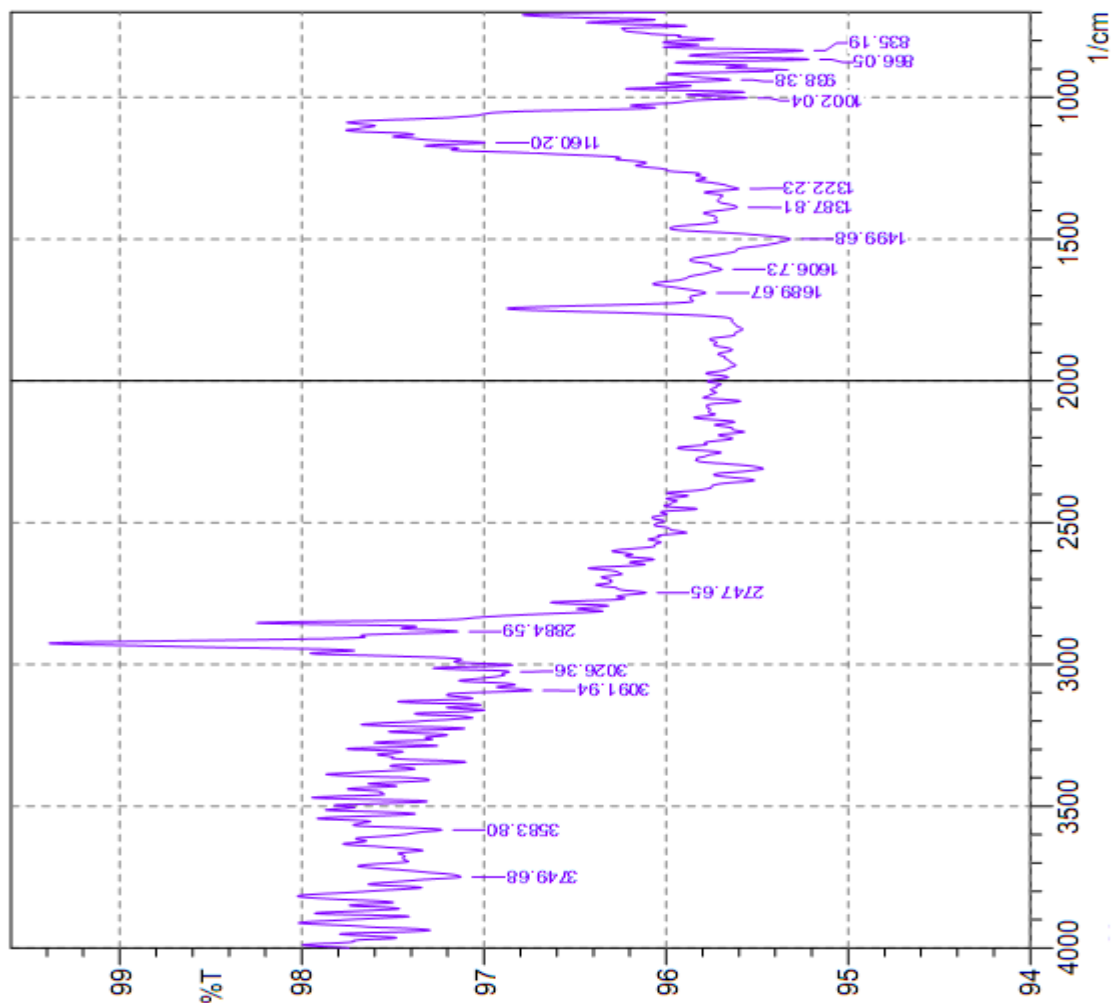
Figure 5.17: FTIR Spectra of Pyrolytic Liquid from Sole Pyrolysis at 250°C

For 250°C, the strong absorbance peak of C-H vibrations is between 2872-2961 cm⁻¹, 1379-1460 cm⁻¹ and 1073-1123 cm⁻¹ which indicate the presence of alkanes. The absorbance peaks for C-O stretching vibration is between 1274-1379 cm⁻¹, indicates the presence of primary, secondary and tertiary alcohols, phenol, esters and ethers. The possible presence of aromatics are indicated by the absorbance peaks between (1460-1601 cm⁻¹), (1601-1937 cm⁻¹) and (744-966 cm⁻¹) presenting Csp² = Csp² stretching vibration. The strong absorbance peaks between 3064-3541 cm⁻¹ represent the O-H stretching vibration; indicate the presence of alcohol, phenol, carboxylic acid. There are no strong absorbance peaks of the HC≡CH and N-H stretching vibration; indicate the presence of alkynes group and specifies the amines respectively.

The absorption frequency spectra representing the functional group composition analysis of the waste shoe/sandal sole pyrolytic solid are summarized in Table 5.9 and presented in Figure 5.18 for 250°C.

Table 5.9: FTIR Functional Groups and Indicated Compound of Pyrolytic Solid Derived from Sole Pyrolysis at 250°C

| Absorbance Range (cm ⁻¹) | Functional Group | Class of Compounds | Pyrolysis Solid |
|--------------------------------------|------------------|---|-----------------|
| 3200-3650 | O-H | Alcohol, Phenol, Carboxylic acid | 3583-3749 |
| 3300-3500 | N-H | Amines | - |
| 2850-2960 | C-H | Alkanes and Alkyl Group | 2747-3091 |
| 1660-2000 | C=C | Aromatic | 1606-1689 |
| 1450-1600 | C-H | Alkanes | 1499-1606 |
| 1325-1425 | | | 1387-1499 |
| 1175-1300 | C-O | Primary, secondary and tertiary alcohols, phenol, esters and ethers | 1160-1322 |
| 1000-1150 | C-H | Alkanes | 1002-1160 |
| 875-950 | HC≡CH | Alkynes | 866-938 |
| 600-950 | | Aromatic compound | 835-866 |



| Peak | Intensit | Corr. | In Base | H Base | (L Area | Corr. Ar |
|------|----------|---------|---------|---------|---------|----------|
| 1 | 835.19 | 95.2485 | 0.7079 | 852.55 | 822.65 | 0.5838 |
| 2 | 866.05 | 95.217 | 0.6977 | 877.63 | 852.55 | 0.4919 |
| 3 | 938.38 | 95.6484 | 0.3812 | 951.89 | 919.1 | 0.6063 |
| 4 | 1002.04 | 95.5579 | 0.4234 | 1029.04 | 990.46 | 0.7108 |
| 5 | 1160.2 | 96.9951 | 0.3887 | 1170.81 | 1138.99 | 0.3871 |
| 6 | 1322.23 | 95.6011 | 0.2038 | 1335.73 | 1293.29 | 0.8097 |
| 7 | 1387.81 | 95.6105 | 0.1471 | 1409.02 | 1364.66 | 0.8504 |
| 8 | 1499.68 | 95.3188 | 0.623 | 1573.94 | 1462.07 | 2.1855 |
| 9 | 1606.73 | 95.6941 | 0.1188 | 1658.81 | 1595.16 | 1.1738 |
| 10 | 1689.67 | 95.7826 | 0.1516 | 1704.14 | 1658.81 | 0.8264 |
| 11 | 2747.65 | 96.1101 | 0.1612 | 2761.15 | 2732.21 | 0.487 |
| 12 | 2884.59 | 97.143 | 0.4145 | 2898.1 | 2873.02 | 0.2916 |
| 13 | 3026.36 | 96.8606 | 0.1731 | 3033.11 | 3013.83 | 0.2562 |
| 14 | 3091.94 | 96.7374 | 0.318 | 3105.45 | 3080.37 | 0.3408 |
| 15 | 3583.8 | 97.2317 | 0.4825 | 3615.63 | 3566.44 | 0.5482 |
| 16 | 3749.68 | 97.127 | 0.5317 | 3775.72 | 3712.07 | 0.734 |

Figure 5.18: FTIR Spectra of Pyrolytic Solid from Sole Pyrolysis at 250°C

For 250°C, the strong absorbance peak of C-H vibrations is between 2747-3091 cm⁻¹, 1387-1499 cm⁻¹ and 1002-1160 cm⁻¹ which indicate the presence of alkanes. The absorbance peaks for C-O stretching vibration is between 1160-1322 cm⁻¹, indicates the presence of primary, secondary and tertiary alcohols, phenol, esters and ethers. The possible presence of aromatics are indicated by the absorbance peaks between (1499-1606 cm⁻¹), (1606-1689 cm⁻¹) and (835-866 cm⁻¹) presenting Csp² = Csp² stretching vibration. The strong absorbance peaks between 3583-3749 cm⁻¹ represent the O-H stretching vibration; indicate the presence of alcohol, phenol, carboxylic acid. The strong absorbance peaks of HC≡CH vibrations are between 866-938 cm⁻¹ which indicates the presence of alkynes group. There are no strong absorbance peaks of the N-H stretching vibration; indicate the presence of the amines.

Thermo Gravimetric Analysis

The TG Analysis of the waste sole pyrolysis liquid are summarized in Table 5.10 and presented in Figure 5.19 for 250°C.

Table 5.10: TGA of Pyrolytic Liquid Derived from Waste Soles at 250°C

| Observation No. | Heating Rate (°C/min) | Flow Rate (mL/min) | Sample Weight (mg) | Time (min) | Yield of Volatile (%) | Range of Degradation (°C) | Temperature (T _{max}) (°C) |
|-----------------|-----------------------|--------------------|--------------------|------------|-----------------------|---------------------------|--------------------------------------|
| 1 | 10 | 10 | 3.332 | 0.00 | 100 | 26.55 | 600 |
| 2 | | | | 4.25 | 83.64 | 83.40 | 600 |
| 3 | | | | 13.03 | 55.44 | 168.01 | 600 |
| 4 | | | | 22.96 | 24.16 | 268.90 | 600 |
| 5 | | | | 46.69 | 7.32 | 507.28 | 600 |
| 6 | | | | 55.94 | 3.96 | 599.60 | 600 |

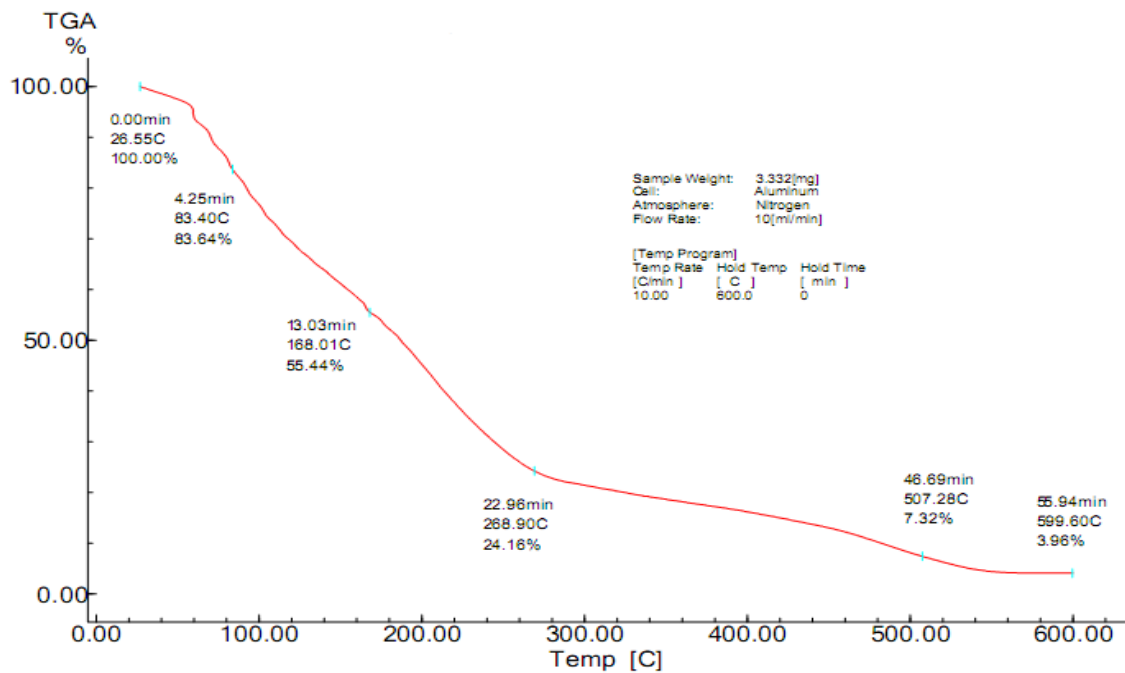


Figure 5.19: TGA of Pyrolytic Liquid Derived from Waste Sole at 250°C

The experiment with nitrogen flow rate of 10 mL/min has been conducted within the heating range (26°C-600°C) at heating rate of 10°C/min. Sample weight was 3.332 mg. The pyrolysis was taken place in the thermal range from $\approx 25^\circ\text{C}$ to $\approx 550^\circ\text{C}$. This method was used to determine the loss of mass and kinetic parameters. Thermo gravimetric analysis of shoe/sandal sole pyrolysis involves the thermal degradation of the pyrolytic oil in an inert atmosphere obtaining simultaneously the weight loss values of the pyrolytic oils with increasing temperature at a constant heating rate. The aim of the thermo gravimetric analysis is to assess the thermal behavior under pyrolysis conditions of each feedstock and the waste shoe/sandal sole blend. The temperature ranges for pyrolysis of shoe/sandal sole overlap at temperatures from 200 to 250°C. From this temperature the experimental curve of weight loss lays over the theoretical one, decreasing abruptly the difference up to 300°C and slightly decreasing at higher temperatures. The facts described above are more accurately observed in the rate of weight loss. The experimental curve is higher from 200 to 300°C, when the rate of weight loss of shoe/sandal sole is higher.

The boiling point distribution of pyrolytic liquids from pyrolysis of shoe/sandal sole waste at the temperature of 250°C is presented in Figure 5.20 and comparison with commercial furnace oil [97] and diesel fuel [98] are also presented in the same.

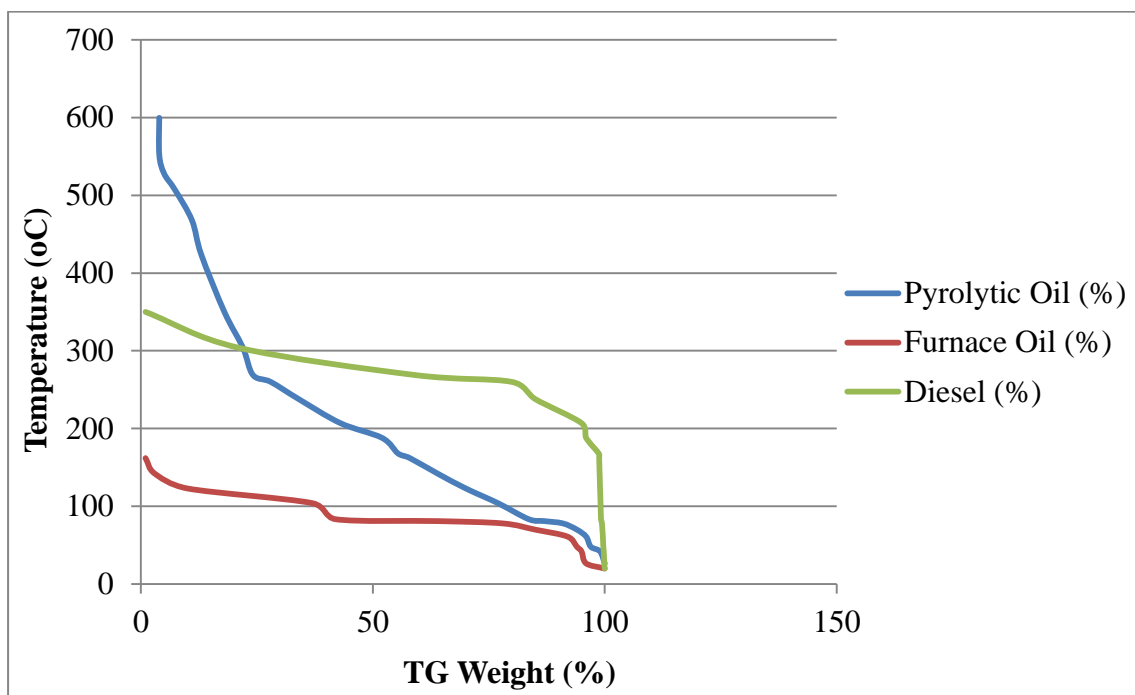


Figure 5.20: Boiling Point Distribution of Pyrolytic Liquids Compared to Petroleum Products

It is to be noted from Figure 5.20 that the boiling point of pyrolytic liquids is higher than that of diesel fuel up to 26% by weight. For the rest 74%, it has lower boiling point than that of diesel. But it has higher boiling point than that of furnace oil for the whole range.

The TG analysis of the waste shoe/sandal sole pyrolytic solid are summarized in Table 5.11 and presented in Figure 5.21 for 250°C.

Table 5.11: TGA of Pyrolytic Solid Derived from Waste Soles at 250°C

| Observation No. | Heating Rate (°C/min) | Flow Rate (mL/min) | Sample Weight (mg) | Time (min) | Yield of Volatile (%) | Range of Degradation (°C) | Temperature (T_{max}) (°C) |
|-----------------|-----------------------|--------------------|--------------------|------------|-----------------------|---------------------------|--------------------------------|
| 1 | 10 | 10 | 4.538 | 0.02 | 100 | 23.95 | 600 |
| 2 | | | | 12.84 | 90.09 | 160.02 | 600 |
| 3 | | | | 32.06 | 84.49 | 350.96 | 600 |
| 4 | | | | 47.12 | 56.82 | 502.26 | 600 |
| 5 | | | | 56.93 | 46.09 | 599.60 | 600 |

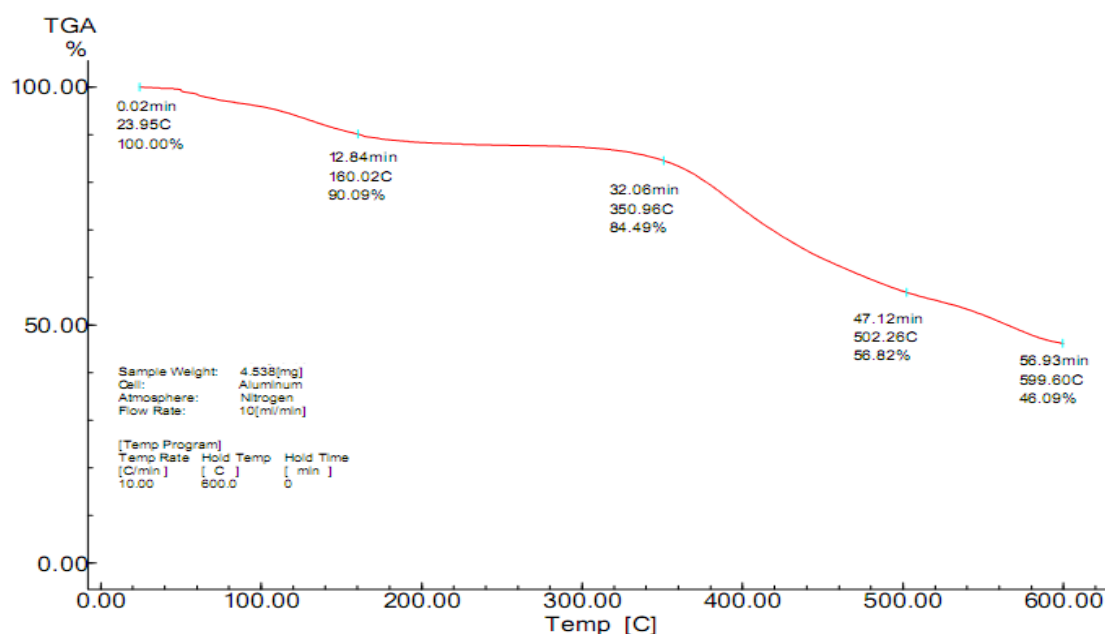


Figure 5.21: TGA of Pyrolytic Solid Derived from Waste Sole at 250°C

In pyrolytic solid, the experiment with nitrogen flow rate of 10 mL/min has been conducted in the heating range (23°C-600°C) at heating rate of 10°C/min. Sample weight was 4.538 mg. The pyrolysis was taken place in the thermal range from $\approx 20^\circ\text{C}$ to $\approx 550^\circ\text{C}$. This method was used to determine the loss of mass and kinetic parameters. Thermo gravimetric analysis of shoe/sandal sole pyrolysis involves the thermal degradation of the pyrolytic solid (char) in an inert atmosphere obtaining simultaneously the weight loss values of the pyrolytic chars with increasing temperature at a constant heating rate. The aim of the thermo gravimetric analysis was to assess the thermal behavior under pyrolysis conditions of the feedstock. The temperature ranges for pyrolysis of shoe/sandal sole overlap at temperatures from 200 to 250°C. From this temperature the experimental curve of weight loss lays over the theoretical one, decreasing slowly the difference up to 300°C and also slightly decreasing at higher temperatures. The facts described above are more accurately observed in the rate of weight loss. The experimental curve is higher from 200 to 400°C, when the rate of weight loss of shoe/sandal sole is higher.

5.6 Comparison of Sole Waste Pyrolysis Products with Petroleum Products

Pyrolytic oil obtained under the different operating conditions was well mixed and homogenized prior to analysis being made. Properties such as, density, flash point, pour

point, boiling point, gross calorific values (GCV) were determined. The oil obtained after thermal pyrolysis of waste shoe/sandal sole 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 shoe/sandal sole were analyzed and compared with that of pyrolytic tyre oil [5], pyrolytic tube oil [4], diesel and furnace oil [99] which is summarized in Table 5.12 and Figure 5.22.

Table 5.12: Comparison of Pyrolytic Sole Oil with Pyrolytic Tyre & Tube Oil, Diesel and Furnace Oil

| Properties | Pyrolytic Oil from Sole | Pyrolytic Oil from Tyre | Pyrolytic Oil from Tube | Diesel | Furnace Oil |
|-------------------------------|-------------------------|-------------------------|-------------------------|----------------|----------------|
| Density (gm/cm ³) | 0.877 to 0.934 | 0.935 | 0.919 | 0.820 to 0.860 | 0.890 to 0.960 |
| Flash Point (°C) | 96 to 108 | 37 | 42 | 55 | 70 |
| Pour Point (°C) | -11 to -12.5 | -7 | -6 | -40 to -1 | 10 to 27 |
| Boiling Point (°C) | 153 to 158 | 362 | 360 | 180 to 360 | 150 to 371 |
| Calorific Value (MJ/kg) | 35 to 38 | 37.98 | 34.51 | 42 to 44 | 42 to 43 |

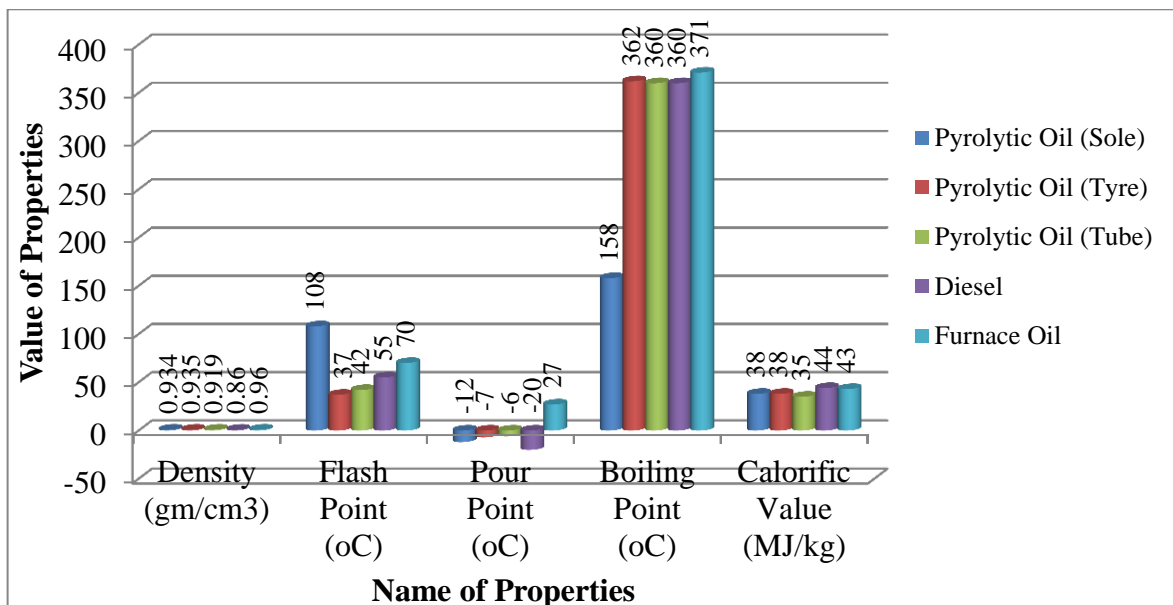


Figure 5.22: Properties of Pyrolytic Oil with Pyrolytic Tyre & Tube Oil, Diesel and Furnace Oil

From Table 5.12, it is seen that the density of pyrolytic oil obtained from shoe/sandal sole waste is between 0.877 to 0.934 gm/cm³ which are comparable to pyrolytic tyre oil (0.935 gm/cm³), pyrolytic tube oil (0.919 gm/cm³), commercial furnace oil (0.890 to 0.960 gm/cm³) and diesel (0.820-0.860 gm/cm³). This is attributed to the presence of heavier compounds in the pyrolysis oil. The flash point obtained from the pyrolytic oils derived from shoe/sandal sole waste was higher than that of pyrolytic tyre and tube oil, diesel and furnace oil. The flash point of the pyrolytic oil was between 96 to 108°C. The pour point of the pyrolytic oil is comparatively high compared to the automotive diesel fuel but low to pyrolytic tyre & tube oil and furnace oil. The boiling point of pyrolytic oil is in the range of 153 - 158°C, but the boiling point of pyrolytic tyre oil is 362°C, pyrolytic tube oil is 360°C, diesel is 180 - 360°C and for furnace oil 150 - 371°C. Gross calorific value (GCV) of the pyrolytic oil is 35- 38MJ/kg which is less than that of diesel and furnace oil, but also same that of pyrolytic tyre and tube oil.

From Figure 5.22, it is envisioned that the calorific value of the pyrolytic oil is comparable with pyrolytic tyre & tube oil, diesel or furnace oil. So, it can be used in similar purposes where heating is needed. The boiling point of pyrolytic oil is less than that of pyrolytic tyre & tube oil, diesel and furnace oil. As the flash point of pyrolytic oil is higher than pyrolytic tyre & tube oil, furnace oil and diesel which indicates that these are easy to handle and store. The pour point of pyrolytic oil is higher than that of diesel but lower than pyrolytic tyre & tube oil and furnace oil, so pyrolytic oil is better than pyrolytic tyre & tube oil and furnace oil. The density of pyrolytic oil does not follow a regular manner regarding density variation, boiling point and even GCV with temperature.

The solid char fractions obtained at optimum reactor conditions were of equal sizes which were easily disintegrable into black powder. Properties such as gross calorific values (GCV) of pyrolytic solid were determined. The char obtained after pyrolysis of waste shoe/sandal sole is dark brown in color.

The fuel properties of solid derived from waste shoe/sandal sole were analyzed and compared with that of peat and coal [100] which is summarized in Table 5.13.

Table 5.13: Comparison of Pyrolytic Solid with Peat and Other Coals

| Properties | Pyrolytic Solid | Peat | Lignite Coal | Sub-bituminous Coal | Bituminous Coal | Anthracite Coal |
|-------------------------|-----------------|----------|--------------|---------------------|-----------------|-----------------|
| Calorific Value (MJ/kg) | 11 to 16 | 12 to 16 | 13 to 16 | 19 to 24 | 27 to 34 | 32 to 34 |

From Table 5.13, the gross calorific value (GCV) of the pyrolytic solid ranges between 11 to 16 MJ/kg which is comparable with peat (12 to 16 MJ/kg) and lignite coal (13 to 16 MJ/kg). So, it can be used in similar purposes where heating is needed.

Refer from Table 5.13; the possible reason may be the heterogeneity of the input material. The shoe/sandal soles are highly heterogeneous material when they are collected from different places and different types. So, the composition may vary widely.

5.7 Management of Shoe/sandal Sole Waste

At present, the energy demands are becoming more acute day by day. Rubber containing wastes such as soles of shoes/sandals are organic solid waste which is non-biodegradable. The disposal of such wastes causes some typical problems to the environment as well as to our surroundings. From this point, it comes out that the general criteria normally applied to the waste management problem which encourage recycling of the waste (soles of shoes/sandals) material and/or energy recovery. So, extraction of liquid fuel from such materials by pyrolysis had been developed. Pyrolysis of such materials will indirectly help to manage such non-biodegradable wastes, also low grade liquid fuels may be obtained. Waste sole of shoe/sandal is converted to pyrolysis oil and char as shown in Figure 5.23.

When waste materials were pyrolyzed, they generate oil, char and gas, which are valuable. The maximum yield of pyrolytic oil (about 36% w/w) and solid (about 53% w/w) is produced at around 250°C and 200°C respectively. So, this cause less pollution to environment and manage such wastes by producing oil and char as by product.



Figure 5.23: Waste Sole of Shoe/sandal is converted to Pyrolysis Oil and Char

5.8 Cost Analysis for Present Project

The total cost such as capital cost, operating cost and payback period for present project as pyrolysis of shoe/sandal sole wastes are given below:

5.8.1 Capital Costs

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

2 runs per day and 280 working days per year.

The details of capital costs are shown in Table 5.14:

Table 5.14: Components of Capital Costs

| Name of Material | Amount Taken | Unit Price Tk. | Total Cost (Tk.) |
|--------------------|--------------|----------------|------------------|
| Reactor | 1 pc | 10000 | 10000 |
| N ₂ Gas | Lump Sum | ---- | 2000 |

| | | | |
|---|----------|------|-------|
| Thermocouple Wire with Temperature Recorder | 3 pcs | 1200 | 3600 |
| Asbestos Ropes and Blanket | 1.5 kg | 200 | 300 |
| MS Angle | Lump Sum | ---- | 1000 |
| Condenser Coil | 1 Coil | 2700 | 2700 |
| Condenser Arrangement | 1 pc | 1500 | 1500 |
| Fabrication | Lump Sum | ---- | 400 |
| Wire Mesh for Reactor Bed | Lump Sum | ---- | 100 |
| Glass Beaker (500 ml) | 4 pc | 120 | 480 |
| Total Capital Cost for 5 Year = | | | 22080 |
| Total Capital Cost Per Year = | | | 4416 |

5.8.2 Operating Costs

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 shoe/sandal sole: 1.7 kg @ Tk.10: Tk. 17

Total Electricity required for pyrolysis of 1.7 kg shoe/sandal sole: 2.25 kWh

Charge for electricity @ Tk.6 per kWh: $6 \times 2.25 = \text{Tk.}13.5$

Labor: 2 hr. @ Tk. 75 = Tk.150

Miscellaneous: Tk. 20

Assuming 4 heaters required per year (280 days)

Heater for Reactor (per batch): $(4 \times 1500) / (280 \times 2) = \text{Tk.}10.714$

Total operating cost per batch: Tk.211.214

Total annual operating cost: $280 \times 2 \times 211.214 = \text{Tk.}118279.84$

Total Cost (per year): Total Annual capital cost + Total Annual operation cost = Tk. (4416 + 118279.84) = Tk. 122695.84

Total Cost for 5 Year = Tk. (122695.84 x 5) = Tk.613479.2

5.8.3 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 2 batches per day

Yield of oil per batches: 0.612 kg (for sample size 0.75 x 0.50 cm at 250°C)

Yield of char per batches: 0.627 kg (for sample size 0.75 x 0.50 cm at 250°C)

Annual product (oil) yield: (0.612 kg/run x 2 runs/day x 280 days/yr.) = 342.72 kg/yr.

Annual product (char) yield: (0.627 kg/run x 2 runs/day x 280 days/yr.) = 349.44 kg/yr.

Price of furnace oil: Tk. 45/kg

Price of char coal: Tk. 150/kg

Total annual value of product: Tk. (342.72 x 45) + Tk. (349.44 x 150) = Tk. 67838.4

Payback period: (122695.84) % (67838.4) = 1.9 yrs.

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. Waste shoe/sandal sole is increasing day by day and it is dumping on various places in our cities. Dumped waste shoe/sandal sole 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 shoe/sandal wall. So, if the environment issues are considered for operating cost, it could be viable.

CHAPTER VI

Conclusions and Recommendations

6.1 Conclusions

From this study, pyrolysis of shoe/sandal soles would be a process for conversion of the same in to solid, liquid and gaseous products though product distribution depends on the operating variables such as temperature, heating rate and soles composition. From the experiment of pyrolysis of waste shoe/sandal soles, test and analysis of pyrolytic oil and char, the following conclusions could be made:

- i. The maximum yield of pyrolytic oil from the waste shoe/sandal soles was 36.0 % (by weight) at a temperature of 250°C with soles size of 0.75×0.50 cm for loading of 1.7 kg waste.
- ii. The maximum yield of pyrolytic solid from the waste shoe/sandal soles was 53.0 % (by weight) at a temperature of 200°C with soles size of 1.25×1.0 cm for loading of 1.7 kg waste.
- iii. The calorific value of pyrolytic oil and char is about 37 MJ/kg and 16 MJ/kg respectively.
- iv. The FTIR tests shows that four groups: alkane, alkenes, alkynes and aromatic compound were found from the pyrolysis of the waste shoe/sandal soles.
- v. The liquid pyrolytic oil could be used as low grade fuel and can be a substitute of furnace oil.
- vi. The solid char could be used as fuel after making them solid lump by mixing with some kind of binder or can be used as activated carbon.
- vii. Pyrolysis reduces the problem of disposal of waste shoe/sandal soles. It could be a source of alternative energy and chemicals. Therefore, as a potential source of energy and chemicals, pyrolytic-oil is an emerging alternative to the depleting fossil fuels.

Considering all these results, it can be concluded that the oil obtained from pyrolysis of shoe/sandal sole wastes could be used as alternative fuel or chemical feedstock after some treatment and also reduce the environmental hazards from the unmanaged disposal wastes.

6.2 Recommendations for Future Work

Better experimental model could be used to improve the quality and quantity of products.

- i. The optimum temperature for pyrolysis could be found by conducting experiments with some higher temperature.
- ii. Catalyst could be added to the feed materials to find the performance.
- iii. More efficient fractionating columns could be used for separation of pyrolysis oil into different fractionates.
- iv. Different kinetic methods and models could be used for designing a suitable reactor to maximize the oil production.
- v. Optimization of the process to achieve an economical and eco-friendly method could be attempted.

REFERENCES

1. Islam, M.R., Tushar, M.S.H.K and Haniu, H., 2008, "Production of Liquid Fuels and Chemicals from Pyrolysis of Bangladeshi Bicycle/Rickshaw Tire Wastes", *Journal of Analytical and Applied Pyrolysis*, Elsevier, Vol. 82, pp.96-109.
2. "Wikipedia", Electricity sector in Bangladesh [Online]. Available: https://en.wikipedia.org/wiki/Electricity_sector_in_Bangladesh.
3. Islam, M.R., Haniu, H., Alam, M.R.B. and Takai, K., 2008, "Preliminary Investigation for Engine Performance by Using Tyre Derived Pyrolysis Oil-Diesel Blended Fuels", *Journal of Power and Energy Systems*, pp.1359-1372.
4. Ali, M.H., 2014, "Extraction of Pyrolytic Fuel from Non- biodegradable Solid Waste", M.Sc Engineering Research Report, Department of Mechanical Engineering, KUET.
5. Hossain, M.S. and Rahman, A.N.M.M., 2015, "Production of Liquid Fuel from Pyrolysis of Waste Tires", *International Journal of Scientific & Engineering Research*, Vol. 6, pp.1224-1229.
6. Soling for Low Cost Footwear. *World Footwear*, pp.18–20, July/August 2006 (Shoe Trades, Cambridge, Massachusetts).
7. The Future of Polyurethane Soling. *World Footwear*, pp.18–20, January/February 2005 (Shoe Trades, Cambridge, Massachusetts).
8. The Federal Environmental Protection Authority, *Environmental impact Assessment Guideline for Tanneries*.
9. <http://www.radiantenergyltd.com>. Access in: 21st October, 2018.
10. Stefanović, S., Jefremović, V., Kiss, I. and Stanojević, D., 2014, "Basic Strategy of Tire Recycling with the Emphasis on the Tire Industry", *International Journal of Engineering*, Vol.12 (3), pp.235-238. ISSN 15842665.
11. Abbas, A.Y., 2004, "Recycling of Rubber Waste", *Polymer-Plastics Technology*, Vol.43 (6), pp.1735-1754. DOI: 10.1081/PPT-200040086. ISSN 03602559.
12. Ramírez-Hernández, A. and Conde-Acevedo, J., 2013, "Tyres: Destination End", *International Journal of Environmental Technology*, Vol.16 (4), pp. 279-289. DOI: 10.1504/IJETM.2013.054822. ISSN 14662132.
13. Singh, S., Nimmo, W., Gibbs, B.M. and Williams, P.T., 2009, "Waste Tyre Rubber as a Secondary Fuel for Power Plants", *Fuel*, Vol.88 (12), pp.2473-2480. DOI: 10.1016/j.fuel.2009.02.026. ISSN 00162361.

14. Antoniou, N. and Zabaniotou, A., 2013, "Features of an Efficient and Environmentally Attractive Used Tyres Pyrolysis with Energy and Material Recovery", *Renewable*, Vol.20, pp.539-558. DOI: 10.1016/j.rser.2012.12.005. ISSN 13640321.
15. Tatáno, F., Acerbi, N., Monterubbiano, Ch., Pretelli, S., Tombari, L. and Mangani, F., 2012, "Shoe Manufacturing Wastes: Characterization of Properties and Recovery Options", *Resources and Conservation*, Vol.66, pp.66-75. DOI: 10.1016/j.resconrec.2012.06.007, ISSN 09213449.
16. Janovská, K., Vilamová, Š., Besta, P., Samolejová, A. and Vozňáková, I., 2012, "Determination of Complex Energy Consumption of Metallurgical Production on the Base of Mathematical Modeling of Interdisciplinary Linkages", *Metalurgija, Croatia: Croatian Metallurgical Soc.*, Vol.51 (4), pp.571-573. ISSN 0543-5846.
17. Laresgoiti, M.F., Caballero, B.M., Marco, I., Torres, A., Cabrero, M.A. and Chomon, M.J., 2004, "Pyrolysis", *Journal of Analytical and Applied Pyrolysis*, Vol.71, pp.917-934.
18. Islam, M.R., Joardder, M.U.H., Hasan, S.M., Takai, K. and Haniu, H., 2011, "Feasibility Study for Thermal Treatment of Solid Tire Wastes in Bangladesh by Using Pyrolysis Technology", *Waste Management*, pp.2142-2149.
19. Rodriguez, I.M., Laresgoiti, M.F., Cabrero, M.A., Torres, A., Chomon, M.J. and Caballero, B., 2001, "Pyrolysis of Scrap Tires", *Fuel Processing Technology*, Vol.72, pp.9-22.
20. Cunliffe, A.M. and Williams, P.T., 1998, "Composition of Oils Derived from the Batch Pyrolysis of Tires", *Journal of Analytical and Applied Pyrolysis*, Vol.44, pp.131-52.
21. Barbooti, M.M., Mohamed, R.J., Hussain, A.A. and Abas, F.O., 2004, "Optimization of Pyrolysis Conditions of Scrap Tires under Inert Gas Atmosphere", *Journal of Analytical and Applied Pyrolysis*, Vol.72, pp.165-170.
22. Pakilel, H., Roy, C., Aubin, H., Jean, G. and Coulombe, S., 1992, "Formation of Limonene in Used Tire Vacuum Pyrolysis Oils", *Environ. Sci. Technology*, Vol.9, pp.16-46.
23. Indian Rubber Industry at a Glance. <http://allindiarubber.net>.
24. United Nations Industrial Development Organization (UNIDO), 2000, "Wastes Generated in the Leather Footwear Industry", 14th Session of the Leather and Leather Products Industry Panel, Czech Republic.

25. Hashem, M.A., Paul, A.C., Hosen, S. and Hasan, A., 2017, “Renewable energy from the waste soles through thermal pyrolysis-A novel approach”, *Bangladesh Journal of Scientific and Industrial Research*, BCSIR, Vol.52 (2), pp.141-146.
26. Isler, A., Sundu, S., Tuter, M. and Karaosmanoglu, F., 2010, “Transesterification Reaction of the Fat Originated from Solid Waste of the Leather Industry”, *Waste Management*, Vol.30, pp.2631–2635.
27. “Anatomy of the Shoe”, [Online]. Available: https://www.shoeguide.org/shoe_anatomy.
28. “The History of Your Shoes”, [Online]. Available: <https://shoeinfonet.com/shoe-history/history-your-shoes>.
29. Harvey, A., 1982, “Footwear Materials and Process Technology”, Lassa Publications, New Zealand.
30. Cleaner Production Institute, Simplified Life Cycle Assessment - Hot Spot Identification in the Leather Production Chain, 2009.
31. Garveri, T., 2012, Livscykelvärdering Av Olika Garvningsmetoder - En Förstudie.
32. Prevodnik, A., 2009, Bad Shoes Stink.
33. IndustriAll, Social and Environmental Report - the European Leather Industry, Brussels, 2012.
34. Group, N., 2012, Hållbarhetsrapport.
35. Albers, K., Canepa, P. and Miller, J., 2008, “Analyzing the Environmental Impacts of Simple Shoes: A Life Cycle Assessment of the Supply Chain and Evaluation of End-of-Life Management Options”, University of Santa Barbara.
36. European Commission, Legislation, Luxembourg, 2013.
37. Group, A., 2001, “A National Approach to Waste Tyres”.
38. www.wikipedia.org/wiki/Synthetic_rubber.
39. NIIR Project Consultancy Services, www.niir.org.
40. Norgate, T.E., Jahanshahi, S. and Rankin, W.J., 2007, “Assessing the Environmental Impact of Metal Production Processes”, *Journal of Cleaner Production*, Vol.15 (8-9), pp.838–848.
41. United Nations Industrial Development Organization (UNIDO), 2000, “Wastes Generated in the Leather Footwear Industry”, 14th Session of the Leather and Leather Products Industry Panel, Czech Republic.

42. Amari, T., Themelis, N. J, and Wernick, I.K., 1999, “Resource Recovery from used Rubber Tyres”, *Resources Policy*, Vol.25 (3), pp. 179-188.
43. “Wikipedia”, [Online] Available: <http://en.wikipedia.org/wiki/EPA>.
44. “Wastage Management Technique on Footwear Industries”, [Online]. Available: https://issuu.com/md.papon/docs/wastage_management_technique_on_foo_0b0c0e675519b8.
45. Bouvier, J.M. and Gelus, M., 1996, “Pyrolysis of Rubber Wastes in Heavy Oils and Uses of the Products”, *Resources and Conservation*, Vol.12, pp.77-93.
46. Wicks, R. and Bigsten, A., 1996, “Used Clothes as Development Aid: the Political Economy of Rags”, <http://ideas.repec.org/p/hhs/gunwpe/0017.html>.
47. Bridgwater, A.V., 1997, “Developments in Thermochemical Biomass Conversion”, pp.1-802, First Edition.
48. Horng, J.L., Chia, L.T. and Jim, S.L., 2004, “A Model for Predicting the Flash Point of Ternary Flammable Solutions of Liquid”, *Combust Flame*, Vol.138, pp.308–19.
49. Bozbas, K., 2008, “Biodiesel as an Alternative Motor Fuel: Production and Policies in the European Union”, *Renew Sustain Energy Rev.*, Vol.12, pp.542–52.
50. “Wikipedia”, [Online]. Available: https://en.wikipedia.org/wiki/Boiling_point.
51. “Wikipedia”, [Online]. Available: https://en.wikipedia.org/wiki/Heat_of_combustion.
52. Alkhatib, R., 2014, “Development of an alternative fuel from waste of used tires by pyrolysis”, PhD Thesis Report, Environmental Engineering, Ecole des Mines de Nantes.
53. “Wikipedia”, [Online]. Available: https://en.wikipedia.org/wiki/Fourier-transform_infrared_spectroscopy.
54. Coelho, A., Costa, L., Marques, M.M., Fonseca, I.M., Lemos, M.A.N.D.A. and Lemos, F., 2012, “The Effect of ZSM-5 Zeolite Acidity on the Catalytic Degradation of High-density Polyethylene Using Simultaneous DSC/TG Analysis”, *Applied Catalysis A: General*, pp.413-414 and pp.183-191. <http://dx.doi.org/10.1016/j.apcata.2011.11.010>.
55. Aguado, J., Serrano, D.P., Miguel, G.S., Escola, J.M. and Rodríguez, J.M., 2007, “Catalytic Activity of Zeolitic and Mesostructured Catalysts in the Cracking of Pure and Waste Polyolefins”, *Journal of Analytical and Applied Pyrolysis*, Vol.78 (1), pp.153-161. <http://dx.doi.org/10.1016/j.jaap.2006.06.004>.
56. Singh, S., Wu, C. and Williams, P., 2012, “Pyrolysis of Waste Materials Using TGA-MS and TGA-FTIR as Complementary Characterization Techniques”, *Journal of*

- Analytical and Applied Pyrolysis, Vol.94, pp.99-107.
<http://dx.doi.org/10.1016/j.jaap.2011.11.011>.
57. Islam, M.N. and Ani, F.N., 2000, “Techno-economics of rice husk pyrolysis, conversion with catalytic treatment to produce liquid fuel”, *Bioresource Technology*, Elsevier, Vol.73, pp.67-75.
58. FCM., 2004, “Solid Waste as a Resource, Review of Waste Technologies”, Federation of Canadian Municipalities, pp.111. Available on: http://www.sustainablecommunities.ca/filesCapacity_Building__Waste/SW_Guide_Technology.pdf.
59. DEFRA., 2007, Department for Environment, Food and Rural Affairs; Incineration of Municipal Solid Waste, Waste Management Technology Brief, the New Technologies Work Stream of the Defra Waste Implementation Programme.
60. Energy, Research Progress of Biomass Pyrolysis Processes, National Resources Management and Environment, China, 2012.
<http://www.fao.org/docrep/T4470E/t4470e0a.htm>.
61. Salman, Z., 2009, Biomass Pyrolysis. <http://www.altenergymag.com>.
62. Abbas-Abadi, M.S., Haghghi, M.N. and Yeganeh, H., 2012, “The Effect of Temperature, Catalyst, Different Carrier Gases and Stirrer on the Produced Transportation Hydrocarbons of LLDPE Degradation in a Stirred Reactor”, *Journal of Analytical and Applied Pyrolysis*, Vol.95, pp.198-204.
<http://dx.doi.org/10.1016/j.jaap.2012.02.007>.
63. Demirbas, A., 2004, “Pyrolysis of Municipal of Plastic Wastes for Recovery of Gasoline-range Hydrocarbons”, *Journal of Analytical and Applied Pyrolysis*, Vol.72 (1), pp.97-102. <http://dx.doi.org/10.1016/j.jaap.2004.03.001>.
64. López, A., Marco, I.D., Caballero, B.M., Adrados, A. and Laresgoiti, M.F., 2011, “Deactivation and Regeneration of ZSM-5 Zeolite in Catalytic Pyrolysis of Plastic Wastes”, *Waste Management (New York, N.Y.)*, Vol.31 (8), pp.1852-1858.
<http://dx.doi.org/10.1016/j.wasman.2011.04.004>. PMID: 21530221.
65. López, A., Marco, I.D., Caballero, B.M., Laresgoiti, M.F. and Adrados, A., 2010, “Pyrolysis of Municipal Wastes: Influence of Raw Material Composition”, *Waste Management (New York, N.Y.)*, Vol.30 (4), pp.620-627.
<http://dx.doi.org/10.1016/j.wasman.2009.10.014>. PMID: 19926462.

66. Lopez-Urionabarrenechea, A., Marco, I.D., Caballero, B.M., Laresgoiti, M.F. and Adrados, A., 2012, "Catalytic Stepwise Pyrolysis of Packaging Plastic Waste", *Journal of Analytical and Applied Pyrolysis*, Vol.96, pp.54-62. <http://dx.doi.org/10.1016/j.jaap.2012.03.004>.
67. Donaj, P.J., Kaminsky, W., Buzeto, F. and Yang, W., 2012, "Pyrolysis of Polyolefins for Increasing the Yield of Monomers Recovery", *Waste Management* (New York, N.Y.), Vol.32 (5), pp.840-846. <http://dx.doi.org/10.1016/j.wasman.2011.10.009>. PMID: 22093704.
68. "Cracking Mechanism Of Higher Hydrocarbons Fuel And Combustion", [Online]. Available: <https://blog.oureducation.in/cracking-mechanism-of-higher-hydrocarbonsfuel-and-combustion>.
69. "Wikipedia", [Online]. Available: https://en.wikipedia.org/wiki/Catalytic_reforming.
70. Williams, P.T., Elbaba, I.F., Wu, C. and Onwudili, J.A., 2010, "High Yield Hydrogen from the Pyrolysis-Catalytic Gasification of Scrap Tires", *Third International Symposium on Energy from Biomass and Waste*, Venice, Italy.
71. Islam, M.R., Parveen, M., Haniu, H. and Sarker, M.R.I., 2010, "Innovation in Pyrolysis Technology for Management of Scrap Tires: a Solution of Energy and Environment", *International Journal of Environmental Science and Development*, Vol.1 (1), pp.89-96.
72. Williams, P.T. and Brindle, A.J., 2002, "Catalytic Pyrolysis of Tyres: Influence of catalytic Temperature", *Fuel*, Vol.81, pp.2425-2434.
73. Brindle, A.J., 2003, "Aromatic Chemicals from the Catalyst Pyrolysis of Scrap Tyres", *Journal of Analytical and Applied Pyrolysis*, Vol.67, pp.143-164.
74. Rocca, P.A.D., Cerella, E.G., Bonelli, P.R. and Cukierman, A.L., 1999, "Pyrolysis of Hardwoods Residues: on Kinetics and Chars Characterization", *Biomass and Bioenergy*, Vol.16, pp.79-88.
75. Bridgwater, A.V. and Peacocke, G.V.C., 2000, "Fast Pyrolysis Processes for Biomass", *Renewable and Sustainable Energy Reviews*, Vol.4, pp.1-73.
76. Williams, P.T. and Cunliffe, A.M., 1998, "Composition of Oil Derived from the Batch Pyrolysis of Tyres", *Journal of Analytical and Applied pyrolysis*, Vol.44, pp.131-152.
77. Islam, M.R., Haniu, H. and Alam, M.R.B., 2008, "Oil Fuels and Chemicals from Pyrolysis of Motorcycle Tyre Waste Product Yields, Compositions and Related Properties", *Fuel*, Vol.87, pp.3112-3122.

78. Bajus, M., 2010, *Petroleum and Coal*, 52 (1) 1-10, 52 (3) 164-172, 52 (3) 207-214, http://www.vurup.sk/sites/vurup.sk/archivedsite/www.vurup.sk/pclvol52_2010/issue1pdf/pc_1_2010_bajus_050.pdf.
79. Pakdel, H. and Roy, C., 1994, "Simultaneous Gas Chromatographic-Fourier Transform Infrared Spectroscopic-mass Spectrometric Analysis of Synthetic Fuel Derived from Used Tyre Vacuum Pyrolysis Oil, Naphtha Fraction", *Journal of Chromatography*, Vol.683, pp.203-214.
80. Chang, Y.M., 1996, "On Pyrolysis of Waste Tyre Degradation Rate and Product Yields", *Resources Conservation and Recycling*, Vol.77, pp.125-139.
81. Sobko, A.A., 2008, "Generalized Vander Waals-Berthelot Equation of State", *Dokl Phys*, Vol.53, pp.416-9.
82. Lopez, G., Olazar, M., Aguado, R. and Bilbao, J., 2010, "Continuous Pyrolysis of Scrap Tires in a Conical Spouted Bed Reactor", *Fuel*, Vol.89, pp.1946-1952.
83. Murata, K., Sato, K. and Sakata, Y., 2004, "Effect of Pressure on Thermal Degradation of Polyethylene", *Journal of Analytical and Applied Pyrolysis*, Vol.71, pp.569-89.
84. Dr. Ing. Heino Vest, 2000, "Recycling of Used Car Tires", www.gtz.de/gate/gateid.afp.
85. Onenç, S., Brebu, M., Vasile, C. and Yanik, J., 2012, "Co-pyrolysis of Scrap Tires with Oily Wastes", *Journal of Analytical and Applied Pyrolysis*, Article in Press.
86. Abbas-Abadi, M.S., Haghghi, M.N., Yeganeh, H. and McDonald, A.G., 2014, "Evaluation of Pyrolysis Process Parameters on Polypropylene Degradation Products", *Journal of Analytical and Applied Pyrolysis*, Vol.109, pp.272-7.
87. Puna, J.F. and Santos, T.M., 2010, "Thermal Conversion Technologies for Solid Wastes: A New Way to Produce Sustainable Energy", Lisbon, High Institute of Engineering of Lisbon, Chemical Engineering Department.
88. Cheremisinoff, N.P., 2003, "Handbook of Solid Waste Management and Waste Minimization Technologies", USA, Elsevier Science.
89. Moustakas, K. and Loizidou, M., 2010, "Solid Waste Management through the Application of Thermal Methods", Athens, National Technical University of Athens.
90. Studija Mogucnosti Koriscenja Komunalnog Otpada U Energetke Svrhe (Waste to Energy), Departman Za Inzenerstvo Zastite Zivotne Sredine, Srbija, 2008, (<http://www.psemr.vojvodina.gov.rs>).
91. Incineration of Municipal Solid Waste, Department for Environment Food & Rural Affairs, London, 2013 (<https://www.gov.uk>).

92. Young, G.C., 2010, "Municipal Solid Waste to Energy Conversion Processes: Economic", Technical and Renewable Comparison, USA, John Wiley & Sons, Inc.
93. Aylon, E., Fernandez-Colino, A., Murillo, R., Grasa, G., Navarro, M.V., Garcia, T. and Mastral, A.M., 2010, "Waste Tire Pyrolysis: Modelling of a Moving Bed Reactor", *Waste Management*, Vol.30, pp.2530-2536.
94. Charpenay, S., Wojtowicz, A.M. and Serio, A.M., "Pyrolysis Kinetics of the Waste Tires Constituents: Extender Oil, Natural Rubber, and Styrene-butadiene Rubber", *Advanced Fuel Research*.
95. Czajczynska, D., Anguilano, L., Ghazal, H., Krzyzynska, R., Reynolds, A.J., Spencer, N. and Jouhara, H., 2017, "Potential of pyrolysis processes in the waste management sector", *Thermal Science and Engineering Progress*, Elsevier, Vol.3, pp.171-197.
96. "Wikipedia", [Online]. Available: <http://en.wikipedia.org/wiki/Pyrolysis>.
97. Fan, C., Zan, C., Zhang, Q., Ma, D., Chu, Y., Jiang, H., Shi, L. and Wei, F., 2014, "The oxidation of heavy oil: Thermogravimetric analysis and non-isothermal kinetics using the distributed activation energy model", *Fuel Processing Technology*, Elsevier, Vol.119, pp.146-150.
98. Haarlemmer, G., Guizani, C., Anouti, S., Déniel, M., Roubaud, A. and Valin, S., 2016, "Analysis and comparison of bio-oils obtained by hydrothermal liquefaction and fast pyrolysis of beech wood", *Fuel*, Elsevier, Vol.174, pp.180-188.
99. Khan, M.Z.H., Sultana, M., Al-Mamun, M.R. and Hasan, M.R., 2016, "Pyrolytic Waste Plastic Oil and Its Diesel Blend: Fuel Characterization", *Journal of Environmental and Public Health*, pp.1-6.
100. Imam, B., 2013, "Energy Resources of Bangladesh", pp.201-282, Second Edition.

APPENDIX

A-1: Details of Sample used in Various Run

| Serial No. | Sample Size (cm × cm) | Weight of Charge (kg) |
|------------|--------------------------|--------------------------|
| 1 | 1.25 × 1.0 | 1.70 |
| 2 | 1.0 × 0.75 | 1.70 |
| 3 | 0.75 × 0.50 | 1.70 |

A-2: Pyrolysis Data of Waste Soles with Sample Size 1.25 × 1.0 cm at 200°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|------------------------------|-------------------------------|-------------------------|------|-----|-------------------------|
| Sample No. | Starting Temperature (°C) | Operating Temperature (°C) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 1 | 94 | 200 | 371 | 880 | 449 | 107 |
| 2 | 100 | 200 | 342 | 921 | 437 | 104 |
| 3 | 98 | 200 | 348 | 900 | 452 | 104 |

A-3: Pyrolysis Data of Waste Soles with Sample Size 1.25 × 1.0 cm at 225°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|------------------------------|-------------------------------|-------------------------|------|-----|-------------------------|
| Sample No. | Starting Temperature (°C) | Operating Temperature (°C) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 4 | 98 | 225 | 464 | 780 | 456 | 156 |
| 5 | 100 | 225 | 453 | 793 | 454 | 150 |

A-4: Pyrolysis Data of Waste Soles with Sample Size 1.25 × 1.0 cm at 250°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|------------------------------|-------------------------------|-------------------------|------|-----|-------------------------|
| Sample No. | Starting Temperature (°C) | Operating Temperature (°C) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 6 | 100 | 250 | 534 | 707 | 459 | 165 |

| | | | | | | |
|---|----|-----|-----|-----|-----|-----|
| 7 | 99 | 250 | 545 | 698 | 457 | 173 |
|---|----|-----|-----|-----|-----|-----|

A-5: Pyrolysis Data of Waste Soles with Sample Size 1.0×0.75 cm at 200°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|---|--|----------------------|------|-----|----------------------|
| Sample No. | Starting Temperature ($^{\circ}\text{C}$) | Operating Temperature ($^{\circ}\text{C}$) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 8 | 92 | 200 | 391 | 859 | 450 | 103 |

A-6: Pyrolysis Data of Waste Soles with Sample Size 1.0×0.75 cm at 225°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|---|--|----------------------|------|-----|----------------------|
| Sample No. | Starting Temperature ($^{\circ}\text{C}$) | Operating Temperature ($^{\circ}\text{C}$) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 9 | 92 | 225 | 498 | 747 | 455 | 152 |

A-7: Pyrolysis Data of Waste Soles with Sample Size 1.0×0.75 cm at 250°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|---|--|----------------------|------|-----|----------------------|
| Sample No. | Starting Temperature ($^{\circ}\text{C}$) | Operating Temperature ($^{\circ}\text{C}$) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 10 | 93 | 250 | 578 | 662 | 460 | 168 |

A-8: Pyrolysis data of Waste Soles with Sample Size 0.75×0.50 cm at 200°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|---|--|----------------------|------|-----|----------------------|
| Sample No. | Starting Temperature ($^{\circ}\text{C}$) | Operating Temperature ($^{\circ}\text{C}$) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 11 | 86 | 200 | 424 | 825 | 451 | 102 |

A-9: Pyrolysis data of Waste Soles with Sample Size 0.75×0.50 cm at 225°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|---|--|----------------------|------|-----|----------------------|
| Sample No. | Starting Temperature ($^{\circ}\text{C}$) | Operating Temperature ($^{\circ}\text{C}$) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 12 | 87 | 225 | 534 | 710 | 456 | 148 |

A-10: Pyrolysis Data of Waste Soles with Sample Size 0.75×0.50 cm at 250°C

| Feed Materials: 1.7 kg | | | | | | |
|------------------------|---|--|----------------------|------|-----|----------------------|
| Sample No. | Starting Temperature ($^{\circ}\text{C}$) | Operating Temperature ($^{\circ}\text{C}$) | Yields Products (gm) | | | Operating Time (Min) |
| | | | Oil | Char | Gas | |
| 13 | 88 | 250 | 612 | 627 | 461 | 164 |

A-11: Effect of Temperature on Product Yield of Shoe/sandal Sole Pyrolysis

| Serial No. | Weight of Shoe/sandal Soles (kg) | Temperature ($^{\circ}\text{C}$) | % of Product Yield (w/w) | | |
|------------|----------------------------------|------------------------------------|--------------------------|-------|-------|
| | | | Oil | Char | Gas |
| 1 | 1.7 | 200 | 20.80 | 52.96 | 26.24 |
| 2 | | 225 | 26.98 | 46.27 | 26.75 |
| 3 | | 250 | 31.74 | 41.33 | 26.93 |
| 4 | | 200 | 23.00 | 50.53 | 26.47 |
| 5 | | 225 | 29.30 | 43.94 | 26.76 |
| 6 | | 250 | 34.00 | 38.94 | 27.06 |
| 7 | | 200 | 24.94 | 48.53 | 26.53 |
| 8 | | 225 | 31.41 | 41.77 | 26.82 |
| 9 | | 250 | 36.00 | 36.88 | 27.12 |

A-12: Effect of Feed Size on Product Yield of Shoe/sandal Sole Pyrolysis

| Serial No. | Weight of Sole Waste (kg) | Feed Size (cm \times cm) | % of Product Yield (w/w) | | |
|------------|---------------------------|----------------------------|--------------------------|-------|-------|
| | | | Oil | Char | Gas |
| 1 | 1.7 | 1.25×1.0 | 20.80 | 52.96 | 26.24 |
| 2 | | | 26.98 | 46.27 | 26.75 |

| | | | | | |
|---|--|-------------|-------|-------|-------|
| 3 | | 1.0 × 0.75 | 31.74 | 41.33 | 26.93 |
| 4 | | | 23.00 | 50.53 | 26.47 |
| 5 | | | 29.30 | 43.94 | 26.76 |
| 6 | | | 34.00 | 38.94 | 27.06 |
| 7 | | 0.75 × 0.50 | 24.94 | 48.53 | 26.53 |
| 8 | | | 31.41 | 41.77 | 26.82 |
| 9 | | | 36.00 | 36.88 | 27.12 |

A-13: Effect of Operating Time on Product Yield of Shoe/sandal Sole Pyrolysis

| Serial No. | Weight of Sole Waste (kg) | Operating Time (Minutes) | % of Product Yield (wt %) | | |
|------------|---------------------------|--------------------------|---------------------------|-------|-------|
| | | | Oil | Char | Gas |
| 1 | 1.7 | 105 | 20.80 | 52.96 | 26.24 |
| 2 | | 153 | 26.98 | 46.27 | 26.75 |
| 3 | | 169 | 31.74 | 41.33 | 26.93 |
| 4 | | 103 | 23.00 | 50.53 | 26.47 |
| 5 | | 152 | 29.30 | 43.94 | 26.76 |
| 6 | | 168 | 34.00 | 38.94 | 27.06 |
| 7 | | 102 | 24.94 | 48.53 | 26.53 |
| 8 | | 148 | 31.41 | 41.77 | 26.82 |
| 9 | | 164 | 36.00 | 36.88 | 27.12 |