

CHAPTER 1

INTRODUCTION

1.1 Overview:

The energy crisis is the concern that the world's demands on the limited natural resources that are used to power industrial society are diminishing as the demand rises. These natural resources are in limited supply. While they do occur naturally, it can take hundreds of thousands of years to replenish the stores. Governments and concerned individuals are working to make the use of renewable resources a priority, and to lessen the irresponsible use of natural supplies through increased conservation. The energy crisis is a broad and complex topic. Most people don't feel connected to its reality unless the price goes up. The energy crisis is something that is ongoing and getting worse, despite many efforts [1]. Bangladesh is passing through a very critical juncture of its history. A nation of about 150 million living in a country of 58,000 square kilometers is struggling against all possible odds that a nation has to encounter for survival. Very difficult global situation of worsening food security and very tight energy security has made its struggle all the more difficult [2]. In Bangladesh renewable energy still remains unused. Most of the energy comes from non-renewable sources like coal which is still remains the top choice to produce energy. Unless we give renewable energy a serious thought, the problem of energy crisis cannot be solved. Renewable energy sources can reduce our dependence on fossil fuel and also helps to reduce greenhouse gas emissions. The reason for the energy crisis are overconsumption, overpopulation, poor infrastructure, unexplored renewable energy options, delay in commissioning of power plants, wastage of energy, poor distribution system, major accidents and natural calamities, wars and attacks etc [3]. Move towards renewable resources is the possible solution of the energy crisis. The Footwear Industry in Bangladesh has started since the colonial era, although its modernization took place only in the late 1980s [4]. The footwear industry is a manufacturing sector which utilizes a wide variety of materials and processes to produce a range of distinctly different products, from sandals to specialized safety footwear. A range of distinctly different materials such as leather, synthetic materials, rubber and textile are commonly used in shoe manufacturing, among them the percentage of rubber used as a form of

full vulcanized or semi vulcanized is about 7% of material consumption in average shoe (%wt) [5].

Vulcanized rubber is non-biodegradable and that's why it has an environmental impact and it is a source of solid waste. Through pyrolysis process these waste sole was using to produce renewable energy. Sometimes scrap rubber is used as a fuel through pyrolysis process. Pyrolysis is one of the thermal approaches to recovering energy and basic materials from waste rubber. Technically, the term 'pyrolysis' covers all forms of heat decomposition, including combustion, although in practice it is normally understood to mean thermal decomposition in a non-reactive (anaerobic, or in the absence of oxygen) atmosphere [6].

This thesis was conducting to reduce the amount of industrial waste throughout the country and try to use those kind of waste as a renewable energy.

1.2 Objectives:

The objectives of this thesis are

- Try to produce renewable energy through pyrolysis process.
- Identification of physio-chemical properties of crude oil.

1.3 Motivation:

There are many footwear industry in Bangladesh and also large amount of wastes are producing. This kind of wastes are very harmful for the environment. Basically, this thesis was conducted to use that kind of wastes as a valuable product as well as reduce the environmental impact.

1.4 Organization of the thesis:

Chapter 1: This chapter is contented with overview and objective of this thesis .There is a briefing of present situation of energy crisis, importance of generation of renewable energy and way of producing energy from waste sole of footwear industries.

Chapter 2: This chapter is contented with compounding ingredient of sample material, it's features and environmental impact. There is a description of methods of recovering energy from waste, design of pyrolysis plant and test analysis (FTIR & TGA).

Chapter 3: This chapter contented with sample collection and preparation, experimental procedure, flow chart of pyrolysis and experimental data.

Chapter 4: This chapter is contented with experimental result and discussion. There is discussion about effect of temperature and time on product yield during pyrolysis, comparison of products yield during pyrolysis and test analysis (FTIR & TGA) of extracted crude oil.

Chapter 5: This chapter is contented with conclusion, future scope and limitation of this thesis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction:

In this chapter try to discuss about vulcanized rubber, feature of vulcanized rubber, ingredient of vulcanized rubber. Besides, solid waste management and physio-chemical analysis for example, Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) are also describe.

2.2 Vulcanized rubber:

Vulcanized rubber is a material that undergoes a chemical process known as vulcanization. This process involves mixing natural rubber with additives such as sulfur and other curatives. Vulcanization makes rubber much stronger, more flexible, and more resistant to heat and other environmental conditions. Vulcanized rubber makes both soft and hard objects, ranging from rubber bands to bowling balls. In fact, almost any rubber object consists of vulcanized rubber [7].

2.2.1 Preperation of vulcanized rubber:

It is necessary to use vulcanization to make commercial-grade rubber because natural rubber is not stable enough to produce goods with. In fact, natural rubber melts when warm, breaks apart when cold, and is very sticky. This is because natural rubber consists of independent polymer chains that allow the rubber to be deformed. Vulcanization creates bridges between these polymer chains, allowing the rubber to be deformed when stress is applied and to return to its original position when the stress is removed. There are two common vulcanizing processes [7].

2.2.1.1 Pressure vulcanization:

This process involves heating the rubber with sulphur under pressure at a temperature of 150°C. Many articles are vulcanized in moulds that are compressed by a hydraulic press.

2.2.1.2 Free vulcanization:

Used where pressure vulcanization is not possible, such as with continuous, extruded products, it is carried out by applying steam or hot air. Certain types of garden hose, for example, are coated

with lead, and are vulcanized by passing high-pressure steam through the opening in the hose [8].

2.2.2 Features of vulcanized rubber [7]:

- Vulcanized rubber is stronger than non-vulcanized rubber.
- Vulcanized rubber stand up more stress and damage.
- Vulcanized rubber is more rigid, more stretch-resistant than non-vulcanized rubber.
- Crack resistance is good.
- Slip resistance is high.
- Heat and oil resistance is good.
- Normal specific gravity (density) range is 1.05 – 1.35 for solid and for cellular 0.3 – 1.1
- Vulcanized rubber may be soft or hard.
- Can be compounded to gain desirable properties.
- Versatility leads to diverse application.

2.2.3 Compounding of vulcanized rubber:

2.2.3.1 Raw rubber:

As a raw rubber natural rubber, SBR (Styrene-Butadiene Rubber), nitrile and polychloroprene rubber can be used, either separately or in blend.

Natural rubber is aelastic substance which is obtained from the exudations of certain tropical plants. The commercial source of natural rubber (sometimes called Pará rubber) is the tree *Heveabraziliensis*. The only other plant under cultivation as a commercial rubber source is guayule (*Partheniumargentatum*), a shrub native to the arid regions of Mexico and the SW United States [9].

Styrene-butadiene or styrene-butadienerubber (SBR) describe families of synthetic rubber derived from styrene and butadiene. These materials have good abrasion resistance and good aging stability when protected by additives [10].

Nitrile rubber (NBR), also called nitrile-butadiene rubber, an oil-resistant synthetic rubber produced from a copolymer of acrylonitrile and butadiene. In the production of NBR, acrylonitrile ($\text{CH}_2=\text{CHCN}$) and butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) are emulsified in water and then polymerized (their single-unit molecules linked into large, multiple-unit molecules) through the action of free-radical initiators. The amount of acrylonitrile present in the final copolymer varies from 15 to 50 percent [11].

Neoprene (CR), also called polychloroprene or chloroprene rubber, synthetic rubber produced by the polymerization (or linking together of single molecules into giant, multiple-unit molecules) of chloroprene. A good general-purpose rubber, neoprene is valued for its high tensile strength, resilience, oil and flame resistance, and resistance to degradation by oxygen and ozone; however, its high cost limits its use to special-properties applications [12].

2.2.3.2 Accelerators [13]:

Accelerators are any of numerous chemical substances that causes vulcanization of rubber to occur more rapidly or at lower temperatures by controlling the speed of the reaction between sulfur and rubber. Many classes of compounds act as accelerators, the most important being organic materials containing sulfur and nitrogen, especially derivatives of benzothiazole. Accelerators are used to decrease the quantity of sulfur necessary for vulcanization, improve processing characteristics, give better mechanical properties, give better resistance to ageing and will reduce discoloration caused by light. Accelerators are also classified as primary and secondary accelerators based on the role they play in a given compound.

Generally, thiazoles and sulfenamide accelerators play a role of being primary accelerators due to their characteristics such as good processing safety, a broad vulcanization plateau and optimum cross link density as well as desired reversion delay that they offer.

The basic accelerators such as guanidines, thiurams, and di-thio-carbamates etc are used as secondary accelerators to activate the primary accelerators. The use of secondary accelerators increases the speed of vulcanization substantially but at the expense of scorch safety. The dosages of the secondary accelerators are generally between 10-40% of the primary accelerator.

2.2.3.3 Accelerator activators/ retarders:

These additives used to improve the processing and final vulcanizate properties. In natural rubber formulations, the activator most commonly used is the zinc oxide. This metal oxide is sulfurating agent that transfer the sulfur to the hydrocarbon chains [14].

2.2.3.4 Antidegradants:

Anti-degradants are used to inhibit the actions of degradants such as oxygen and ozone which can alter the network structure when react with elastomers. The function of Antioxidants can be chemically or physically. Chemical protectants react directly with degradants whereas physical protectants migrate to the surface to provide a barrier to any reaction or action by degradants. Amines, phenolics and phosphites are commonly used chemical protectants. Various waxes have been used as physical protectants [15].

2.2.3.5 Reinforcing filler:

One kind of chemicals include carbon blacks, silica and resins, which increase the strength and improve the elastic property of rubber by creating a cross-linking effect. It also reduce the cost of the end product and modifies the electrical and optical properties of the polymer matrix [14].

2.2.3.6 Cheapening filler:

These are available in the form of powder which are added to the compound. They tend to stiffen the product and reduce its strength, stretch and elasticity. Common examples are soft clays, calcium carbonate etc [14].

2.2.3.7 Extenders:

Extenders are added to stiffen rubber composition as well as to reduce cost. Oil extension of rubber is widely used in tyre treads which permits the use of elastomers with higher filler levels and higher molecular weight. Other examples of extenders are clay, calcium carbonate and ground coal. Oil levels of 30-40 phr are typical [15].

2.2.3.8 Tackifiers [15]:

Tackifiers are added to improve the ability of two materials to resist separation under pressure which is known as tack. In natural rubber, tackifiers are added to prevent tack degradation in the range of 1 to 10 phr. In Styrene-butadiene rubber, tackifiers increase initial tack as well as prevent tack degradation. Following are the types of tackifiers:

- a) Alkyl-modified phenol-formaldehyde resins
- b) Coumarone-indene resins obtained from coal coke oven lights consist of indene, coumarone, styrene and other hydrocarbons.
- c) Chemical mixtures of abietic acids known as rosin derivatives
- d) Terpene oligomers
- e) Aliphatic petroleum resins

2.2.3.9 Softeners:

To ease the process of mixing of rubber compounds, softeners are used to provide lot of energy for the process. Mineral oils are most important softener. Animal and vegetable oils are also some examples of softener [15].

2.2.4 Environmental impacts:

Vulcanized rubber does not have great impact on environment but does exhibit several negative attributes. Rubber is mildly toxic when burned and cools quickly after being melted, making it somewhat hazardous to those handling it. Generally, the only way for rubber to harm someone in this way is if he/she purposely burns it [7].

2.3 Solid waste management [5]:

In footwear industry solid waste management is performed in following ways -

- Recycling the waste
- Reduce the quantity of waste
- Reuse the waste
- Recover energy from the waste

2.3.1 Recovering energy from waste [5]:

Recovering energy from waste is only appropriate for waste that cannot be prevented, reused or recycled with less greenhouse gas emitted. Energy recovery can be a sustainable option for waste that would otherwise go to landfill and create landfill methane emissions. The conventional technologies are—

2.3.1.1 Direct combustion (incineration) of dry biomass [5]:

The heat generated by the following wastes can be used directly to warm homes and buildings or to generate electricity using a steam turbine, or both, through combined heat and power systems:

- direct combustion (incineration) of dry biomass waste such as wood waste, straw and poultry litter
- the biomass part of municipal waste
- some commercial and industrial wastes
- some construction and demolition wastes

Where waste is combusted in a combined heat and power unit, it is possible to produce both heat and power at greater efficiencies.

2.3.1.2 Combustion of waste-derived fuel:

The methane produced from landfill (landfill gas) is a waste-derived fuel. It can be used in the same way as for combustion plants or it can be injected into the national gas grid. Waste derived fuel is also referred to as Solid Recovered Fuel (SRF) or Refuse Derived Fuel (RDF) [5].

2.3.1.3 Anaerobic digestion [5]:

Anaerobic digestion (AD) is a natural process in which micro-organisms break down the organic matter found in wet biomass waste (such as sewage sludge, animal manure and slurry and waste food) in the absence of oxygen, to produce biogas (mainly a mixture of around 60% methane and 40% carbon dioxide) and digestate (a nitrogen rich fertilizer).

The biogas can be burned directly in a gas boiler to produce heat or burnt in a combined heat and power (CHP) unit to produce heat and electricity. Alternatively, the biogas can be cleaned to

remove the carbon dioxide and other substances, to produce biomethane. This can be injected into the national gas grid to be used in the same way as natural gas, or used as a vehicle fuel.

The National Non-food Crops Centre (NNFCC) runs the government's Anaerobic Digestion Portal - a gateway to information on anaerobic digestion, biogas and digestate.

2.3.1.4 Advanced conversion technologies:

A number of innovative advanced, high temperature processes are beginning to emerge. These have the potential to be more efficient than conventional processes and can offer a range of different types of energy from bio-based wastes, including wood waste and municipal wastes [5].

2.3.1.4.1 Gasification:

Gasification is a type of advanced conversion that produces a combustible gas that is a mixture of carbon monoxide, hydrogen, carbon dioxide and methane. This gas can be used directly to generate heat and electricity. Alternatively, it can be upgraded to an ultra clean gas called syngas. This can be used to manufacture either bio-methane, which can be injected into the national gas grid, or transport fuels such as hydrogen, ethanol, synthetic diesel or jet fuel. The energy given off can be harnessed to generate heat and power [5].

2.3.1.4.2 Pyrolysis:

Pyrolysis is the thermal decomposition of fuel into liquids, gases, and char (solid residue) in the absence of oxygen. It is usually understood to be anhydrous (without water). The solid, termed variously as char, bio-char, charcoal or coke, is generally of high carbon content and may contain around half the total carbon of the original organic matter. The volatiles can be partly condensed to give a liquid fraction leaving a mixture of so called 'non-condensable' gases. Pyrolytic products can be used as fuels, with or without prior upgrading, or they can be utilized as feedstock for chemical or material industries. Because of the nature of the process, yield of useful products is high compared to the other processes. In general, pyrolytic products are more refined and therefore can be used with greater efficiency. Materials suitable for pyrolysis processing include coal, animal and human waste, food scraps, paper, cardboard, plastics, rubber and biomass. The process is represented simply in **Figure 2.1**.

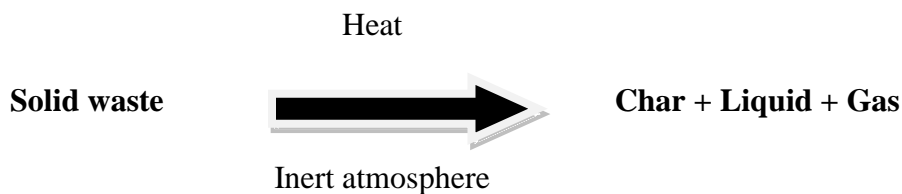


Figure 2.1: Simple representation of pyrolysis process

Pyrolysis is a type of advanced conversion that can be used to produce either a combustible gas, oil or solid char (sometimes known as bio-coal). In the future, it will be possible to upgrade pyrolysis oil to produce petrol and diesel using oil refining techniques. The choice of technology for any project depends on the type of waste available, local circumstances and finance [16].

2.4 Test analysis method:

2.4.1 FTIR (Fourier Transform Infrared Spectroscopy) [17]:

FTIR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. It provides information about the following:-

- It can identify unknown materials.
- It can determine the quality or consistency of a sample.
- It can determine the amount of components in a mixture.

FTIR offers quantitative and qualitative analysis for organic and inorganic samples. Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing

an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. FTIR can be used with other molecular spectroscopy techniques available in Intertek laboratories, including Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Infrared-spectroscopy coupled to Thermogravimetric Analysis (FTIR/TGA), Nuclear Magnetic Resonance Spectroscopy (NMR), Gas Chromatography - Mass Spectrometry (GC/MS), Liquid Chromatography - Mass Spectrometry (LC/MS), UV/Vis spectroscopy, Near Infrared (NIR) and Raman scattering. FTIR combined with these techniques provides complementary data regarding a molecule's molecular structure.

In FTIR analysis, when electromagnetic energy in infrared region passes through the sample it causes atoms and groups of atom of organic compound to vibrate faster which connect them. Due to absorption of infrared radiation by the atoms and groups of atom produces band or peak which is identical for individual material. It is impossible for any two different compound to have precisely same infrared spectrum. Peaks forms in 1500 to 500 cm^{-1} is fixed for particular compound so this region is called finger print region. The chemical bonds present in a compound can be stretched or bended condition. Depending on bond state, symmetric condition of compound, in-plane and out-of-plane vibrations and static and dynamic condition of molecule during molecular vibration infrared spectrum varies. Generally, 3800 to 2400 cm^{-1} region in spectrum called single bond region. Absorption due to O-H, N-H and C-H bond stretches here. They are very high in energy because in such a light atom. The position of the bond depends on strength which increase in the order $\text{C-H} < \text{N-H} < \text{O-H}$. The region between 2300 to 2000 cm^{-1} called triple bond region. These are the strongest bonds, so they occur at higher wavelength than single bond. 1900 to 1500 cm^{-1} is double bond region where – double bond stretches. Finally, 1500 to 500 cm^{-1} region is called fingerprint region where single bond stretches. The bond in an infrared spectrum are classified by intensity: strong, medium, weak and variable. The number of similar group in a molecule changes the relative strength s of the absorption band of spectrum. For example, the stretching bond of single O-H group in a compound displays itself as a relatively strong whereas a single C-H stretch is comparatively weaker.

There is a potentially broad number of molecular fragments that can be considered to be functional groups attached to an organic structure or backbone. This section features the most simple and most common of the functional groups, -C-X, i.e. the halogens (X= F, Cl, Br and I), hydroxy (X=OH), oxy or ether (X=OR, where R=alkyl), and amino (X=NH₂, =NH or ...N). With the exception of the carbonyl functionality, these three basic functional groups cover most of the common occurrences in simple organic compounds. Note that for the oxy/hydroxy and amino functionalities, these are molecular fragments, and they contribute their own set of characteristic absorptions to the spectrum of the compound. In fact, the bonding between the functional group and the backbone is only one part of the overall picture used for the spectral interpretation.

2.4.1.2 Why Infrared Spectroscopy?

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis [17].

2.4.1.3 Principal:

Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has

the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis [17].

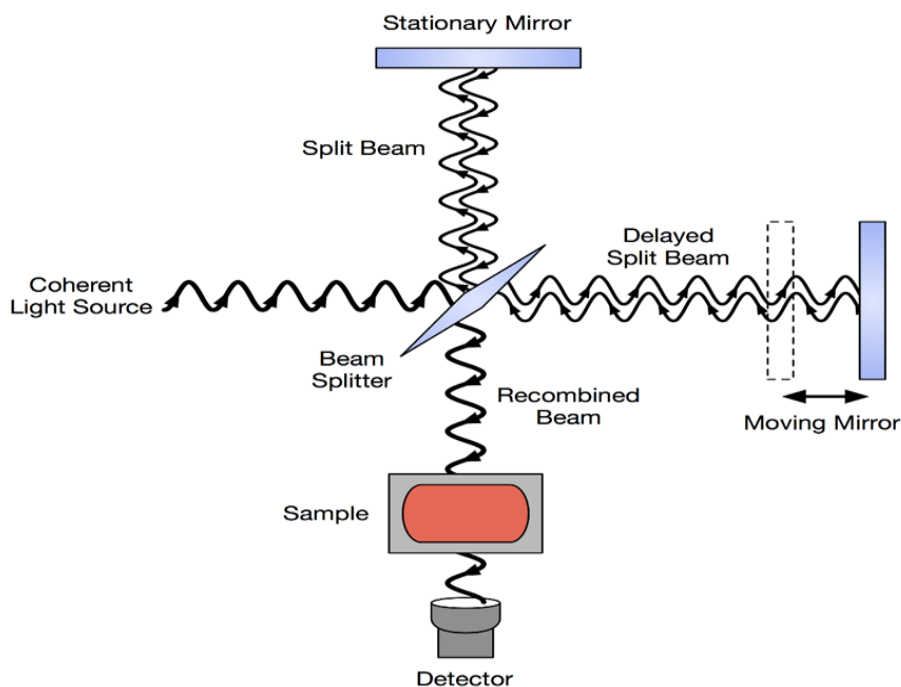


Figure 2.2: Mechanism of FTIR analysis [17]

2.4.1.4 Sample analysis process [17]:

The normal instrumental process is as follows:

- **The Source:**

Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

- **The Interferometer:**

The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

- **The Sample:**

The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

- **The Detector:**

The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

- **The Computer:**

The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation. Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the “percent transmittance.” This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which

are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.

2.4.1.5 Application of FTIR [17]:

Some of the major advantages of FT-IR over the dispersive technique include:

- **Speed:** Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Fellgett Advantage.
- **Sensitivity:** Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Fellgett Advantage) which results in much lower noise levels, and the fast scans enable the coaddition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).
- **Mechanical Simplicity:** The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.
- **Internally Calibrated:** These instruments employ a He, Ne laser as an internal wavelength calibration standard. These instruments are self-calibrating and never need to be calibrated by the user.

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. Thus, it is a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality controller quality assurance applications whether it be batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FT-IR detectors, along

with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis.

Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

2.4.2 TGA (Thermogravimetric Analysis) [18]:

Thermogravimetric analysis or thermal gravim analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Common applications of TGA are

- materials characterization through analysis of characteristic decomposition patterns.
- studies of degradation mechanisms and reaction kinetics.
- determination of organic content in a sample.
- determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints.

2.4.2.1 The TGA Technique [18]:

- TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum.
- Thermal gravimetric analysis can be interfaced with a mass spectrometer RGA to identify and measure the vapors generated, though there is greater sensitivity in two separate measurements.
- Inorganic materials, metals, polymers and plastics, ceramics, glasses, and composite materials can be analyzed.
- Temperature range from 25°C to 900°C routinely. The maximum temperature is 1000°C on our instrument. We have access to an instrument with an upper temperature limit of 1500°C when you need it.
- Sample weight can range from 1 mg to 150 mg. Sample weights of more than 10 mg are preferred, but excellent results are sometimes obtainable on 1 mg of material.
- Weight change sensitivity of 0.01 mg.
- Samples can be analyzed in the form of powder or small pieces so the interior sample temperature remains close to the measured gas temperature.

2.4.2.2 Applications of Thermogravimetry [18]:

- Determines temperature and weight change of decomposition reactions, which often allows quantitative composition analysis.
- May be used to determine water content or the residual solvents in a material.
- Allows analysis of reactions with air, oxygen, or other reactive gases (see illustration below).
- Can be used to measure evaporation rates as a function of temperature, such as to measure the volatile emissions of liquid mixtures.

- Allows determination of Curie temperatures of magnetic transitions by measuring the temperature at which the force exerted by a nearby magnet disappears on heating or reappears on cooling.
- Helps to identify plastics and organic materials by measuring the temperature of bond scissions in inert atmospheres or of oxidation in air or oxygen.
- Used to measure the weight of fiberglass and inorganic fill materials in plastics, laminates, paints, primers, and composite materials by burning off the polymer resin. The fill material can then be identified by XPS and/or microscopy. The fill material may be carbon black, TiO_2 , CaCO_3 , MgCO_3 , Al_2O_3 , $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, talc, Kaolin clay, or silica, for instance.
- Can measure the fill materials added to some foods, such as silica gels, cellulose, calcium carbonate, and titanium dioxide.
- Can determine the purity of a mineral, inorganic compound, or organic material.

CHAPTER 3

METHODOLOGY AND EXPERIMENTAL SETUP

3.1 Introduction:

In this chapter describe the experimental methodology and how the experimental setup for pyrolysis plant had done? Moreover, the FTIR and TGA analysis process also describe.

3.2 Sample collection and preparation:

To perform pyrolysis process, the waste sole was collected (full vulcanized and semi vulcanized) from Bay Rubber Industry, Gazipur, Dhaka. Before carrying out the pyrolysis process, the soling materials were washed out to remove dirt and any kind of contamination. Then waste soles were dried it properly and cut into small pieces to aid the pyrolysis. The amount of sample taken was –

Full vulcanized rubber 850 gm

Semi vulcanized rubber 850 gm

3.3 Design of pyrolysis plant:

The thesis work was performed in a manual designed pyrolysis plant. Pressure cooker was used instead of batch type fixed bed fire tube pyrolysis reactor. The pressure cooker was 5.5 liter and length was 20 cm and opening diameter was about 14 cm. The opening and the vent tube was sealed properly by M-seal. The pressure cooker was insulated by mud to prevent heat loss. A copper pipe of diameter 1 cm was inserted at the top of pressure cooker by M-seal. The copper pipe was wrapped by foam to aid condensation of vapor. One end of the K-type single thread thermocouple was set at the top of the pressure cooker and the other end was connected to the temperature regulator.



Figure 3.1: Overall setup of the pyrolysis plant

3.4 Components of pyrolysis plant:

3.4.1 Pressure cooker:

KIAM brand pressure cooker was used, which was collected from the Khulna town. The photograph of the pressure cooker is presented in **Figure 3.2**



Figure 3.2: Photograph of the pressure cooker

3.4.2 Electric heater:

A double coil electric heater of 2000 W was used. It was placed at the bottom of the cooker. The temperature was increased up to 350°C. The photograph of the electric heater is presented in **Figure 3.3**



Figure 3.3: Photograph of the electric heater

3.4.3 Condenser:

A copper condenser pipe of diameter 1 cm was used. It was bent randomly at seven position to ensure proper liquidification of hot vapor. The photograph of the condenser is presented in **Figure 3.4**



Figure 3.4: Photograph of the condenser

3.4.4 Thermocouple:

K-type single thread thermocouple was used, which was also collected from Khulna town. The photograph of the K-type single thread thermocouple is presented in **Figure 3.5**



Figure 3.5: Photograph of the K-type single thread thermocouple

3.4.5 Temperature regulator:

XMTD type temperature regulator was used, which was also collected from Khulna town. The photograph of the temperature regulator is presented in **Figure 3.6**



Figure 3.6: Photograph of the temperature regulator

3.5 Experimental procedure:

850 gm semi vulcanized rubber and 850 gm full vulcanized rubber was take into the pressure cooker accordingly one after another. Before dosing, the cooker with cover handle the flow of nitrogen gas was supplied to ensure oxygen free atmosphere. The pyrolysis process was carried out between 250°C – 350° C. Then the heater was switched on and the temperature of the pressure cooker was allowed to increase to the value of 250° C, 300° C, 350° C indicated by temperature regulator. The K-type single thread thermocouple was placed in the pressure cooker for the purpose of temperature record which was connected to the temperature regulator. At the same time temperature was controlled by temperature regulator. During pyrolysis process, the vapor was condensed and collected in a measuring cylinder and weighted. The non-condensable gas was vented through the exhaust pipe. The residue was then collected and weighted after cooling the reactor.

3.6 Process Flow Chart:

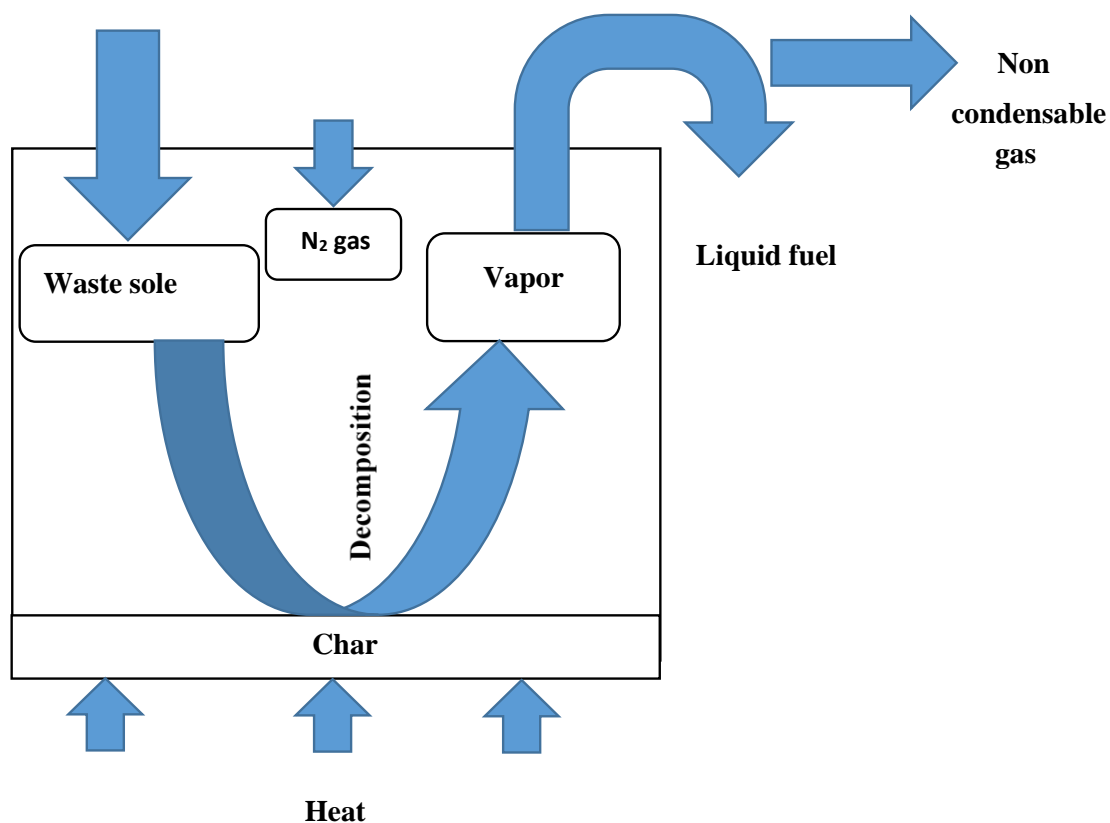


Figure 3.7: Flow diagram of pyrolysis process

3.7 Physio-chemical Analysis:

In order to analyze the extracted crude oil physio-chemically, FTIR and TGA analysis were done.

3.7.1 FTIR Analysis:

The spectrum for crude oil of semi and full vulcanized rubber were recorded with FTIR 8400S Shimadzu spectrophotometer. The spectral range acquired was from 4000-700 cm^{-1} , with an accumulation of 20 scans and resolution of 4 cm^{-1} .

3.7.2 TGA Analysis:

The thermograms for crude oil of semi vulcanized and full vulcanized rubber were recorded with TGA-50, Shimadzu, Japan. For semi and full vulcanized rubber approximately 3.039 mg and 14.224 mg of sample were taken respectively. The test was performed in alluminium cell under an inert nitrogen atmosphere at a heating rate of 10°C/min and the flow rate was 10ml/min. The initial temperature was room temperature and the final temperature was 600°C and the hold time was five minutes.

CHAPTER 4

DATA COLLECTION

4.1 Introduction:

In this chapter, only various experimental data are given.

4.2 Experimental data:

In case of semi vulcanized rubber for different temperatures the amount of extracted crude oil, char and effect of temperature on product distribution during pyrolysis process is shown in table 4.1 & table 4.2

Table 4.1 Product yields at different temperature during pyrolysis of semi vulcanized rubber

No. of observations	Temperature in °C	Oil (ml)	Char (kg)	Residence time (min)
01	250	60	0.70	80
02	300	110	0.55	55
03	350	180	0.35	40

Table 4.2: Effect of temperature on product distribution of pyrolysed semi vulcanized rubber

No. of Observations	Temperature in °C	% of product			Residence time (min)
		Oil	Char	Gas	
01	250	7.58	82.35	10.07	80
02	300	12.94	64.70	22.36	55
03	350	21.17	41.17	62.34	40

- In case of full vulcanized rubber for different temperatures the amount of extracted crude oil, char and effect of temperature on product distribution during pyrolysis process is shown in table 5.1 & table 5.2

Table 4.3 Product yields at different temperature during pyrolysis of full vulcanized rubber

No. of Observations	Temperature in °C	Oil	Char	Residence time (min)
01	250	20	0.75	95
02	300	50	0.66	60
03	350	80	0.49	45

Table 4.4: Effect of temperature on product distribution of pyrolysed full vulcanized rubber

No. of Observations	Temperature in °C	% of product			Residence time (min)
		Oil	Char	Gas	
01	250	2.35	88.23	9.42	95
02	300	5.88	77.64	16.48	60
03	350	9.41	57.64	32.95	45

Table 4.5: FTIR spectrum table for crude oil of semi vulcanized rubber for functional group

Peak	Absorption (cm ⁻¹)	Functional group
754.17	770 – 730 and 710 – 690	mono subst. benzenes
889.18	915 – 870	R ₂ C=CH ₂
964.41	1100 – 900	Silicate ion

Peak	Absorption(cm^{-1})	Functional group
1033.85	1130 – 1030	Sulfate ion
1072.42	1130 – 1030	Sulfate ion
1282.66	1350 – 1250	Organic phosphate ion
1381.03	1420 – 1370	Organic sulfates
1454.33	1490 – 1410	Carbonate ion
1600.92	1550 – 1610	Carboxylate
1705.07	1725 – 1700	Acid (RCOOH)
2866.22	2975 – 2850	Alkane(C-H)
2929.87	2975 – 2850	Alkane(C-H)
2956.87	2975 – 2850	Alkane(C-H)
3026.31	3100 – 3020	Alkene (C=C-H)
3064.89	3100 – 3020	Alkene (C=C-H)

Table 4.6: FTIR spectrum table for crude oil of semi vulcanized rubber for type of bond

Peak	Frequency	Type of bond
754.17	790-650 770-735	-C-H(bending)
889.18	895-885	-C-H(out of plane)
964.41	1000-960	-C-H(bending)
1033.85	1250-950	-C-H(bending)
1072.42	1250-950	-C-H(bending)
1282.66	1360-1180	-C-N (stretch)

Peak	Frequency	Type of bond
1381.03	1385-1370	-C-H(bending)
1484.33	1485-1445	-C-H(bending)
1600.92	1680-1600	C=C(stretch)
1705.07	1740-1680	C=O(stretch)
2866.22	3000-2800 3300-2500	C-H(stretch) -O-H(stretch)
2929.87	3000-2800 3300-2500	C-H(stretch) -O-H(stretch)
2956.87	3000-2800 3300-2500	C-H(stretch) -O-H(stretch)
3026.31	3100-3000	C=C(stretch)
3064.89	3100-3000	C=C(stretch)

Table 4.7: FTIR spectrum table for crude oil of full vulcanized rubber for functional group

Peak	Absorption (cm ⁻¹)	Functional group
3375.43	3500-3300	Stretch alkenes
1639.49	1680-1600	Stretch amines

Table 4.8: FTIR spectrum table for crude oil of full vulcanized rubber for type of compound

Peak	Frequency	Type of bond
3375.43	3500-3300	N-H(stretch)
1639.49	1680-1600	C=C(stretch)

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction:

In this chapter results and discussion has described broadly with some graphs and diagrams. During thermal pyrolysis process, 300 ml crude oil from semi vulcanized rubber and 150 ml from full vulcanized rubber was obtained with significant amount of char and gas.

5.2 Effect of temperature and time on product yield:

In case of semi vulcanized rubber the effect of temperature on product shown in following figure 5.1, where horizontal axis present temperature and vertical axis present % of product i,e; crude oil, char, gas. It shows that with increase of temperature the amount of crude oil and gas increased but the amount of char decreased.

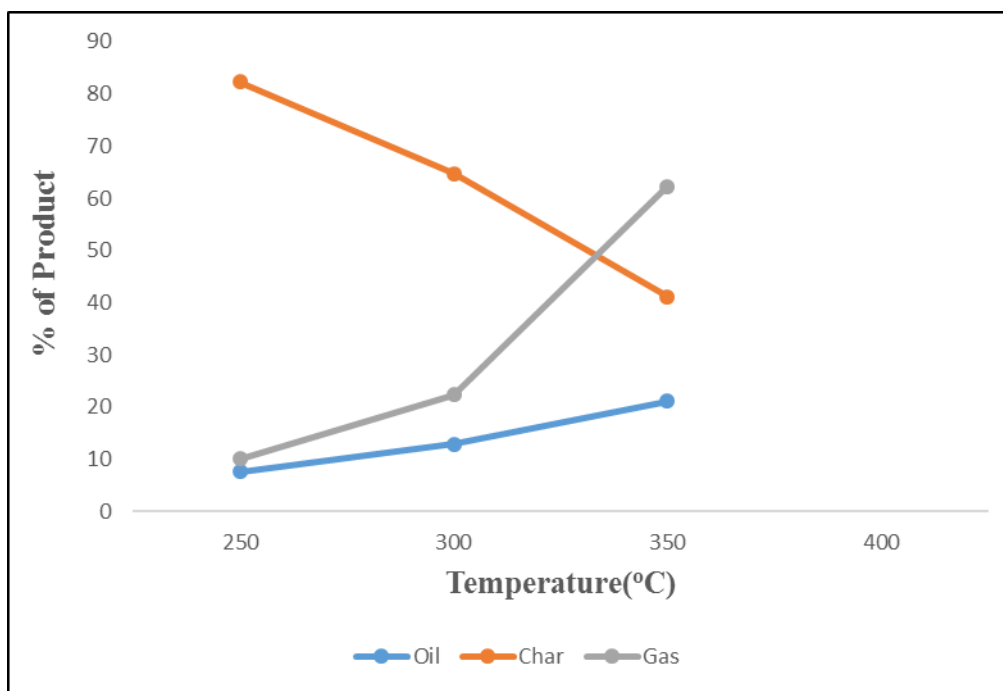


Figure 5.1: Effect of temperature on product for semi vulcanized rubber

The effect of time on product for semi vulcanized rubber is shown in figure 5.2 where horizontal axis present time and vertical axis present % of product i.e; crude oil, gas, char. It shows that with increase of time the amount of crude oil and gas increased but the amount of char decreased.

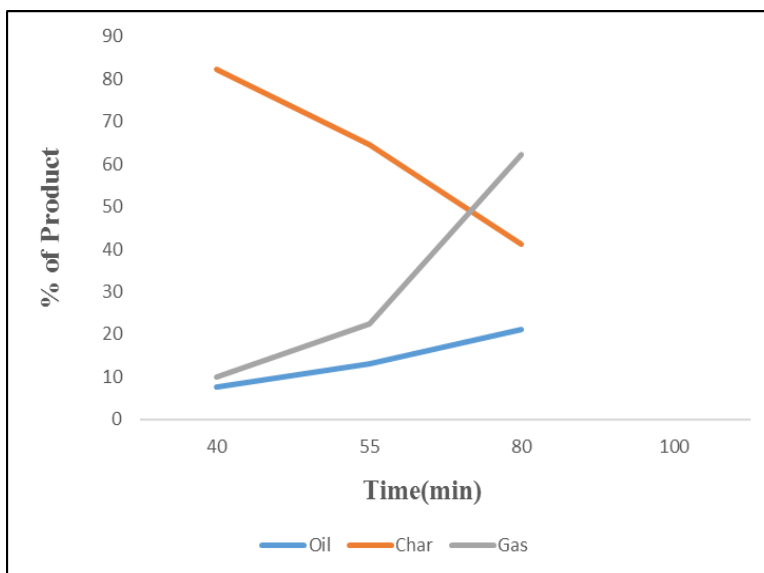


Figure 5.2: Effect of time on product for semi vulcanized pyrolysis

Similarly, in case of full vulcanized rubber the effect of temperature on product shown in following figure 5.3, where horizontal axis present temperature and vertical axis present % of product i.e; crude oil, char, gas. It shows that with increase of temperature the amount of crude oil and gas increased but the amount of char decreased.

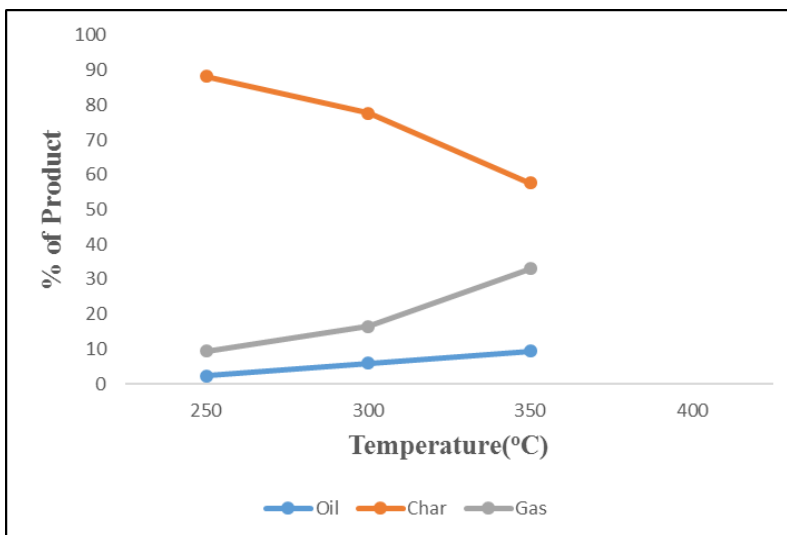


Figure 5.3: Effect of temperature on product for full vulcanized pyrolysis.

The effect of time on product for full vulcanized rubber is shown in figure 5.4, where horizontal axis present time and vertical axis present % of product i.e crude oil, gas, char. It shows that with increase of time the amount of crude oil and gas increased but the amount of char decreased.

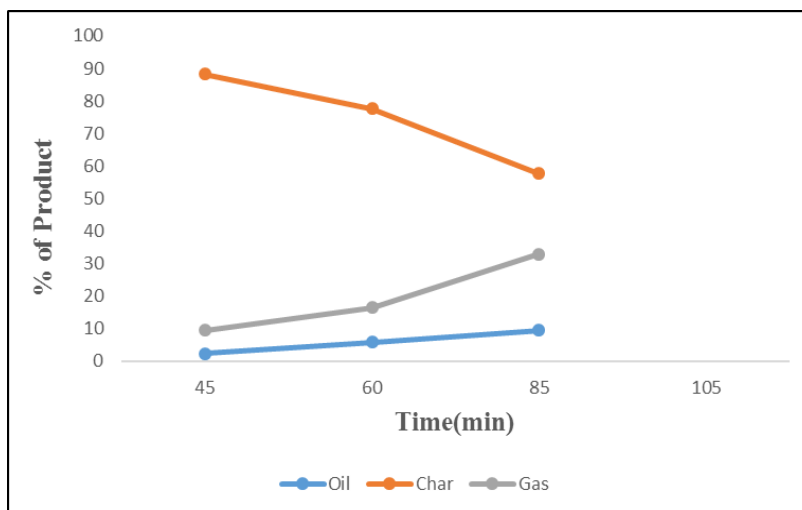


Figure 5.4: Effect of time on product for full vulcanized pyrolysis.

5.3 Comparison of product yield from semi and full vulcanized rubber:

For both semi and full vulcanized rubber the effect of temperature on crude oil is shown in figure 5.5 where horizontal axis presents temperature and vertical axis presents % of oil. It shows that the amount of crude oil increased with temperature for both but the amount of oil extracted from semi vulcanized rubber is greater than full vulcanized.

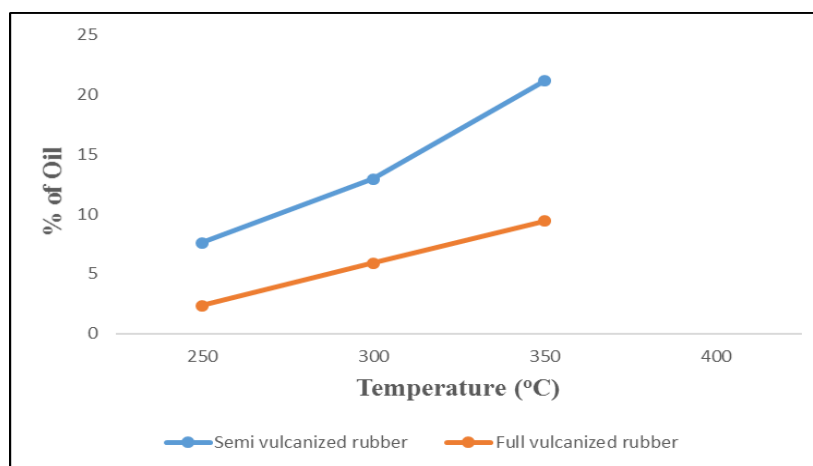


Figure 5.5: Effect of temperature on oil for both semi & full vulcanized rubber

For both semi and full vulcanized rubber the effect of temperature on char is shown in figure 5.6, where horizontal axis presents temperature and vertical axis presents % of char. It shows that the amount of char decreased with temperature for both but the amount of char from full vulcanized rubber is greater than semi vulcanized.

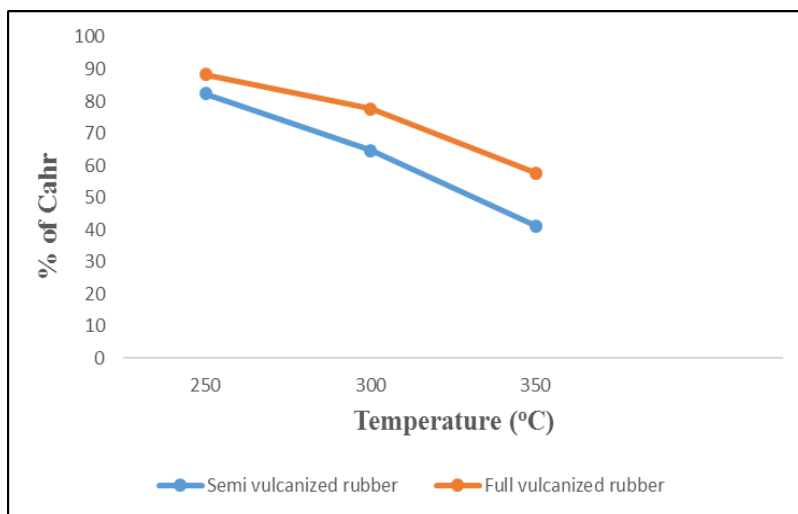


Figure 5.6: Effect of temperature on char for both semi & full vulcanized rubber

For both semi and full vulcanized rubber the effect of temperature on gas is shown in figure 5.7, where horizontal axis presents temperature and vertical axis presents % of gas. It shows that the amount of gas increased with temperature for both but the amount of gas from semi vulcanized rubber is greater than full vulcanized.

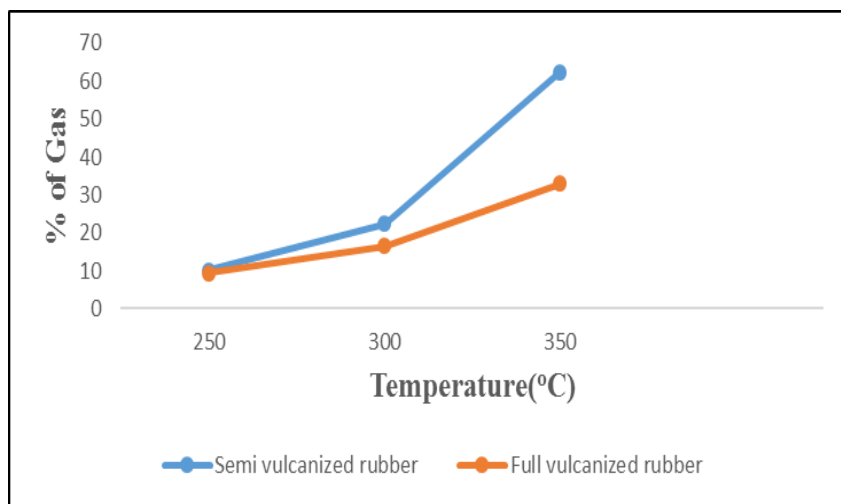


Figure 5.7: Effect of temperature on gas for both semi & full vulcanized rubber

5.4 FTIR analysis:

5.4.1 For Semi vulcanized rubber:

The spectrum of sample is given bellow:

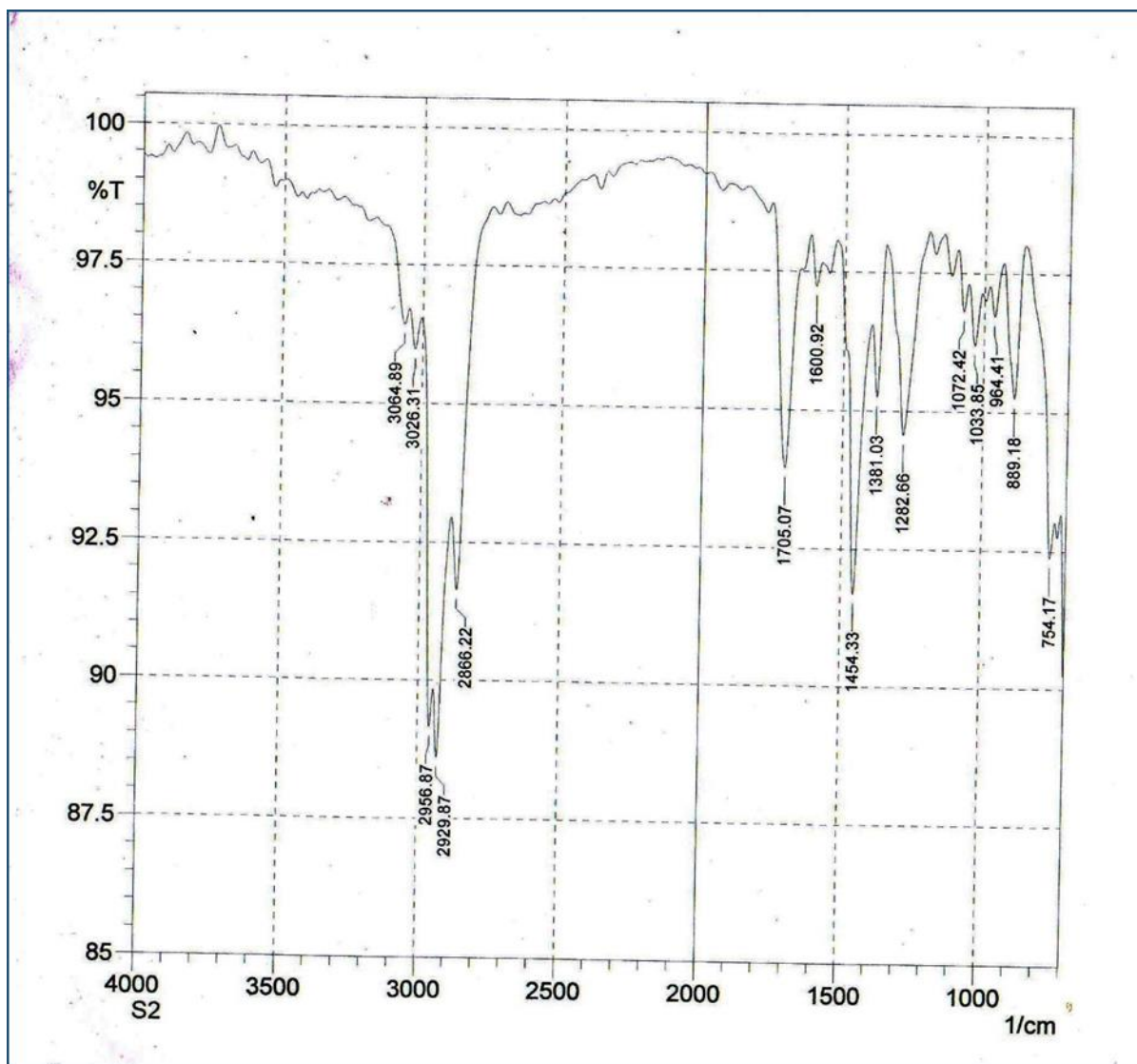


Figure 5.8: Spectra obtained by FTIR Analysis for crude oil of semi vulcanized rubber

Horizontal axis of the diagram represents wavenumber(cm^{-1}) and vertical axis represents transmittance (%). Each dip in the spectrum is called peak. There are 15 peak in the spectrum.

FTIR spectrum of sample shows there are presence of alkane, alkene, carboxylate, organic sulfate, organic phosphate, amino group and various types of chemical bond such as C-H, C-N, C=O etc.

To be a fuel, crude oil must have hydrocarbon group, alkane, alkene, carboxylic acid group. The crude oil extracted from semi vulcanized rubber have all of them.

Beside this crude oil burn itself when it fired like kerosene. 3 ml of this sample burn for 2.45 min and produce temperature of about 328°C. So, we can say that the crude oil extracted from semi vulcanized rubber is a one kind of fuel. Most probably it could be kerosene, because in finger print region of spectrum, it match at a several point beside it smells a little bit like kerosene.

5.4.2 Full vulcanized rubber:

The spectrum of sample is given bellow:

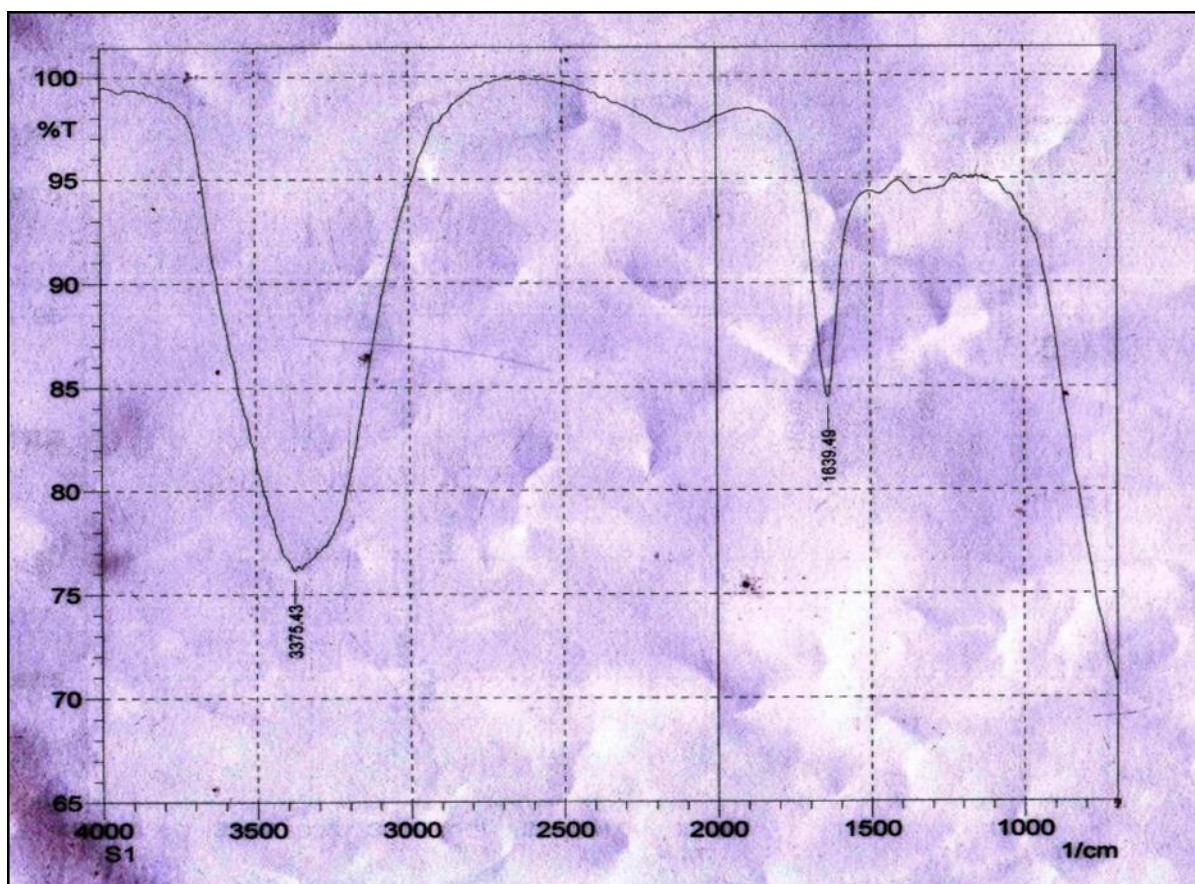


Figure 5.9: Spectra obtained by FTIR Analysis for crude oil of full vulcanized rubber

Horizontal axis of the diagram represents wavenumber(cm^{-1}) and vertical axis represents transmittance(%). Each dip in the spectrum is called peak. There are 2peak in the spectrum.

In the case of full vulcanized rubber, sample FTIR spectrum show there are presence of alkene and amide group.

This crude oil helps to burn when fired but the flame color of fire become greenish. 3 ml of this crude oil sample burn for about one minute.

5. TGA analysis:

5.5.1 For semi vulcanized rubber

The thermogram of the sample is shown in following **figure 5.10**

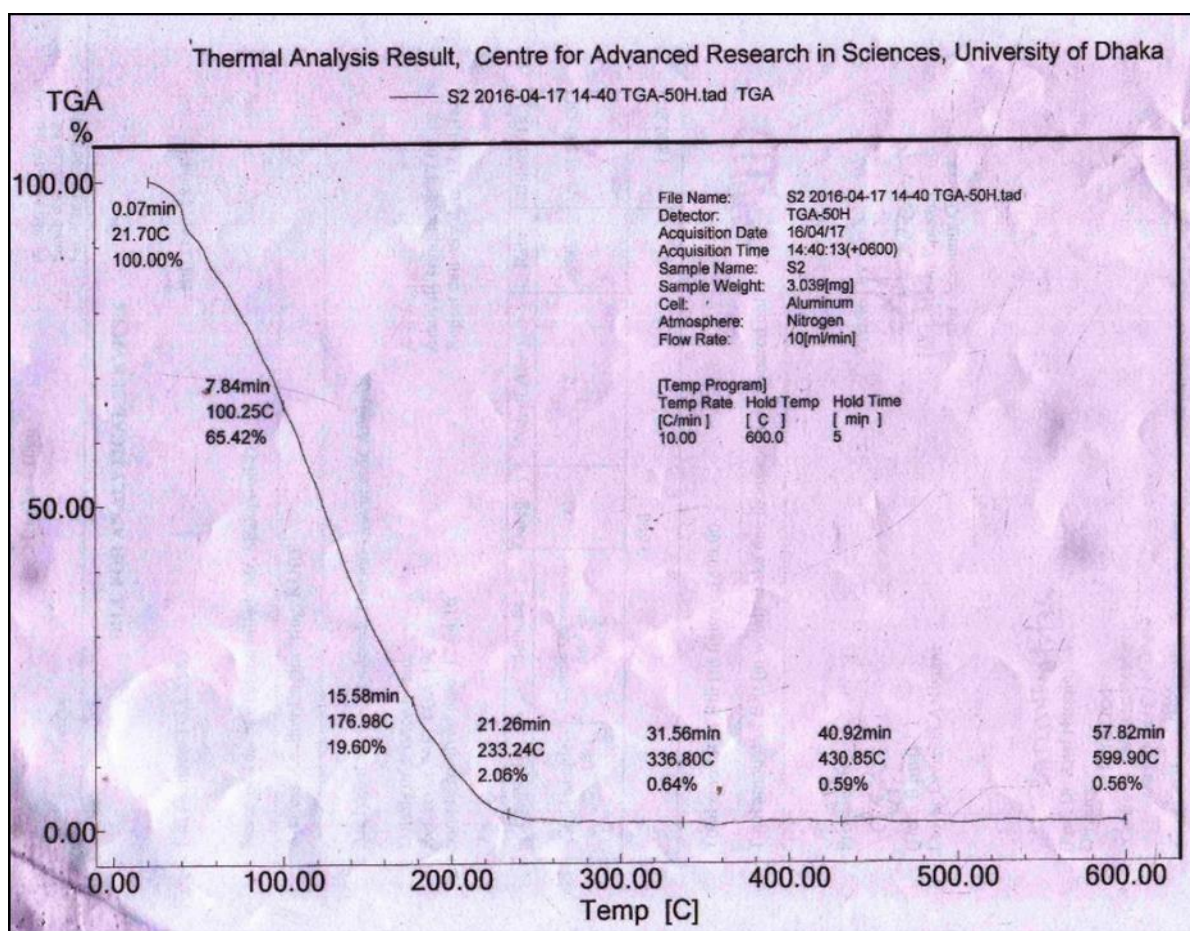


Figure 5.10: Thermogram for crude oil of semi vulcanized rubber

Horizontal axis of the diagram represents percentage of mass loss and vertical axis represents temperature ($^{\circ}\text{C}$). This TGA plot shows the decomposition for crude oil of semi vulcanized rubber. The TGA result shows that the decomposition occurs in one mass loss steps which is a single stage decomposition. The corresponding TGA curve provide the decomposition rate and which is helpful for evaluating the mass loss steps accurately. From the thermogram the crude oil of semi vulcanized rubber undergoes thermal degradation beginning at 21.70°C with a total mass loss of 100.00% and end at 233.24°C with a total mass loss of 2.06%.

5.5.2 For full vulcanized rubber:

The thermogram of the sample is shown in following **figure 5.11**

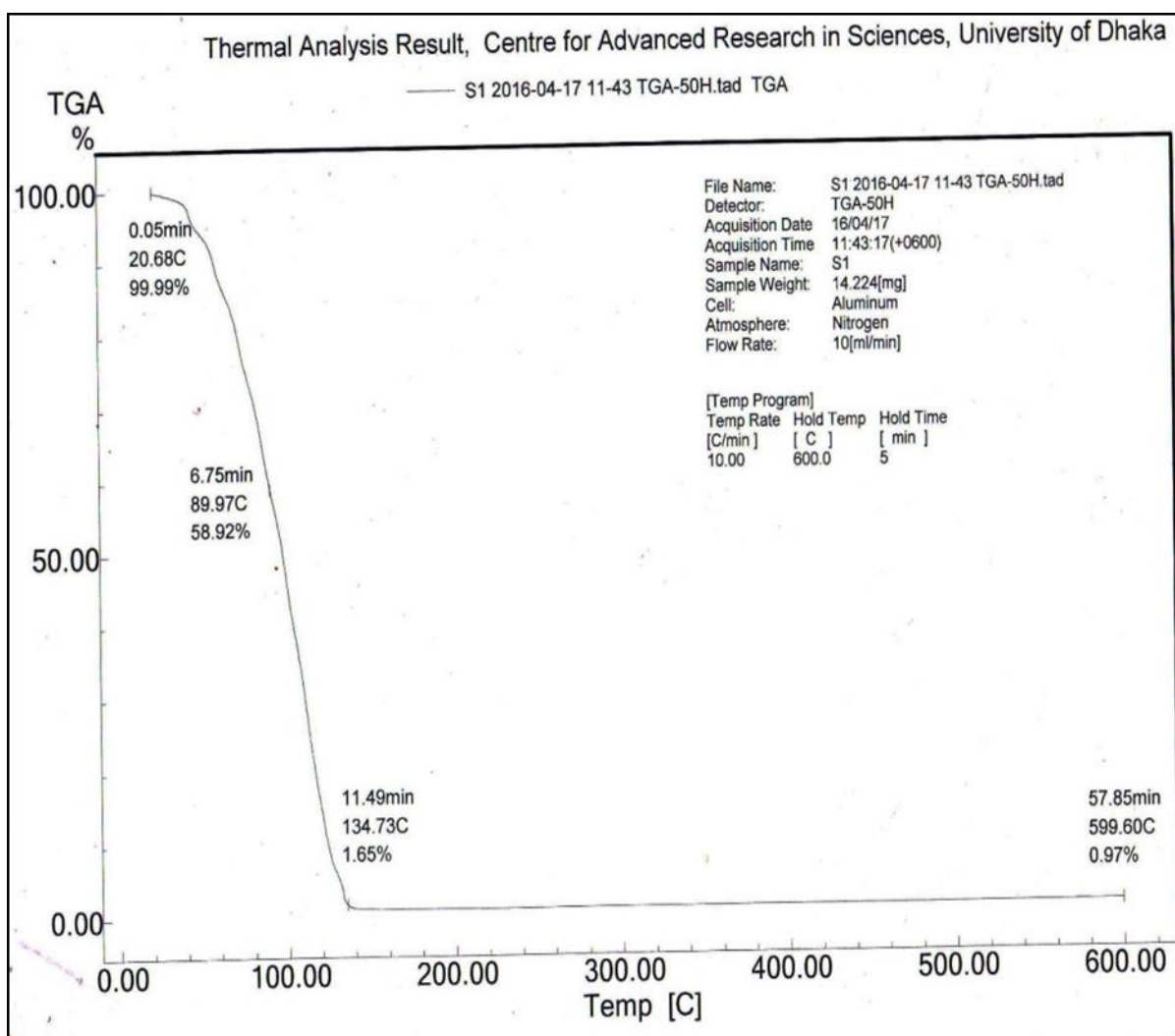


Figure 5.11: Thermogram for crude oil of full vulcanized rubber

This TGA plot shows the decomposition for crude oil of full vulcanized rubber. The TGA result shows that the decomposition occurs in one mass loss steps which is a single stage decomposition. The corresponding TGA curve provide the decomposition rate and which is helpful for evaluating the mass loss steps accurately. From the thermogram the crude oil of full vulcanized rubber rubber undergoes thermal degradation beginning at 20.68°C with a total mass loss of 99.99% and end at 134.73°C with a total mass loss of 1.65%. From the thermogram:

- the horizontal portion indicate the regions where there is not weight change.
- the curve portion is indicate of weight loss.

Thermograms of semi vulcanized and full vulcanized rubber shows that the thermal stability of semi vulcanized rubber is greater than full vulcanized rubber.

CHAPTER 6

LIMITATIONS AND FUTURE SCOPE

6.1 Introduction:

In this chapter limitations of the thesis experiment has described as well as giving probable future scope of the final product.

6.1 Conclusion:

From the study of thermal pyrolysis and test analysis of extracted crude oil following conclusions can be summarized as follow:

- Significant amount of Oil, Char and Gas are obtained from the sample.
- In the temperature range of 250⁰C to 350⁰C oil and gas is increased with the increase of temperature but char is decreased.
- Extracted crude oil from semi vulcanized rubber contains more functional groups and chemical bonds than full vulcanized rubber.
- Extracted crude oil from semi vulcanized rubber is more thermally stable than full vulcanized.
- The extracted crude oil from semi vulcanized rubber can be used as fuel after proper refining.
- Semi vulcanized rubber provides more effective result than full vulcanized rubber.

6.2 Future Scope:

- The gas emitted in the atmosphere during production of fuel can be tested to identify the presence of harmful substance which can be removed through proper treatment.
- The residue char can be recovered and used as solid fuel.
- Energy balance, calorific value, flash point of fuel can be determined.

6.3 Limitation:

- There was no proper arrangement of gas emission.
- There was no adequate supply of nitrogen gas.
- The temperature of source was constant.

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