Study of Thermo-Kinetics and Synergistic Effects on Tri-pyrolysis of Lignite Coal, Rice Straw and Polyethylene Terephthalate

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Supervisor: Dr. Umair Sikandar

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(2024)

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DEDICATION

By the grace of Almighty Allah, who is the most Beneficent and the most merciful.

This research is dedicated to my parents, who have always been my source of guidance and support.

To my supervisor who shared his knowledge, gave advice, and encouraged me to fulfill my tasks.

And to all my fellows, with whom I worked with and shared good memories.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

A	Ash
CV	Calorific Value
EDX	Energy Dispersive X-Ray
FC	Fixed Carbon
FTIR	Fourier Transform Infrared Spectroscopy
GCV	Gross Calorific Value
HDPE	High Density Polyethylene
HHV	Higher Heating Value
L_c	Lignite Coal
LDPE	Low Density Polyethylene
LHV	Lower Heating Value
M	Moisture
PC	Polycarbonate
P_{ET}	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
R_s	Rice Straw
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
VM	Volatile Matter
XRD	X-Ray Diffraction

ABSTRACT

The fast depletion of non-renewable energy sources, environmental concerns, and energy security are demanding less and effective use of fossil fuels. Due to these concerns, more focus is required on biofuels to be obtained from thermochemical and biochemical conversion processes. Biofuels obtained from biomass, coal, and waste plastic have gained much attention to be used as the replacement to fossil fuels. This utilization of waste biomass and plastic also serves as a solution to domestic solid waste. Pyrolysis is one of the potential thermochemical processes being focused for this purpose. Thermogravimetric Analyzer (TGA) is one of the important technologies helpful in studying the kinetic and thermodynamic parameters and synergistic effects in the process. The synergistic effects have also been studied here in tri-pyrolysis of feedstock blends. Starting from basic introduction, the samples preparations, blending, characterization and analysis, thermo-kinetics, and synergistic effects have been studied in this research work.

This thesis report basically presents the research work on tri-pyrolysis of lignite coal, rice straw, and polyethylene terephthalate for different blend ratios. It presents a comparison for pyrolysis of individual samples and blend ratios. It also presents a study of increase in conversion and yields in case of blend ratios due to the presence of materials particle interactions and synergistic effects. The study reports first time the tri-pyrolysis of lignite coal, rice straw, and PET plastic blends. Study was carried out in TGA. Samples were placed in TGA, and temperature was raised from ambient to 900 °C. TGA curves were obtained for weight loss % against temperature. Based on the results of TGA, the thermo-kinetic analysis, and synergistic effects in different blend ratios were studied. Model-Fitting Kinetic models were applied for detailed Thermo-Kinetics study of the tri-pyrolysis of blends at a single constant heating rate of 10 °C/min. During the whole process, an inert atmosphere was provided inside TGA with N_2 inert gas with flow rate of 30 mL/min. Finally, the results were concluded providing a lead for effective biofuels production applications.

Keywords: Tri-pyrolysis; Blends; TGA; Thermo-Kinetics; Synergistic effects; Biofuels

CHAPTER 1: INTRODUCTION

1.1 Background

Waste disposal and energy supply are the two major concerns due to the large-scale urbanization, industrialization and population growth now a days [1, 2]. Energy is considered one of the essential commodities required for the well-being of human beings. Today, whole the world is facing global energy crisis. Affordable and sustainable energy supply is one of the major concerns of all developing nations [3]. World is facing challenges to meet the needs of energy supply due to the rapid increase in urbanization, industrialization and population growth [4]. Similarly, the rapid increase in world population and large scale urbanization and industrialization are causing generation of huge amounts of solid waste [5, 6]. Countries with the rapid growth in economy, industrialization, urbanization and population are the main contributors towards the generation of large amounts of solid waste (SW) [7]. These countries include many Asian nations with growing economy. According to a review, India with the population of over 1.2 billion generates 0.5 kg of solid waste per person every single day [8]. China is also facing an issue of huge amounts of solid waste generation. The waste generation rate in China was 0.5 kg/capita/day back in year 1980. This solid waste generation rate increased to 0.98 kg/capita/day in year 2006 [9]. Meanwhile this rate of solid waste generation has increased rapidly in past few years not only in China but also in other countries with rapidly growing population and economy.

Municipal solid waste (MSW) produced because of rapid population growth, urbanization, and industrialization, mainly includes waste plastic, biomass, municipal waste, industrial refuse, agricultural waste, paper, wood, glass, rubber, litter, leather, textiles, waste food, metals, and garbage [10]. Waste disposal is one of the major issues in developing countries. Municipal solid waste generated at high rate, requires a proper management and utilization. Mostly the municipal solid waste (MSW) is disposed in the landfills [11]. For the ultimate and easy disposal of solid waste, landfilling has been considered as the most dominant technology from ancient times [12]. But, landfilling technologies are not a proper solution to this problem as in most cases the leachate produced from landfills requires further treatments [13]. Similarly landfills become a cause of leachate inclusion to ground water and ground water is getting polluted and contaminated [14]. There are also many other environmental impacts of landfills caused because of gas and leachate generation [15]. Besides environmental impacts of landfills, there are also some socio-economic impacts of landfills [16]. Therefore, it is required to properly utilize this municipal solid waste which includes biomass, waste plastic, and agricultural and crop residues by using modern technologies because landfills are not a proper solution to municipal solid waste disposal. Crop residues which include the remains left after harvesting like leaves, roots, and stalks, are also not being utilized properly. These residues can also be utilized properly by using technology.

Fast depleting fossil fuels are also a major concern worldwide [17-19]. Fossil fuels are being used as a main source of energy worldwide [19-21]. Fossil fuels include natural gas, crude oil, and coal [20]. Natural gas is a gaseous fossil fuel. Coal falls in the category of solid fossil fuels and all the crude oil fractions fall in the list of liquid phase fossil fuels. They are being used as a primary source of energy for centuries to meet the energy needs of world. But use of fossil fuels as a source of energy, is causing environmental impacts [22]. Huge amount of greenhouse gases like carbon dioxide, carbon monoxide, oxides of nitrogen and oxides of sulfur are being added to our atmosphere [23, 24]. All these gases are harmful and causing rise of Earth temperature, global warming, and climate changes [22, 25]. Besides the environmental impacts, the fast depletion of these fossil fuels is also an area of major concern worldwide. Fossil fuels are depleting at very high rate. Therefore, world needs a permanent solution to these two major problems that are environmental concern and fast depletion of fossil fuels. They must be replaced with sustainable, non-conventional and environmental friendly fuels [26]. Biofuels are being considered as a replacement to these conventional fossil fuels [27-29]. These biofuels can be produced from the municipal solid waste, biomass, and coal. Biofuels are sustainable, and environmentally friendly fuels which can replace these conventional fossil fuels [30].

Biofuels are the fuels produced through biochemical and thermochemical conversion processes [31]. Biochemical conversion processes include aerobic and anaerobic digestion, and fermentation [32-34]. On the other hand, thermochemical routes include gasification, pyrolysis, torrefaction, and carbonization [35]. Gasification gives gaseous biofuels as the main products [36]. Syn-gas is the gaseous biofuel which contains carbon monoxide and hydrogen gases. Carbon monoxide gas is separated out from hydrogen gas and hydrogen gas is then used as a sustainable, environmentally friendly fuel for fuel cells mainly. Fuel cells using hydrogen as a fuel, are used to generate electrical energy [37]. Pyrolysis gives liquid biofuel as the main product [38, 39]. Carbonization and torrefaction give solid biochar as their main product. All these biochemical and thermochemical conversion routes are used to convert biomass, solid waste including waste plastics, and solid fossil fuels like coal into the biofuels. The produced biofuels can be used to replace those conventional and rapidly depleting fossil fuels. Hydrogen, biochar, and biodiesel are the most common biofuels that can be used for energy supply in recent times [40]. Bio-oil or biodiesel is the most common liquid biofuel produced by pyrolysis [41-43].

Therefore, fast depletion of non-renewable energy sources, environmental concerns, and energy security is demanding less and effective use of fossil fuels [18, 44]. Solid waste disposal is other major concern worldwide. Due to these concerns more attention is being given to thermochemical and biochemical conversion processes to produce biofuels. Biofuels obtained from biomass, coal, and waste plastic have gained much attention as these fuels can be used as a replacement to conventional high carbon emitting fossil fuels [45]. Pyrolysis with liquid biofuel as its main product, is one of the thermochemical processes being focused for this purpose. The pyrolytic thermochemical conversion of a feedstock is carried out inside a pyrolyzer [46]. This conversion can be studied in a Thermogravimetric Analyzer (TGA) where we can analyze the conversion rates of the biofuel products. Thermogravimetric Analyzer (TGA) coupled with Fourier Transform Infrared Spectrometer (FTIR) is the important technology helpful in analyzing the conversion rates, controlling the greenhouse emissions, and replacing fossil fuels by biofuels. TGA coupled with FTIR is used for the online detection of the mass loss of feedstock during conversion and for detecting the kinetic parameters of the process [47-49].

1.2 Bio-fuels Demand

The three main fossil fuels are oil, natural gas, and coal. Coal is considered to be the second largest consumable fossil fuel in the world [18]. The research work shows that coal will remain the second largest source of primary fuel till 2030 [50]. The worldwide consumption of fossil fuels from 1965 to 2030 is shown in Figure 1.1. The world's crude oil reserves have been estimated to be diminished by the year 2030. And it has also been estimated that coal will be the only fossil fuel left after year 2042. It means that all other fossil fuels will be completely depleted by the year 2042. After that, the utilization of coal for energy purpose will jump to higher extent. It has been estimated that world's coal reserves are also enough to provide energy only till year 2112 [18]. Therefore, there must be an alternate source of energy to be considered. Biofuels are being considered as a main replacement. Biofuels are being paid attention at research scale for being considered as an important source of energy in future and they will be in much demand after world's conventional fossils fuels depletion.

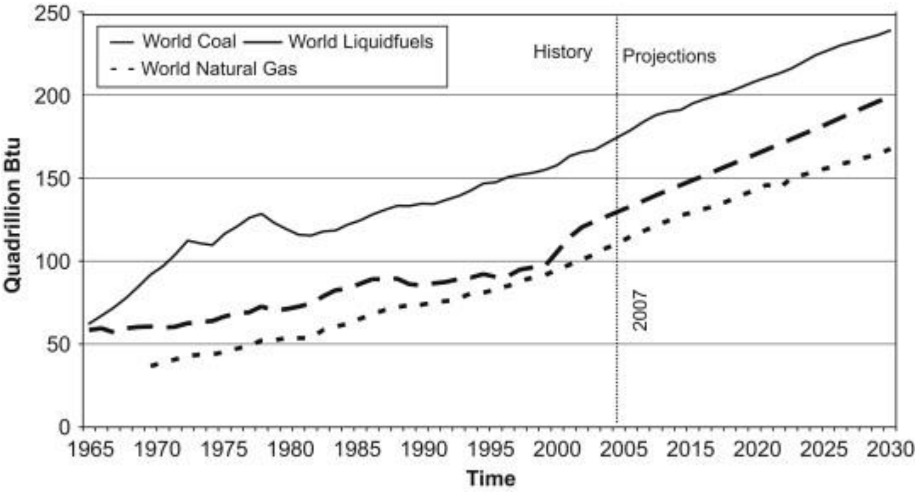

Figure 1.1: The worldwide consumption of fossil fuels from 1965 to 2030 [18].

1.3 Feedstock

Low ranked lignite coal, rice straw (a crop residue), and PET plastic waste are under consideration as feedstock materials in this study. Before preparing the samples, all these three samples are required to be collected. Coal is collected from a specific region. Waste plastic is available easily at domestic scale. It can be collected from MSW. While the crop residues can be collected from fields e.g., rice straw (R_S) and wheat straw (W_S) can be collected from fields easily.

1.3.1 Chemical Structure

Coal is one of the major fossil fuels of world. Its formation occurs over millions of years through a process that is called carbonation. Coal is mostly formed from the accumulation of large amounts of plant debris under Earth crust. The plant debris are degraded and broken down to the simpler compounds by the microbiological activity or abiotically. The debris are then gradually covered by the silts or thick inorganic sediments which provide a shield against the further degradation of this matter. Then this matter is chemically altered by heat to form coal when the matter is continuously compacted by the overburden pressures. This is how the buried remains of plants are converted to coal under earth crust [51].

The plants that undergo decay to form coal are composed of mainly carbohydrates, glycosides, proteins, waxes, fats, resins, alkaloids, enzymes, chitins, pigments, purines, cellulose, hemicellulose, and lignin. During the degradation process, the plant waxes, fats, and resins generally resist the microbial degradation and undergo the oxygen-promoted polymerization under the strong aerobic activity. Cellulosic matter is quickly broken down to the simple sugars. While the pigments survive the alteration for long time. Lignin is oxidized to form complex 'humic acids' which are then converted to derivatives of water soluble benzenoids. Glycosides are hydrolyzed to give sugars. And the proteins are denatured to give free amino acids and undefined slimes. All these processes convert the plant matter to form 'humus'. Then this residue is further altered when the degradation products interact with each other. This rate of decay generally increases with the increase of temperature under the Earth crust. The microbiological decay can be of two types, aerobic and anaerobic decay. Aerobic decay is based on the interaction of oxygen. While the anaerobic decay is in the absence of oxygen, and it is mostly carried out by bacterial hydrolysis and reduction. The abiotic alteration takes place when the decay matter is buried under the sediments. It is carried out by the compaction, dehydration, stripping, and condensation reactions taking place in series. Finally, coal is formed from the plant debris after all these decay and degradation processes under high pressure and temperature conditions beneath Earth crust [51].

Coal is mainly composed of carbon with some minor amounts of other elements including hydrogen, oxygen, nitrogen and sulfur. The molecular structure of coal with molecular formula $C_{169}H_{128}O_{10}N_2S$ is shown in Figure 1.2 and Figure 1.3 shown below.

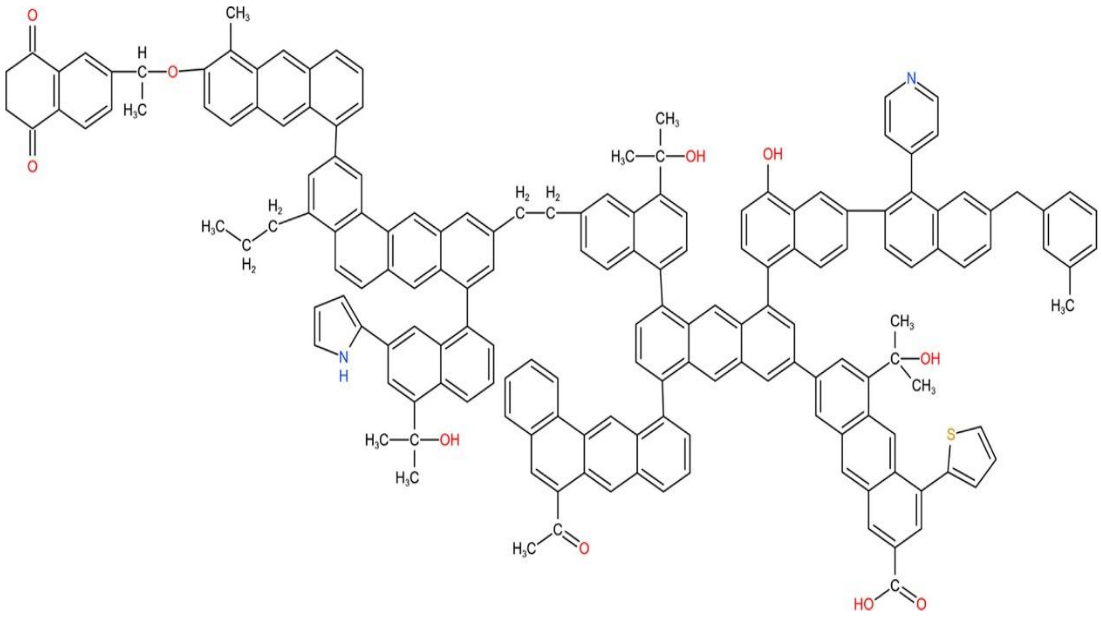

Figure 1.2: Molecular structure of coal with molecular formula $C_{169}H_{128}O_{10}N_2S$ [51].

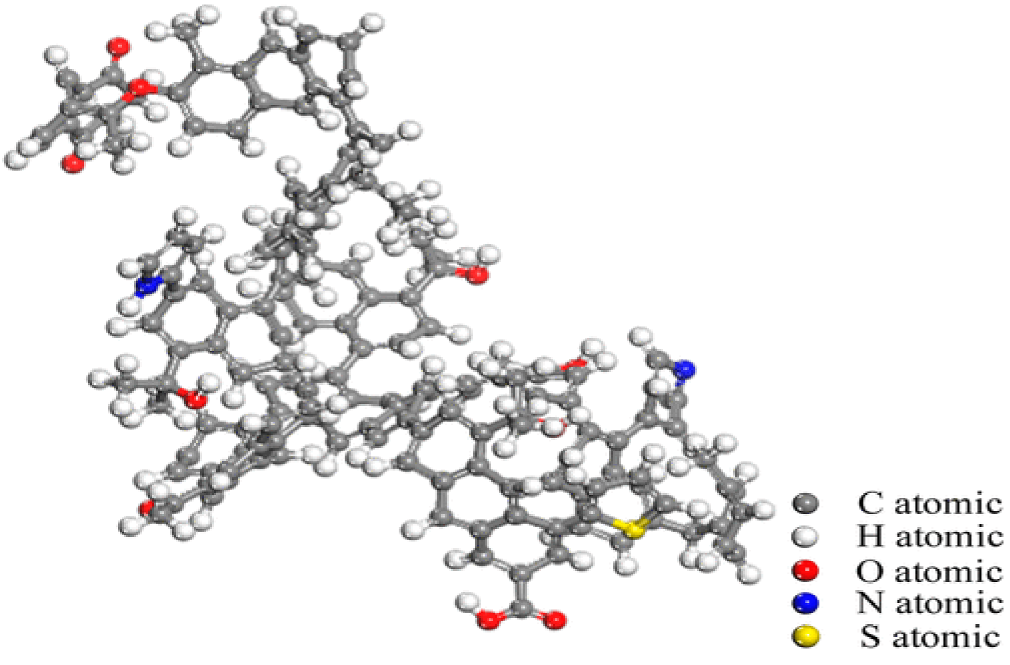

Figure 1.3: Molecular structure of coal with molecular formula $C_{169}H_{128}O_{10}N_2S$ in 3D [51].

Polyethylene terephthalate (PET) plastic is a polymer of ethylene terephthalate monomers. The chemical formula of this monomer is $C_{10}H_8O_4$. So, the PET polymer is composed of these alternating $C_{10}H_8O_4$ monomer units and PET polymer has formula $[C_{10}H_8O_4]_n$. PET plastic is mainly used to prepare PET bottles which are used for carbonated drinks. The chemical structure of PET plastic is shown in Figure 1.4.

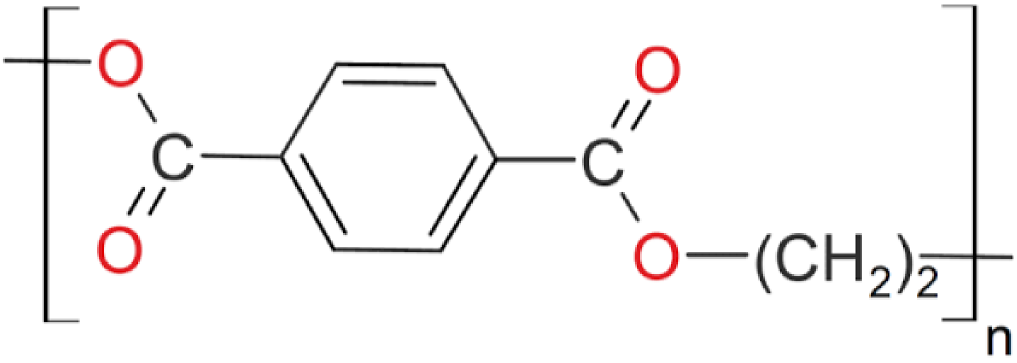

Figure 1.4: Chemical structure of polyethylene terephthalate polymer $[C_{10}H_8O_4]_n$ [92].

The Figure 1.5 given below shows the terephthalate group and ethylene group present in the chemical structure of a monomer of PET plastic.

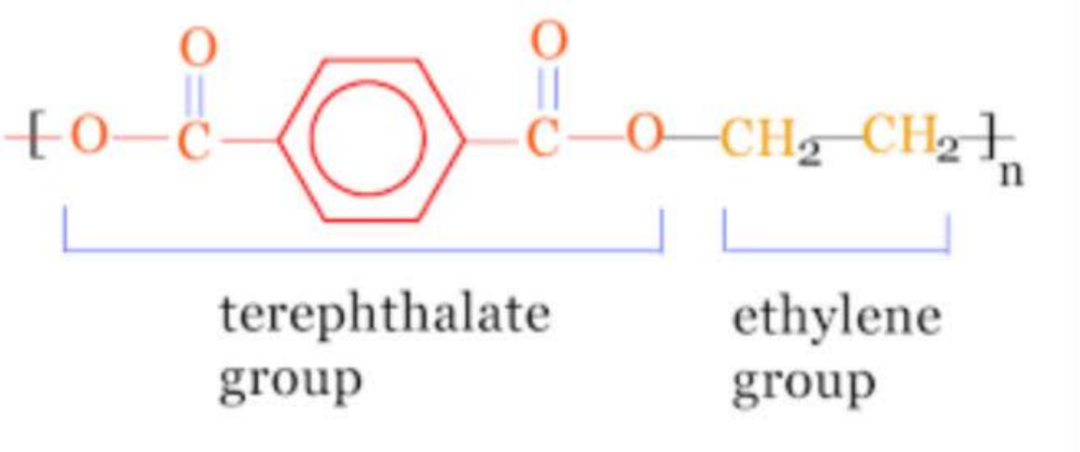

Figure 1.5: The terephthalate group and ethylene group present in a monomer of PET [92].

Rice straw is mainly a lignocellulosic biomass. It contains 12% lignin, 25% hemicellulose and 38% cellulose. While the ash and extractives % varies as 7.45±0.31% and 11.93±0.11% (% by w/w dry biomass) respectively. Figure 1.6 and Figure 1.7 show the chemical structure and composition of rice straw.

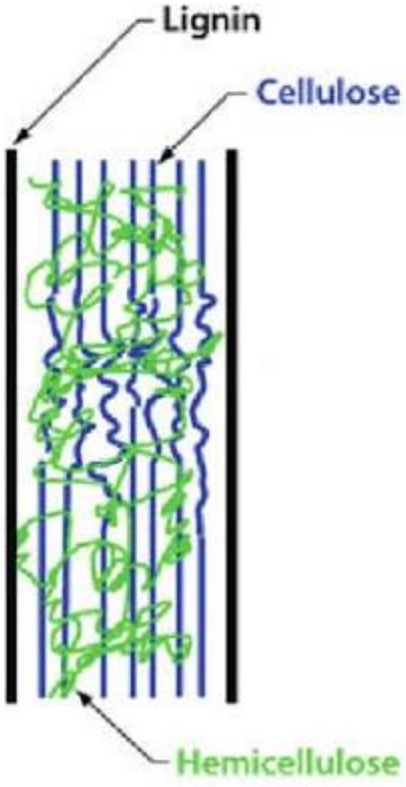

Figure 1.6: Chemical structure and composition of lignocellulosic rice straw biomass [70].

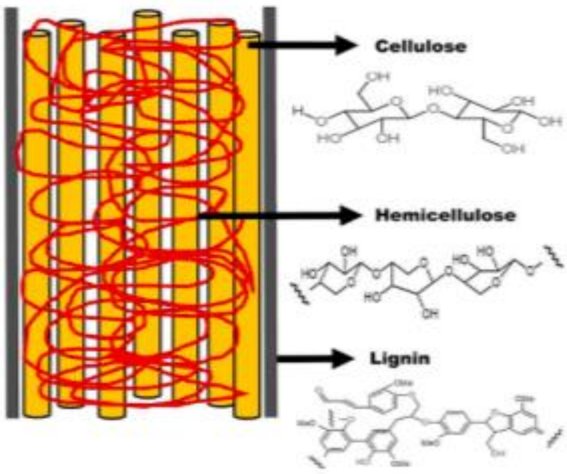

Figure 1.7: Chemical structure of rice straw and the components present in its structure [71].

1.3.2 Blends and Blend Ratios

After collecting the feedstock materials, the first step is the sample preparation. The samples preparation involves the individual size reduction of all three feedstock materials being used. After the size reduction, the next step is individual sieving of all three samples. So, we get the screened feed material. Then the individual characterization analysis of all three samples is carried out. Now, the three samples are ready to be used as a feedstock for the study of pyrolysis effect in TGA [106]. Then the blends of the three samples in different blend ratios of 2:2:6, 2:6:2, 4:1:5, 4:5:1, 6:1:3 and 6:3:1, are to be prepared to study the blend ratios effects in TGA.

1.4 Pyrolysis

Pyrolysis is one of the processes being adopted for biofuels production. Biofuels are fuels produced through biochemical and thermochemical conversion processes [31]. Biochemical conversion processes include aerobic and anaerobic digestion, and fermentation [32-34]. On the other hand, thermochemical routes include gasification, pyrolysis, torrefaction, and carbonization [31, 35, 98-101]. Gasification gives gaseous biofuel (Syn-gas) as the main product [36]. While pyrolysis gives liquid biofuel as the main product [38, 39]. On the other hand, carbonization and torrefaction give solid biochar as their main product. All these biochemical and thermochemical conversion routes are used to convert biomass including crop residue, solid waste including waste plastic, and solid fossil fuels like coal into the biofuels. The produced biofuels can be used to replace those conventional and rapidly depleting fossil fuels. Hydrogen, biochar, and biodiesel are the most common biofuels being considered for energy supply in recent times [40]. Biodiesel is the most common liquid biofuel produced by pyrolysis [41-43].

Pyrolysis has 3 main modes or types. These are slow, fast, and ultra-fast or flash pyrolysis. These are differentiated based on their heating rate, time for the process, and main product [102].

Slow pyrolysis is characterized by long time, low heating rate and low temperature pyrolytic degradation. The main product of slow pyrolysis is solid biochar [103]. Usually, carbonization and torrefaction are considered as the slow pyrolysis processes as both has solid biochar as their main product. Slow pyrolysis takes place at 150-350 °C. Slow pyrolysis takes almost 90 minutes. This is the reason it is considered as slow.

The heating rate is from 1 to 30 °C per minute. The process is carried out at atmospheric pressure [103]. Fast pyrolysis is characterized by the short time, high heating rate and high temperature pyrolytic degradation. The main product of fast pyrolysis is liquid biofuel. Fast pyrolysis takes place at 350 °C and above and it takes a few minutes. This is the reason it is considered as fast pyrolysis. The heating rate in fast pyrolysis is 10-3000 °C/s [104]. Flash/ultrafast pyrolysis is characterized by the extremely short time, much high heating rate and high temperature pyrolytic degradation. The main product of ultrafast pyrolysis is also liquid biofuel. Ultrafast pyrolysis takes place at temperature above 650 °C and it takes a few seconds. It is completed in a flash of time. This is the reason it is considered as flash/ultrafast pyrolysis. The heating rate is up to 20000 °C/s. The pressure is up to 3 MPa [105].

The basic process overview of pyrolysis conversion process is shown in Figure 1.8 given below.

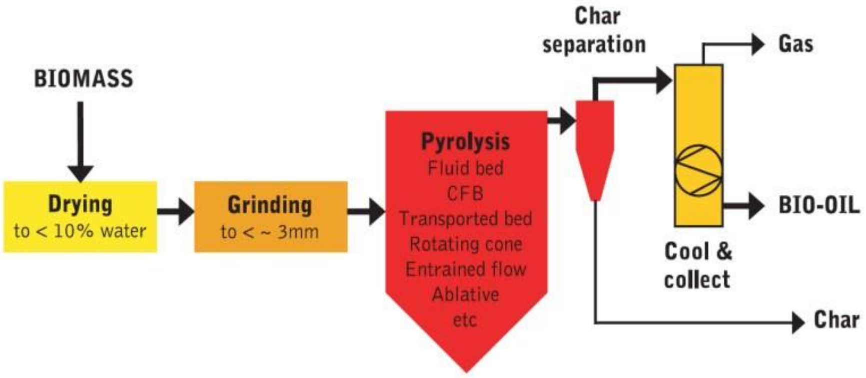

Figure 1.8: The pyrolysis process overview for conversion of a feedstock to biofuels [103].

1.5 Problem Statement

Today, the whole world is facing global energy crisis. Affordable and sustainable energy supply is one of the major concerns of all developing nations. Similarly, the rapid increase in world population, large scale urbanization and industrialization are causing generation of huge amounts of solid waste. Considering these problems, there is a need for utilizing the municipal wastes and it is also a need of time to have an alternative source of energy that can reduce environmental issues and may replace conventional fossil fuels. Bio-fuels have the capacity of reducing the use of fossil fuels due to their environment-friendly behavior and are biodegradable. Tri-pyrolysis process has capacity to be used to convert municipal solid wastes and biomass into useful, environment friendly and sustainable bio-fuels.

1.6 Research Objectives

To overcome the existing challenges in the field of energy supply, following objectives were identified:

1. To study the effect of different blend ratios of the feedstock on the overall conversion and rate of process.
2. To analyze the thermo-kinetic parameters of the pyrolytic conversions in TGA.
3. To study the synergistic effects while converting feedstock into biofuel products through pyrolysis and tri-pyrolysis by using TGA.

1.7 Scope of Study

The following scope was established to ensure that the research would be carried out in the time available:

- The study was limited to Lignite Coal, PET plastic and Rice Straw blends only.
- The analysis of physiochemical properties was carried out for limited samples.
- The TGA analysis was limited to the study of product yields at a fixed heating rate and fixed pressure for different blend ratios.
- Kinetics, thermodynamics and synergistic effects models' study was carried out to limited extent.

1.8 Chapters Summary

This thesis comprises of five chapters. The overview of each chapter is given below:

- **Chapter 1:** delivers vision of the subject, background and contemporary problems related to the work. It also clarifies the problem statement, research objectives and scope of the planned study.
- **Chapter 2:** will sketch the literature review achieved to describe the previous work done on the pyrolytic conversion of municipal waste and biomass. It also includes review based on feedstock and properties of different blend materials.
- **Chapter 3:** covers the methodology related to the sample preparation and characterization and physiochemical properties. It will also give the related

information about experimental procedure and the main equipment contributing to the experimental investigations.

- **Chapter 4:** delivers results and discussions of all characterization techniques, results of TGA study as well as thermo-kinetics and synergistic effects results.
- **Chapter 5:** reviews all the findings and conclusions in the current study and provides the future recommendations for the related work.

CHAPTER 2: LITERATURE REVIEW

Lignite coal (L_c), rice straw (R_s), and Polyethylene Terephthalate (P_{ET}) plastic are under consideration as feedstock materials in this study. Before preparing the samples, all these three samples are required to be collected. Coal was collected from a specific region. Waste plastic is available easily at domestic scale. It was collected from MSW. While the crop residues can be collected from fields e.g., rice straw (R_s) and wheat straw (W_s) can be collected from fields easily.

2.1 Coal

The three main fossil fuels are oil, natural gas, and coal. Coal is considered to be the second largest consumable fossil fuel in the world [18]. The research work shows that coal will remain the second largest source of primary fuel till 2030 [50]. The worldwide consumption of fossil fuels from 1965 to 2030 is shown in Figure 1.1. The world's crude oil reserves have been estimated to be diminished by the year 2030. And it has also been estimated that coal will be the only fossil fuel left after year 2042. It means that all other fossil fuels will be completely depleted by the year 2042. After that, the utilization of coal for energy purpose will jump to higher extent. It has been estimated that world's coal reserves are enough to provide energy till year 2112 [18]. Therefore, coal is being paid attention at research scale as it is being considered as an important source of energy in future.

The study of remaining reserves of fossil fuels shows that coal shares almost 65% of the remaining reserves of the world's fossil fuels. While both the oil and gas just have 35% share in the remaining reserves of the world. Similarly, coal reserves are distributed throughout the world. Coal reserves have been found in more than 70 countries across the world. While oil and gas reserves are mostly distributed in the middle east countries [18]. On the basis of these facts and figures, coal gained attention in research field throughout this world.

2.1.1 Origins and Formation

Coal is mostly formed from the accumulation of large amounts of plant debris under Earth crust. The plant debris are degraded and broken down to the simpler compounds by the microbiological activity or abiotically. The debris are then gradually covered by the silts or thick inorganic sediments which provide a shield against the further degradation of this matter. Then this matter is chemically altered by heat to form coal when the matter is continuously compacted by the overburden pressures. This is how the buried remains of plants are converted to coal under earth crust [51].

The plants that undergo decay to form coal are composed of mainly carbohydrates, glycosides, proteins, waxes, fats, resins, alkaloids, enzymes, chitins, pigments, purines, cellulose, hemicellulose, and lignin. During the degradation process, the plant waxes, fats, and resins generally resist the microbial degradation and undergo the oxygen-promoted polymerization under the strong aerobic activity. Cellulosic matter is quickly broken down to the simple sugars. While the pigments survive the alteration for long time. Lignin is oxidized to form complex 'humic acids' which are then converted to derivatives of water soluble benzenoids. Glycosides are hydrolyzed to give sugars. And the proteins are denatured to give free amino acids and undefined slimes. All these processes convert the plant matter to form 'humus'. Then this residue is further altered when the degradation products interact with each other. This rate of decay generally increases with the increase of temperature under the Earth crust. The microbiological decay can be of two types, aerobic and anaerobic decay. Aerobic decay is based on the interaction of oxygen. While the anaerobic decay is in the absence of oxygen, and it is mostly carried out by bacterial hydrolysis and reduction. The abiotic alteration takes place when the decay matter is buried under the sediments. It is carried out by the compaction, dehydration, stripping, and condensation reactions taking place in series. Finally, coal is formed from the plant debris after all these decay and degradation processes under high pressure and temperature conditions beneath Earth crust [51].

2.1.2 The Coal "Series"

All coals, regardless of their age, origin, and type can be arranged in an ascending order of their carbon contents (organically bound carbon). It is called the coal 'Series'. It is shown below:

Peat → Lignite Coal → Subbituminous Coal → Bituminous Coal → Anthracite Coal

With this concept, the end point of this series is graphite which resembles anthracite coal. The coal 'series' is basically a metamorphic development process of coal in which peat matures to be converted to lignite, lignite to subbituminous, subbituminous coal to bituminous coal, and finally bituminous coal matures itself to be converted to anthracite. It is called coalification. Peat contains least amount of carbon content, while anthracite contains the highest amount of carbon content. The series shows the order of carbon content increase from peat to anthracite coal [51].

2.1.3 Rank of Coal

Rank is the qualitative measure of carbon content of the coal. It also indicates the degree or extent of maturation of coal. The coal series gives an important framework for ranking the different kinds of coal. The suitability of a particular kind of coal for its end-use is determined and assessed with the help of rank of coal. There are two main ranks of coal. These are low ranked coal and high ranked coal. Lignite and subbituminous coal are considered as the low rank coal. While bituminous and anthracite coal are considered as the high rank coal. Lignite and subbituminous coal are also named as soft coals. While bituminous and anthracite coal are called hard coals [51].

Anthracite is black lustrous in color. Bituminous coal is shiny and smooth. Sub-bituminous coal is dull, black, and not shiny. While Lignite is brown in color. Low ranked coal is available in abundant amount because of their large deposits across the world. Low ranked coal can be used as a feedstock to undergo thermochemical conversions to convert it into useful biofuel.

The rank of coal must not be confused with the grade of coal. Grade of coal refers to the quality of coal. The low ranked coal may also have higher quality and can be preferred over high rank coal for some applications [51]. Therefore, the grade of coal and the rank of coal are two different parameters, and they are not synonymous with each other.

2.1.4 Ultimate and Proximate Analysis

The ultimate and proximate analysis of the different types of the coal gives the information regarding the chemical composition and properties of the different types of the coal. One such ultimate and proximate analysis is shown in Table 2.1.

Table 2.1: Ultimate and proximate analysis of different types of coal (weight % on dry basis) [52].

Sample	Proximate Analysis			Ultimate Analysis				
	Ash	Volatile Matter	Fixed Carbon	C^{daf}	H^{daf}	N^{daf}	O^{daf}	S^{daf}
Anthracite	2.5	7.8	89.7	94.6	2.3	1.2	1.3	0.6
Bituminous	16.3	24.8	58.9	83.7	5.0	1.7	8.9	0.7
Sub-Bituminous	12.6	43.5	43.9	68.5	5.8	1.5	16.6	7.6
Lignite	31.6	42.7	25.7	61.3	5.4	1.1	30.8	1.4

2.1.5 Coal Utilization Routes

Coal is being used in two main ways in recent times. Direct combustion and conversion into biofuels are these two ways. Direct combustion of coal as the source of energy is the major way of coal utilization. Coal can also be utilized as a source of energy by converting it into biofuels which are then used for energy and power generation purposes [53, 54].

2.1.5.1 Direct Combustion

The direct combustion of coal is one of the ancient ways of getting energy for domestic as well as industrial purpose [55]. Coal can be combusted at domestic level for steam generation and getting energy required for household purposes. The generated steam is used for radiators and heaters at domestic levels. While at industrial scale, coal is used in boiler systems to generate steam for power generation, as well as it is also used in furnaces as the source of heat and energy. Boilers generate steam from water by using the energy obtained from the direct combustion of coal. Then this generated steam is used for running turbines in power plants. The mechanical rotation of turbines produces electricity. This is how coal is used for power generation purpose in power plants [56, 57].

The direct combustion of coal for getting energy, produces a large amount of harmful greenhouse gases like CO_2, CO, NO_x, and SO_x. They are directly released into the atmosphere causing air pollution, rise in temperature, climate change, global warming, and greenhouse gas effect. All these issues are directly related to the direct combustion of coal both at the domestic scale as well as at the industrial scale [58]. It requires a lot of carbon capture and flue gases clean-up for the flue gases being produced because of direct coal combustion. These emissions can also be minimized by the clean coal technologies use [59].

2.1.5.2 Conversion to Biofuels

On the other hand, coal is converted to gaseous, liquid, and solid biofuels by using different thermochemical conversion routes. These routes are gasification, pyrolysis, and liquefaction. All these routes are used to convert solid coal into the biofuels which can replace those conventional fossil fuels as a source of energy [55, 60].

Coal gasification is used to convert coal to gaseous biofuel that is called syn-gas. The main product is the syn-gas along with the small percentages of liquid biofuel and solid char. The main product is syn-gas, and it contains CO and H_2. CO can be separated out before H_2 is used as a clean fuel being used as a source of energy. Similarly, coal can be also converted to liquid biofuels by using pyrolysis and liquefaction processes. The produced liquid biofuels can replace conventional fossil fuels and these biofuels add small amounts of emissions to environment [60, 61].

2.2 Crop Residue

Crop residue is one of the agricultural wastes. Agricultural waste is the unwanted waste and residue obtained from the growing and processing of raw agricultural products like crops, vegetables, fruits, poultry, meat, and dairy products [62]. The major agricultural wastes are crop residues, weeds, leaf, sawdust, forest waste, and livestock waste. Agricultural wastes can be in different forms. They can be in the form of liquids, solids, or slurries. It depends on the nature of agricultural activities. Agricultural wastes can be used to manufacture biofuels, animal feed, and other chemicals by the means of biochemical and thermochemical conversion routes [63].

2.2.1 Generation

Agri-waste is mostly generated in the form of crop residues. It includes remains of crops like roots, stems, and no-seedy parts of crops and plants. It also includes the remains of fruits and vegetables. Wheat straw, rice straw, sugarcane bagasse, corn stalk etc. are some examples of remains of crops. These remains are obtained because of processing and harvesting of crops. Wheat straw, sugarcane bagasse, and rice straw are the most common crop residues that are produced in bulk amounts. They are considered as the waste and are considered as of no use remains of crops. But they can be utilized and can be converted to biofuels by using different thermochemical conversion processes like gasification, pyrolysis, carbonization, and torrefaction [64]. These biofuels are useful products obtained from the crops residues and these biofuels can replace depleting fossil fuels in near future. They have less emissions and do not increase the carbon content of our atmosphere at large scale [65].

Deforestation also produces residual waste. Increase in population growth and urbanization are the main reasons for deforestation. Deforestation is the cutting of trees. It involves the cutting of forests as a whole or partially a few parts of a forest. Deforestation also produces a huge amount of residue and remains of trees and bushes as a waste. They are also the Agri-waste, and this waste is usually considered as of no use. But this waste can also be converted into biofuels by using pyrolysis, gasification, and other thermochemical conversion routes. Pyrolysis is one of those conversion routes that can be used for the conversion of this waste into useful biofuel [66, 67].

Similarly, sawdust is obtained during the woodwork. It is also one of the Agri-waste as sawdust is basically the remains of wood and wood is obtained from plants and trees. It is also usually considered as a waste of no use. But it can be also used as a feedstock for thermochemical conversion processes and this waste can be converted to useful biofuels [68]. It is one of the best uses of this waste. It not only utilizes this waste, but also gives us the sustainable and useful biofuels that are being considered as the replacement to the conventional fossil fuels.

2.2.2 Compositional Analysis

Crop residues are one of the main agricultural wastes. The typical examples of the crop residues are cornstalk, sugarcane bagasse, wheat, and rice straw etc. The compositional analysis of different crop residues has been shown in Table 2.2.

Table 2.2: Compositional Analysis of different crop residues (by weight %).

Sample	Hemicellulose	Cellulose	Lignin	Ash	Reference
Wheat Straw	39.1	28.8	18.6	13.5	[69]
Corn Cob	32	52	15	1	[69]
Corn Stover	30.7	51.2	14.4	3.7	[69]
Olive Husk	23.6	24	48.4	4	[69]

Tobacco Stalk	28.2	42.4	27	2.4	[69]
Wood Bark	29.8	24.8	43.8	1.6	[69]
Husk of Rice	40	21	22	16	[70]
Rice Straw	25.6	39.9	10.2	19.6	[71]
Cane Bagasse	28.46	44.14	20.17	2.41	[72]

2.2.3 Ultimate and Proximate Analysis

The ultimate and proximate analysis of different crop residues is shown in Table 2.3 given below.

Table 2.3: Ultimate and proximate analysis of different types of crop residues (weight % dry basis).

Sample	Proximate Analysis			Heating Value (MJ/Kg)	Ultimate Analysis					Ref.
	A	V.M	F.C		C^{daf}	H^{daf}	N^{daf}	O^{daf}	S^{daf}	
Wheat Straw	7.3	87.8	4.9	17-18.9	41.7-46.7	5.1-6.3	0.4-0.5	34.1-51.4	0.1-0.3	[73]
Rice Straw	8.2	84.0	7.8	14.5-15.5	34.0-41.5	4.6-6.7	0.2-0.8	38.8-41.2	0.1-0.2	[73, 74]
Maize Straw	4.2	92.7	3.1	16.2-16.5	35.2-45.6	5.4-6.3	0.3-0.8	4.34-45.7	0.1-0.3	[73]

2.2.4 Utilization Routes for Crop Residues

2.2.4.1 Animal Feed

Agri-waste like crop residues is being utilized as an animal feed from centuries. The remains of crops mainly rice straw and wheat straw are being used as a feed for cows and buffaloes. These crop residues are added in their feed. The use of crop residues as an animal feed is one of the better uses of crops remains as it improves milk yields and meat production from animals like cows and buffaloes. There is no harmful effect in using this residue as animal feed [75, 76].

2.2.4.2 Improving Soil Fertility

The crop residues are burnt in the fields to improve the fertility of soil. Burning these residues in the fields produces solid char that is best suited for the cultivation of any crop. Soil gets enough fertility which is best suited for the proper growth of crops. This concept is being adopted for years in villages to improve the fertility of the soil [77]. Besides providing the fertility to soil, the burning of remains of crops also produces greenhouse gases that are much harmful. These gases are added to our atmosphere and causing the rise of temperature.

2.2.4.3 Adsorbent in Elimination of Heavy Metals

There is an excessive release of harmful heavy metals in the environment. The heavy metals like zinc, copper, chromium, lead, and mercury are harmful to environment and there is no harmless end-product of these heavy metals by their degradation. They are toxic and much harmful for health. They do not undergo biological degradation and do not degrade into the harmless products. Therefore, these metals are required to be eliminated from our environment to reduce the amounts of these toxic metals in our environment. Crop residues serve as the adsorbents to eliminate such toxic heavy metals from our environment [78]. The toxic heavy metals can be removed from the wastewater being produced at industrial scale. The treatment of wastewater by using crop residues as the adsorbents is one of the useful methods for removal of toxic heavy metals from water before the water is added to canals and streams. This is one of the uses of crop residues [79].

2.2.4.4 Direct Combustion

Crop residues are also burnt directly for domestic heating and cooking purposes in villages where there is no supply of natural gas. This use of crop residues is not being considered as a wise move as it produces harmful gaseous emissions into the atmosphere. We are getting energy at the cost of polluting our environment and adding greenhouse gases to our atmosphere. It is also one of the uses of crop residues [62, 80].

2.2.4.5 Conversion to Biofuel

Crop residues are converted into biofuels by using different thermochemical conversion routes. Pyrolysis is one such route. The pyrolysis of crop remains produces biofuels that can replace the conventional fossil fuels. This is also one of the uses of crop residues. This use of crop residues is the most advisable and best use as it gives biofuels as the end-products. Biofuels are environment friendly fuels that have potential to replace the depleting fossil fuels [81].

2.3 Plastic Waste

Plastic is a valuable material due to its use for many functions. Plastic is being used for improving food quality, food packaging, food storage and other domestic and industrial purposes [82]. Plastic use has revolutionized our lives [83]. But with the rapid increase in population growth, the demand and use of plastic has increased within last few decades causing addition of a large amount of waste plastic on earth surface. This addition of large amounts of plastic wastes in our ecosystems, is causing harmful effects on human as well as other terrestrial life, wildlife, and life in our oceans [84].

The rate of plastic waste generation per person is much larger in high income countries than those countries with low income [82]. The rate of plastic waste generation also depends on the population growth rate. Higher the population, higher is the use of plastic, higher is the rate of plastic waste generation. Waste plastic includes all the plastic items being used in our daily life. Waste plastic not only causes land pollution, but also effects our aqueous life when this waste plastic is added to oceans [84]. Almost 20% of the waste plastic that is being added to oceans, comes from different marine sources. In 1950, world was producing 2 million tons of plastic waste annually. In 2010, the global plastic waste production was almost 275 million tons and there has been a large annual increase in this rate in last few years. In 2015, the global waste plastic production was 381 million tons. This is how the use of plastic has increased from 1950 to recent years and it caused a rapid increase in waste plastic production globally [82]. The globally Mismanaged Plastic Waste (MPW) generation in year 2015 is shown in Figure 2.1.

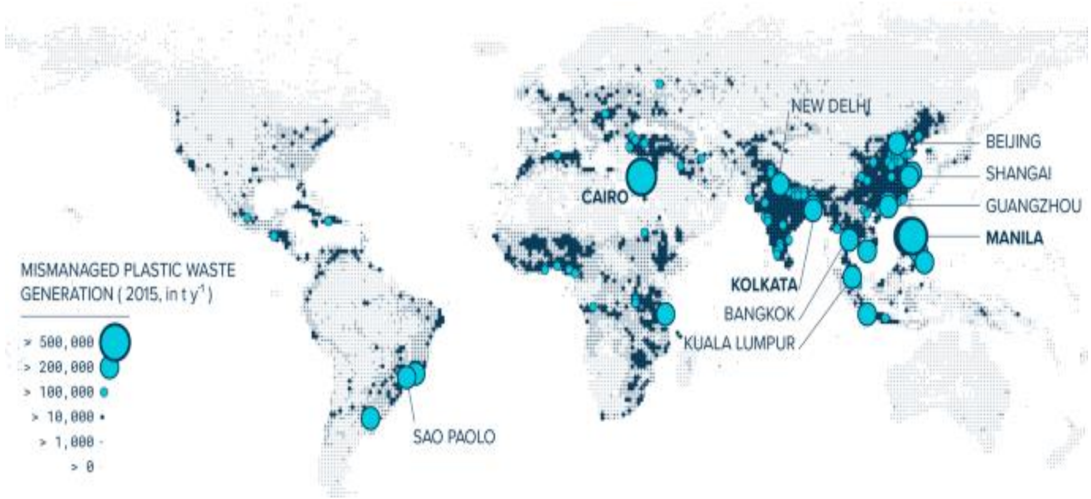

Figure 2.1: The globally Mismanaged Plastic Waste (MPW) generation in 2015 [85].

2.3.1 Types of Plastic

Plastic has seven different types. These are Polyethylene Terephthalate (PET), High Density Polyethylene (HDPE), Polyvinyl Chloride (PVC), Low Density Polyethylene (LDPE), Polypropylene (PP), Polystyrene (PS), and Polycarbonate (PC) [86].

2.3.2 Ultimate and Proximate Analysis

The ultimate and proximate analysis of different types of plastic is shown in Table 2.4.

Table 2.4: Ultimate and proximate analysis of different types of plastic (dry weight % basis).

Sample	Proximate Analysis			Ultimate Analysis					HHV (KJ/Kg)	Ref.
	A	V.M	F.C.	C^{daf}	H^{daf}	N^{daf}	O^{daf}	S^{daf}		
PE	0.15	99.85	0.00	85.45	14.32	0.16	0.00	0.07	46318	[87]
HDPE	0.60	99.40	0.00	85.50	14.20	0.00	0.00	0.30		[88]
LDPE	0.30	99.70	0.00	85.50	14.30	0.00	0.00	0.20		[88]
PP	0.16	99.84	0.00	84.30	14.44	0.18	1.05	0.03	45769	[89]

PS	0.51	99.49	0.00	91.08	7.68	0.00	1.24	0.00		[90]
PVC	0.32	91.25	8.43	41.79	4.84	0.09	0.00	0.02	21732	[91]
PET	0.31	94.09	5.60	62.26	4.06	0.00	33.69	0.00		[92]

2.3.3 Plastic Waste Utilization Routes

2.3.3.1 Recycling

The first route for the utilization of waste plastic is its recycling. Recycling of waste plastic is carried out for carrying out the reuse of waste plastic. The use of plastic and waste plastic is inevitable. Therefore, the recycling of waste plastic is essential. It is essential for the proper waste plastic management. Waste plastic recycling is one of the best utilizations of waste plastic. It is also important from the socioeconomic point of view [93].

2.3.3.2 Conversion into Biofuel

The second method of waste plastic management is the conversion of waste plastic into biofuels by using different thermochemical conversion routes [94]. Pyrolysis is one of those routes being used to convert the waste plastic into liquid biofuel such as biodiesel [95-97]. The large amounts of plastic wastes are much difficult to be handled and managed. The recycling of waste plastic involves machinery and costs of recycling. To avoid such costs, the waste plastic can be easily utilized by using it as a feedstock to produce biofuels. Plastic can be added to other biomass feedstocks for their effective conversion into liquid biofuels through pyrolysis. Plastic addition to biomass feedstock increases the yield of liquid biofuel [95]. Therefore, waste plastic can be utilized by its conversion into biofuels.

2.4 Pyrolysis

Pyrolysis is one of the processes being adopted for biofuels production. Biofuels are fuels produced through biochemical and thermochemical conversion processes [31]. Biochemical conversion processes include aerobic and anaerobic digestion, and fermentation [32-34]. On the other hand, thermochemical routes include gasification, pyrolysis, torrefaction, and carbonization [31, 35, 98-101]. Gasification gives gaseous biofuel (Syn-gas) as the main product [36]. While pyrolysis gives liquid biofuel as the main product [38, 39]. On the other hand, carbonization and torrefaction give solid biochar as their main product. All these biochemical and thermochemical conversion routes are used to convert biomass including crop residue, solid waste including waste plastic, and solid fossil fuels like coal into the biofuels. The produced biofuels can be used to replace those conventional and rapidly depleting fossil fuels. Hydrogen, biochar, and biodiesel are the most common biofuels being considered for energy supply in recent times [40]. Biodiesel is the most common liquid biofuel produced by pyrolysis [41-43].

2.4.1 Modes of Pyrolysis

Pyrolysis has 3 main modes or types. These are slow, fast, and ultra-fast or flash pyrolysis. These are differentiated based on their heating rate, time for the process, and main product [102].

Slow pyrolysis is characterized by long time, low heating rate and low temperature pyrolytic degradation. The main product of slow pyrolysis is solid biochar [103]. Usually, carbonization and torrefaction are considered as the slow pyrolysis processes as both has solid biochar as their main product. Slow pyrolysis takes place at 150-350 °C. Slow pyrolysis takes almost 90 minutes. This is the reason it is considered as slow. The heating rate is from 1 to 30 °C per minute. The process is carried out at atmospheric pressure [103]. Fast pyrolysis is characterized by the short time, high heating rate and high temperature pyrolytic degradation. The main product of fast pyrolysis is liquid biofuel. Fast pyrolysis takes place at 350 °C and above and it takes a few minutes. This is the reason it is considered as fast pyrolysis. The heating rate in fast pyrolysis is 10-3000 °C/s [104]. Flash/ultrafast pyrolysis is characterized by the extremely short time, much high heating rate and high temperature pyrolytic degradation. The main product of ultrafast pyrolysis is also liquid biofuel. Ultrafast pyrolysis takes place at temperature above 650 °C and it takes a few seconds. It is completed in a flash of time. This is the reason it is considered as flash/ultrafast pyrolysis. The heating rate is up to 20000 °C /s. The pressure is up to 3 MPa [105].

2.4.2 Pyrolysis Applications

Pyrolysis can serve this world in many ways as discussed one by one here. These applications include:

1. Biofuels produced by the pyrolysis process, can serve as a sustainable replacement to fossil fuels being used worldwide. Fossil fuels emissions are a major health and environmental concern these days. Biofuels are a clean and green source of energy and can be used in future to overcome this issue.

2. All organic food waste can also be utilized to be converted into biofuels through pyrolysis process and in this way, we can also overcome one of the major waste food problems throughout this world.

3. Pyrolysis can also serve as a solution to municipal solid waste management that is one of the major concerns in all developing and developed states of the world. Waste can be converted into biofuels to serve us through fulfilling our energy demands.

4. Biofuels produced through the process of pyrolysis can be used in near future as a sustainable source of energy throughout this world. Fossil fuels are depleting. Therefore, there is always a need of shifting to some sustainable sources of energy worldwide.

5. Biofuels produced through the process of pyrolysis can be used to replace depleting fossil fuels in near future as the world fossil fuels are going to deplete by 2060s as per some scientific research.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

The raw material which was used in this research study is local lignite coal, local rice straw (a crop residue), and PET from plastic waste. These three raw materials are under consideration as feedstock materials in this study. Before preparing the samples, all these three samples were collected. Coal was collected from a specific local region. Waste plastic is available easily at domestic scale. It was collected from MSW. While the crop residues can be collected from fields e.g., rice straw (R_s) and wheat straw (W_s) can be collected from fields easily.

3.2 Preparation of Samples Powder

After the collection of all three materials, the next step is the drying of materials for moisture removal before preparation of individual samples and their respective blends of different ratios that are then to be used to analyze the pyrolysis effects by using TGA. Both lignite coal and rice straw were first sun dried for 24 hours. Then 200 gm of both lignite coal and rice straw was desiccated for 12 hours to remove their inbound moisture. After this primary desiccation, both the materials were dried in an electric oven at a heating temperature of 105 °C for 24 hours to further remove their inherent moisture. After drying, then comes individual size reduction of materials. For this purpose, lignite coal was crushed and grinded in ball mill to reduce its size. Rice straw was chopped and grinded to required size with grinder. Waste plastic was shredded in a shredder to reduce its size. After the size reduction, the next step is individual sieving of all three samples. For this purpose, all the three materials powder were sieved through 0.20 mm mesh screen. So, we got the screened feed material in powder form. Now, the three samples are ready to be used as a feedstock for the study of pyrolysis effect in TGA.

3.3 Preparation of Blends

In TGA, the pyrolysis effects of individual samples were first analyzed and then blends of the samples (in different blend ratios) were prepared to study the effects in TGA. The blends were prepared for polyethylene terephthalate, rice straw and lignite coal in blend ratios: 2:2:6, 2:6:2, 4:1:5, 4:5:1, 6:1:3 and 6:3:1 respectively by taking weights in grams and each blend had a weight of 10 gm. Then the uniform mixing of the blends was carried out.

3.4 Material Characterization

Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) characterization techniques were used to analyze physiochemical properties of all three material samples. SEM is used to study and describe the morphology of the material. EDX is used to study and analyze the elements in a specific area or point of the material. FTIR is used to the study the spectra of absorbance with respect to wavenumber (cm^{-1}) to analyze the different molecular bonds and functional groups present inside the sample materials.

3.5 Thermogravimetric Analysis

TGA is in use for this research study. We performed this analysis in TGA 5500 (TA Equipment, USA). Thermogravimetric Analysis (TGA) is a technique which is used to measure the weight loss of a feedstock sample with respect to temperature and time during the process when the sample is undergoing thermochemical degradation in a thermochemical degradation process. The degradation takes place in a controlled temperature and environment. The thermogravimetric analysis of the individual feedstock samples and the blends is carried out inside TGA analyzer [106]. Pyrolytic degradation inside a TGA analyzer is completed in three stages including the first drying stage, the second devolatilization or active pyrolytic stage, and the third solid char formation or the passive pyrolytic stage. Thus, the thermochemical degradation of the feedstock materials in pyrolysis process undergoes three major stages in a TGA analyzer [107]. The operating temperature range of the commercially available TGAs now a days are from ambient to 1000 °C or slightly above [108]. Here, we took a 8-10 mg sample and placed it on to crucible ceramic and heated from ambient to 900 °C at a single constant heating rate of 10 °C/min.

Thermogravimetric Analyzer (TGA) is used to study the degradation effect of feedstock during pyrolysis which is a process being used for the conversion of feedstock into biofuels. TGA is used to study the kinetic parameters during degradation process taking place in pyrolysis. TGA gives the information of activation energy required for individual feedstock pyrolysis, and that required for tri-pyrolysis.

Thus, Thermogravimetric Analyzer is equipment that is used for the study of pyrolytic thermal behavior of the feedstock materials [108].

Thermogravimetric Analyzer consists of a ceramic sample basket/crucible with a circular base. Samples being used as feedstocks are placed inside this ceramic crucible. TGA has an electric oven for heating. This electric oven operates to a specific temperature, and it is operated with the help of a temperature controller. TGA also has a thermocouple which is located near ceramic crucible and it is used for temperature monitoring. It is used for measuring the temperature parameter. It also controls the temperature of electric oven with the help of temperature controller. In this way the kinetic parameters of any pyrolytic degradation process are studied in a controlled temperature and environment by using TGA [108]. A schematic diagram for thermogravimetric analysis is shown below in Figure 3.1.

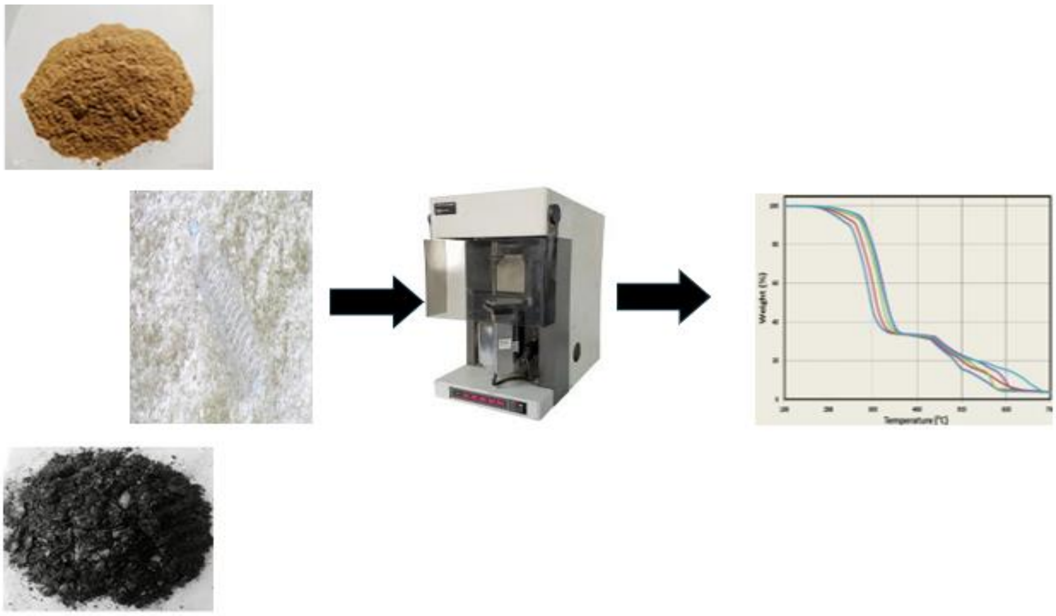

Figure 3.1: Schematic diagram for thermogravimetric analysis of R_s, P_{ET} and L_C.

For studying pyrolytic degradation process in TGA, the first step was sample preparation. Once the material samples and blends were prepared, then comes the placement of 8-10 mg sample inside the ceramic crucible. Nitrogen purging of TGA was carried out for making sure the complete inert atmosphere inside TGA. We used inert N_2 gas at a flow rate of 30 mL/min. After purging, the heating rate of 10 °C /min was set for the electric oven. Heat was provided by the electric oven and the heating rate and temperature were controlled by the help of thermocouple and temperature controller. Heat was provided from ambient temperature to 900 °C and the pyrolysis of the feedstock took place inside the TGA. The thermo-degradation was studied in the form of graphs called thermograms containing weight loss % as a function of temperature.

3.6 Kinetic Study and Models

To study the pyrolytic behavior of the materials, thermogravimetric analysis (TGA) is one of the most effective techniques being used now a days [110]. It is useful to study the kinetic parameters of the reactions being involved in the pyrolytic degradation process with the help of using kinetic models. They give us the information of the activation energy required for the individual feedstock pyrolysis, and tri-pyrolysis of blends in different blend ratios. Previous studies have shown that co-pyrolysis and tri-pyrolysis are the potential methods for obtaining biofuels as compared to pyrolysis of individual feedstocks. It is because the average activation energy required for the pyrolysis of the individual feedstock is higher while comparing it to that required in co-pyrolysis or tri-pyrolysis [106, 107]. Further, the previous studies also show that the conversion increases on increasing temperature during pyrolytic conversion process [109]. Thus, in order to study the kinetics of pyrolytic degradation process, we used TGA and kinetic models.

3.6.1 Kinetic Models

We can analyze and investigate the kinetic parameters of the pyrolysis process by using the kinetic models. These kinetic parameters include the activation energy, order of reaction, reaction mechanism and pre-exponential factor. Pyrolysis process involves many complex reactions, intermediates, and the end products. Therefore, determining the exact pyrolysis reaction mechanism and modeling its kinetics is much more difficult. So, the simplified reactions and the kinetic models are used for this purpose [111]. In this study, the pyrolysis process is described by a single reaction with individual feedstock materials as well as for tri-fuel feedstock blends as raw materials. Volatile gases, tar, and solid biochar are generally its three end products. The degree of transformation or the conversion of the process is given by Eq. (1):

$$\alpha = \frac{m_0 - mt}{m_0 - m_f} \tag{1}$$

Here, α is the degree of conversion, m_t is the mass of solid at given time, m_0 is initial amount of sample and m_f is residual or final amount of sample. While the rate of conversion is given by Eq. (2):

$$\frac{d\alpha}{dt} = K(t)\, f(\alpha) = A\ \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \qquad (2)$$

Here, E_a is the activation energy, R is the universal gas constant, T is temperature, K(t) is the reaction rate constant=$A\ \exp\left(-\frac{E_a}{RT}\right)$ that is taken from Arrhenius equation, A is the pre-exponential factor, and $f(\alpha)$ is the function and it depends on pyrolysis reaction's model.

Thus, we have:

T = temperature [K]

A = Pre-exponential factor [s^{-1}]

R = Gas constant [8.314 J mol^{-1} K^{-1}]

E_a= Activation energy [J mol^{-1}]

The kinetic models used for calculating the kinetic parameters are of two types basically: Model-Fitting Kinetics Models (for single heating rate) and Model-Free kinetics Models or also called Iso-conversional Models (for multiple heating rates). There are four main model-free kinetics models that are basically used when we are using multiple heating rates in TGA. These are: Friedman (Differential method) Model, KAS (Integral method) Model, FWO (Integral method) Model and Vyazovkin (Non-linear equation) Model. Friedman, KAS and FWO models are linear equation models while Vyazovkin model is a non-linear equation model used for multiple heating rates study. On the other hand, there are three main Model-Fitting Kinetics Models which are used for a single heating rate. These are given below:

3.6.1.1 Combined Kinetics Model

This is one of the Model-Fitting Kinetics models. It is basically a differential method of Model-Fitting. It is used for finding out the reaction mechanism.

3.6.1.2 DAEM Model

Distribution Activation Energy Model is also one of the main Model-Fitting Kinetics models. It is basically a non-linear equation-based model.

3.6.1.3 Coats Redfern Model

Coats Redfern is an integral method of Model-Fitting Kinetics study. We have used this Model-Fitting Kinetics technique to study kinetics here. It is based on the constant heating rate. So, for the case of constant heating rate; $\beta=\frac{dt}{dT}$. Thus, from above Eq. (2), we get:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{3}$$

By using integration, we get Eq. (4) as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \tag{4}$$

Here in this Eq. (4), $g(\alpha)$ is in the model integral form. The solution of the right side of this equation is impossible here. So, for solving this complicated part of equation, the different approximation models are used.

The kinetic parameters of samples were calculated through the TGA data using the Coats-Redfern method here in this study. Table 3.1 shows the most used models on the basis of reaction modes. These are used for calculating kinetic parameters like activation energy and pre-exponential factor etc. These models include: phase interfacial reaction models, power law models, nucleation & growth models, diffusion models, and chemical reaction models.

The TG and DTG graphs show the weight loss of samples and blends with respect to time and temperature. The Coats-Redfern model which is a model-fitting model, is often used to estimate A and E and to estimate the order of reaction when dealing with the single constant heating rate. The general form of equation used for Coats-Redfern model is given in Eq. (5).

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{5}$$

In case of the first-order reaction, g(α) is:

$$g(\alpha) = -\ln(1- \ \alpha)$$

So, by putting this value in Eq. (5), we get Eq. (6):

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (6)$$

Table 3.1: Mostly used reaction models, mechanisms, and their corresponding g(α).

Symbol	Function f(α)	g(α)
Chemical Reaction Models or Chemical Processes and Mechanism Non-invoking Equations		
F1	First order (n =1)	-ln (1- α)
F1.5	One and a half order (n = 3/2)	$2[(1-\alpha)^{-1/2}-1]$
F2	Second-order reaction	$(1-\alpha)^{-1}-1$
Diffusional Models or Deceleratory Reaction Mechanism Models		
D1	Parabolic law	α^2
D2	Valansi equation	(1- α) ln (1- α) + α
D3	Jander equation	$[1-(1-\alpha)^{1/3}]^2$
D4	Ginstling equation	$1-(0.67\alpha)-(1-\alpha)^{0.67}$
Phase Interfacial Reaction Models or Phase Boundary Models		
Pl	Contracting cylinder	$1-(1-\alpha)^{1/2}$
Pi	Contracting sphere	$1-(1-\alpha)^{1/3}$
Nucleation and Growth Reaction Mechanism Models		
N1.5	Avrami-Erofeev equation (n= 3/2)	$-\ln(1-\alpha)^{2/3}$
N2	Avrami-Erofeev equation (n= 2)	$-\ln(1-\alpha)^{1/2}$
N3	Avrami-Erofeev equation (n= 3)	$-\ln(1-\alpha)^{1/3}$
Power Law or Acceleratory Reaction Mechanism Models		
PL	Power law (Contacting disk)	α
PL 0.5	Mampel power law (n=1/2)	$\alpha^{1/2}$

At a single heating rate of 10 °C /min, the curve of ln g(α) vs 1/T was obtained under different pyrolysis samples. The slope & the intercepts of the curves ln g(α) vs 1/T were used to calculate the activation energy (E). On the basis of linearity, the curve was split in to two sections. Correlation Coefficient (r^2) value indicates the precision of this model-fitting kinetics. Value closer to 1, more is the precision.

3.7 Thermodynamic Analysis

The thermodynamic parameters which include enthalpy change, Gibbs free energy change, and entropy change, can be obtained from TGA based kinetic data by using the following equations. Based on the kinetic data, these thermodynamic parameters can be estimated from Eq. (7-9):

$$\Delta H = E - RT \tag{7}$$

$$\Delta G = E + RT_m \ln\left(\frac{K_B T}{hA}\right) \tag{8}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{9}$$

Here,

K_B = Boltzmann Constant = $1.381\text{x}10^{-23}$ m² kg s^{-2} K^{-1}.

T_m = Maximum Temperature (K) At which the Decomposition Occurred.

h = Plank's Constant = $6.626\text{x}10^{-34}$ m^2 kg s^{-1}.

R = Gas Constant = 8.3145 J mol^{-1} K^{-1}

3.8 Synergistic Effects

Synergistic effect can be defined as an effect that arises b/w two or more materials and it is greater than the sum of individual effects. Synergistic effect arises because of the interaction of the material particles of different blended materials. The synergistic effect of lignite coal, rice straw and polyethylene terephthalate plastic feedstock blends can be estimated by using experimental and calculated (theoretical) weight loss by considering the given Eq. (10) [107].

$$\Delta W = W_{exp} - W_{cal} \tag{10}$$

Here,

ΔW = Theoretical weight loss difference of the sample

W_{exp} = Experimental weight loss of the sample

W_{cal} = Theoretical or calculated weight loss of the sample

W_{exp} is estimated from experimental thermograph of TGA obtained and W_{cal} can be estimated by Eq. (11) [107].

$$W_{cal} = x_a W_a + x_b W_b + x_c W_c \quad (11)$$

Here, x is representing the mass ratio of each material present in blend, and W having subscripts a, b & c is the mass loss of each sample material.

Estimating the synergistic effects is much important when different materials are being mixed and blended and then they are being pyrolyzed as it gives the information about the positive and negative interactions between particles of different materials that have been blended and pyrolyzed [107].

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Material Characterization Results

4.1.1 SEM and EDX Results

Figure 4.1 and Figure 4.2 show the results of Scanning Electron Microscope (SEM) analysis results and Energy-Dispersive X-Ray Spectroscopy (EDX) analysis results respectively. Meanwhile Table 4.1, Table 4.2 and Table 4.3 present the EDX results for elemental composition analysis of a specific area of material sample of polyethylene terephthalate (P_{ET}), rice straw (R_S) and lignite coal (L_C) respectively.

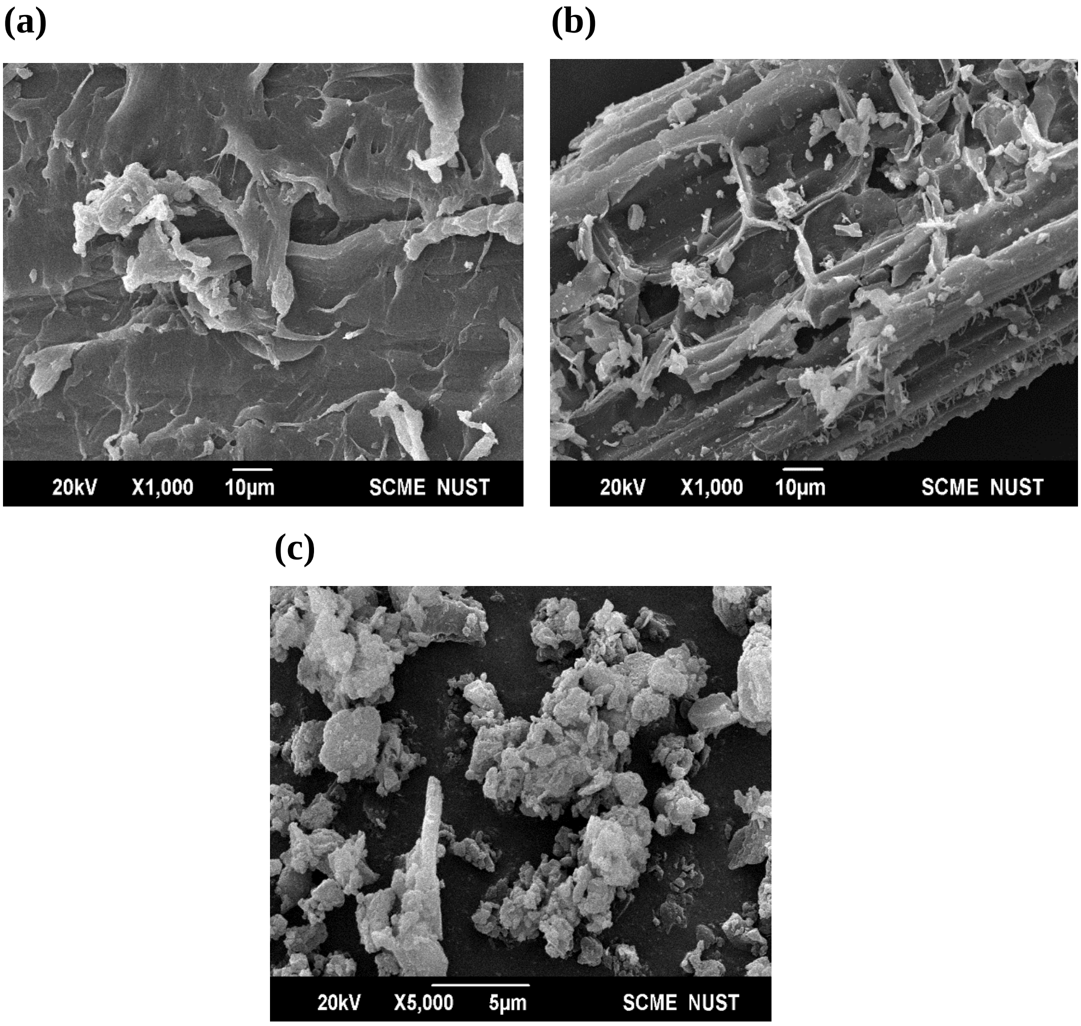

Figure 4.1: SEM analysis results for: (a) polyethylene terephthalate P_{ET}, (b) rice straw R_S and (c) lignite coal L_C.

The morphology of polyethylene terephthalate (PET) plastic shown as a result of SEM analysis in Figure 4.1 (a) actually depicts the multiple alternating monomers of polyethylene terephthalate. PET is basically a polymer of ethylene terephthalate monomers. The chemical formula of this monomer is $C_{10}H_8O_4$. So, the PET polymer is composed of these alternating $C_{10}H_8O_4$ monomer units and PET polymer has a formula $[C_{10}H_8O_4]_n$. Each alternating monomer present inside the polymer contain one ethylene group and one terephthalate group. These two groups combine to form a single monomer and multiple alternating monomers combine to form a polymer of polyethylene terephthalate. While the morphology of rice straw R_s shown as a result of SEM analysis in Figure 4.1 (b) actually depicts its nature as a lignocellulosic biomass. It contains 12% lignin, 25% hemicellulose and 38% cellulose. While the other components that are present in its structure are ash and extractives. The ash and extractives % vary as 7.45±0.31% and 11.93±0.11% (% by w/w on dry biomass basis) respectively. Thus, this type of morphology of rice straw is due to its lignocellulosic biomass nature. Meanwhile the morphology of lignite coal L_C shown as a result of SEM analysis in Figure 4.1 (c) actually depicts its nature as carbon compound which is made up of carbon mainly. Coal is mainly composed of carbon with some minor amounts of other elements including hydrogen, oxygen, nitrogen and sulfur. The molecular formula of coal is $C_{169}H_{128}O_{10}N_2S$. This type of morphology of coal is owing to its nature made up of carbon mainly.

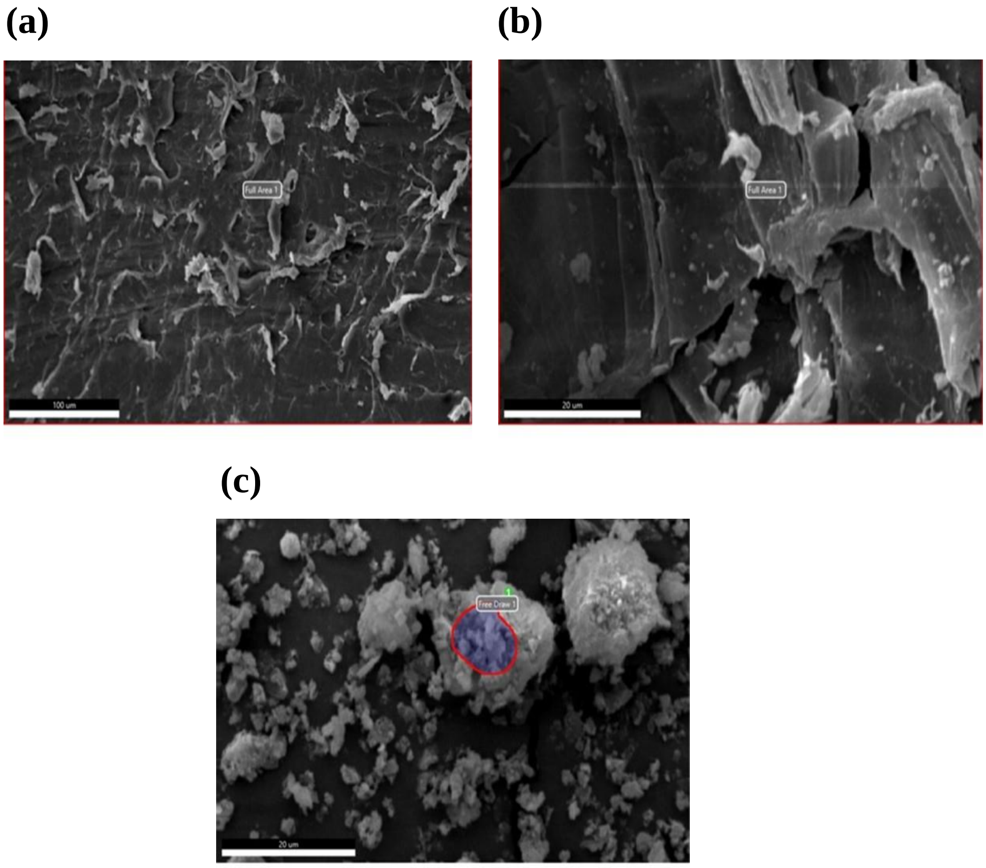

Figure 4.2: EDX analysis of: (a) polyethylene terephthalate P_{ET}, (b) rice straw R_S and (c) lignite coal L_C.

From Figure 4.2 (a), (b), (c) it can be seen that a specific area of the material samples was analyzed in EDX analysis to study the elemental composition of that specific area. These three areas are clearly highlighted. The elemental compositions of these specific areas highlighted above are shown in Table 4.1, Table 4.2, and Table 4.3 respectively. According to the EDX results for elemental composition of P_{ET}, it can be seen in Table 4.1 that the polyethylene terephthalate is composed of majorly two elements that are carbon and oxygen with weight % of 59.3 and 36.6 respectively. In Table 4.2 it can be seen that the rice straw is composed of majorly three elements that are carbon, oxygen and potassium with weight % of 41.2, 43.2 and 9.5 respectively. Table 4.3 shows that the lignite coal has three major elemental components that are carbon, hydrogen and oxygen with their weight % of 85.4, 5.38 and 6.7 respectively.

Table 4.1: The EDX results for elemental composition analysis of polyethylene terephthalate (P_{ET}).

Element	Weight %	MDL	Atomic %	Error %
C	59.3	0.24	45.45	9.8
O	36.6	0.59	18.19	11.2
H	4.2	0.15	36.36	6.2

Table 4.2: The EDX results for elemental composition analysis of rice straw (R_S).

Element	Weight %	MDL	Atomic %	Error %
C	41.2	1.26	52.5	10.9
O	43.2	0.48	41.3	11.1
Si	2	0.11	1.1	7.1
Cl	1.9	0.13	0.8	6.3
K	9.5	0.16	3.7	3.0
Fe	2.3	0.29	0.6	9.3

Table 4.3: The EDX results for elemental composition analysis of lignite coal (L_C).

Element	Weight %	MDL	Atomic %	Error %
C	85.4	0.20	54.52	10.0

H	5.38	0.49	41.28	6.9
O	6.7	0.11	3.23	11.5
N	1.17	0.15	0.65	7.7
S	1.35	0.36	0.32	19.2

4.1.2 FTIR Results

Figure 4.3 shows results of FTIR analysis of sample materials of polyethylene terephthalate, rice straw and lignite coal respectively to analyze the functional groups present in the sample materials. FTIR analysis was carried out to study the main functional groups and bonds present in the sample.

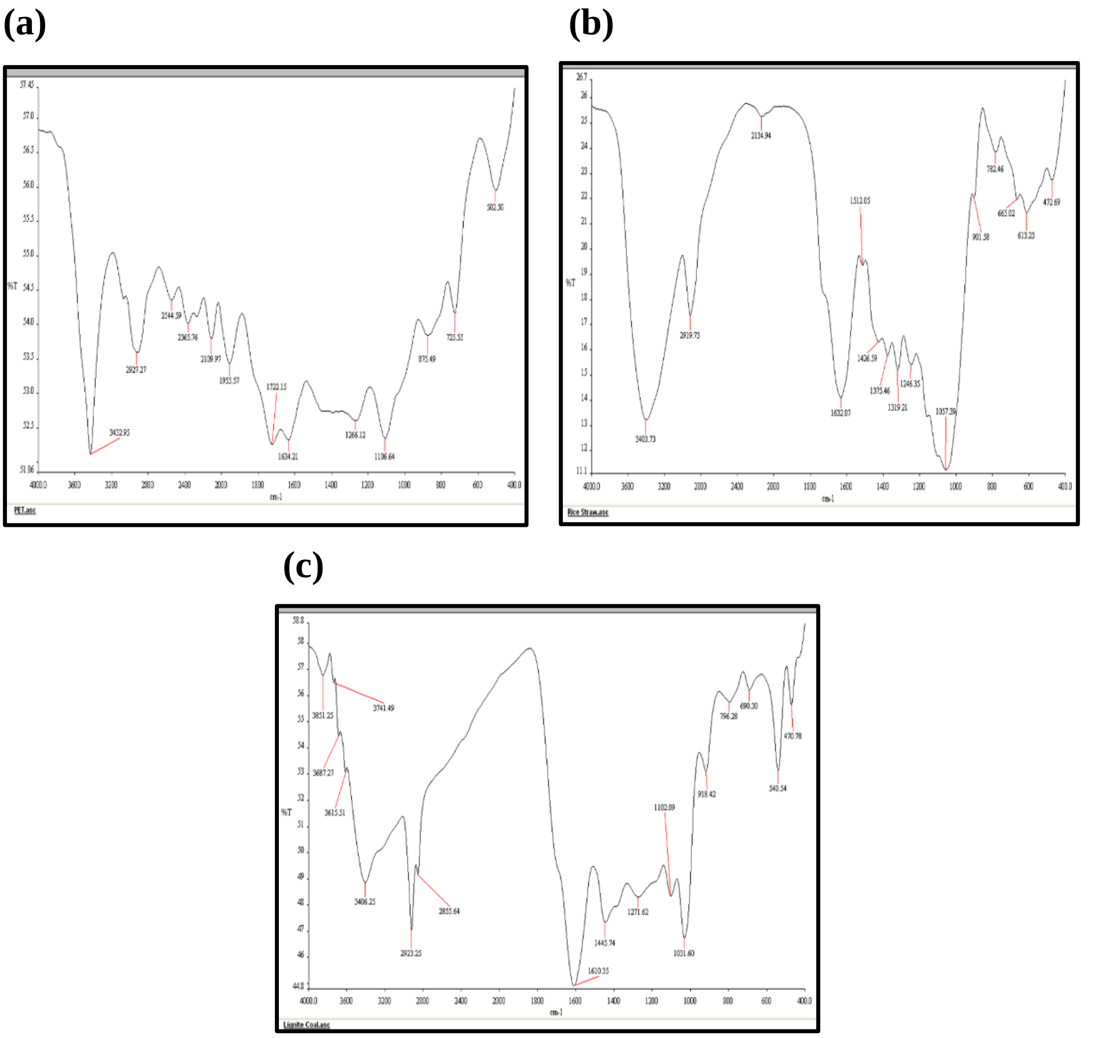

Figure 4.3: FTIR spectra representing absorbance w.r.t wavenumber (cm^{-1}) for: (a) polyethylene terephthalate P_{ET}, (b) rice straw R_S and (c) lignite coal L_C.

FTIR analysis with results shown in Figure 4.3, was actually carried out to study and analyze the chemical composition of the sample materials. It was used to analyze the presence of specific molecular bonds and functional groups like amino groups (-NH), hydroxyl groups (-OH), carboxyl groups (-COOH), phenolic groups (-C_6H_5OH), aromatic rings (benzene, naphthalene), aliphatic chains (methane, ethane), ketone groups (>C=O), ether groups (>C-O-C<) and carbonyl (-CO) groups present in the chemical or molecular structure of the sample material. FTIR analysis actually helps us to analyze the chemical or molecular structure of the sample material as well as the presence of any impurities or contaminants inside the sample.

Figure 4.3 (a) shows the FTIR spectra of polyethylene terephthalate sample. PET contains usually ester groups (CO-O), hydroxyl (-OH) groups, carboxyl groups (-COOH), carbonyl groups (-CO), methylene groups (-CH3), alkyl groups (R-), terephthalate groups (OOCC_6H_4-COO), ethylene groups (-C_2H_4) and aromatic rings (benzene, naphthalene) in its chemical or molecular structure. The characteristic absorption bands located at wavenumber 502.50 cm^{-1}, 725.55 cm^{-1} in Figure 4.3 (a) represent the stretching vibration of the functional group called methylene groups. The absorption band located at 875.49 cm^{-1} is associated with stretching vibration of ethylene groups. The absorption band located at 1106.64 cm^{-1} is associated with stretching vibration of terephthalate groups. The band located at 1266.12 cm^{-1} is associated with ester groups, 1634.21 cm^{-1} associated with aromatic ring, 1722.15 cm^{-1} associated with carboxyl groups, 1955.57 cm^{-1} associated with carbonyl group, 2109.97 cm^{-1} associated with triple bonds (C≡C) or alkynes, 2927.27 cm^{-1} associated with Alkyl group, and the absorption peak located at wavenumber 3432.95 cm^{-1} is associated with hydroxyl groups.

Figure 4.3 (b) shows the FTIR spectra of rice straw sample. Rice straw is a lignocellulosic biomass mainly composed of cellulose, hemicellulose and lignin. Rice straw usually contains uronic ester groups (CO-O) that are found in hemicellulose, hydroxyl (-OH) groups found in both cellulose and hemicellulose, carboxyl groups (-COOH) found in lignin, carbonyl groups (-CO) found in cellulose and hemicellulose, acetyl groups (-$COCH_3$) found in the lignin, ketone groups (>C=O), ether groups (>C-O-C<), sulfur containing groups (e.g. sulfides), nitrogen containing groups (e.g. amines) and aromatic rings (benzene, naphthalene) found in lignin inside its molecular structure. The characteristic absorption band in Figure 4.3 (b) located at wavenumber 472.29 cm^{-1} is associated with metal-oxygen (M-O) bond stretch and Si-O-Si bond presence. The bands at 633.23 cm^{-1} & 665.02 cm^{-1} are associated with C-Cl bond presence and the band at 782.46 cm^{-1} represents the stretching vibrations of weak C-H bond. The absorption band located at 901.58 cm^{-1} is associated with aromatic ring bending vibration in lignin. The absorption peak located at 1057.39 cm^{-1} is associated with stretching vibration of ether groups in cellulose and hemicellulose and carbonyl group in lignin. The bands located at 1246.35 cm^{-1} and 1319.21 cm^{-1} show the existence of C-N bond or nitrogen containing groups. The band at 1375.46 cm^{-1} is associated with sulfur containing groups or S=O stretching vibrations , 1426.59 cm^{-1} associated with C-H bond stretching in lignin, 1512.05 cm^{-1} associated with stretching of carbonyl group in cellulose and hemicellulose and aromatic ring stretching in lignin, 1632.07 cm^{-1} associated with carboxyl group in lignin, 2134.94 cm^{-1} associated with acetyl group in lignin, 2919.73 cm^{-1} associated with C-H bond stretching in cellulose and hemicellulose, and the absorption peak located at wavenumber 3403.73 cm^{-1} is associated with hydroxyl groups.

Figure 4.3 (c) shows the FTIR spectra of lignite coal sample. Lignite coal usually contains hydroxyl (-OH) groups, carboxyl groups (-COOH), carbonyl groups (-CO), phenolic group (C_6H_5OH), aromatic rings (benzene, naphthalene), aliphatic groups/chains (C-H chains), ketones (>C=O), ethers (>C-O-C<), sulfur containing groups (S=O, S-C), and nitrogen containing groups (N-H bonds, C-N bonds) in its molecular structure. The characteristic absorption band located at wavenumber 470.78 cm^{-1} in Figure 4.3 (c) represent the stretching vibration of the sulfur containing groups. The absorption band located at 540.54 cm^{-1} is associated with stretching vibration of S-C bond stretching. The absorption band located at 690.30 cm^{-1} is also associated with stretching vibration of sulfur containing groups. The bands located at 796.28 cm^{-1} and 918.42 cm^{-1} are associated with the aromatic ring bending, 1031.60 cm^{-1} associated with S=O stretching, 1102.09 cm^{-1}

associated with ether group, 1271.62 cm^{-1} associated with aliphatic chain CH_2 bending , 1445.74 cm^{-1} associated with aromatic rings stretching or the presence of phenolic groups, 1610.35 cm^{-1} associated with carboxyl groups as well as ketones, 2855.64 cm^{-1} and 2923.25 cm^{-1} associated with aliphatic group/chain C-H stretching, and the absorption peaks located at wavenumber 3406.25-3851.25 cm^{-1} are associated with the presence of hydroxyl group.

4.2 TGA Results

Figure 4.4 and Figure 4.5 given below show the TGA and the DTG thermograms of pyrolysis of individual samples of polyethylene terephthalate (P_{ET}), rice straw (R_S), lignite coal (L_C) and their respective different blend ratios (B_R) under the study.

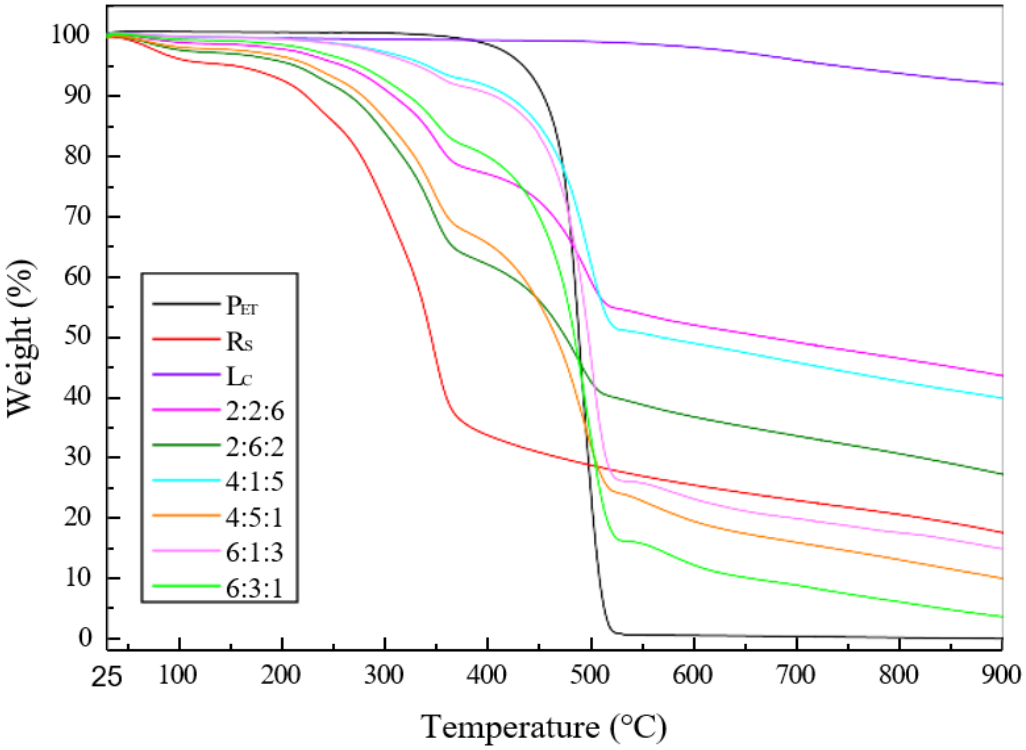

Figure 4.4: The TG (weight % vs temperature) thermograms of individual samples of polyethylene terephthalate (P_{ET}), rice straw (R_S), lignite coal (L_C), and TG thermograms of their respective six blend ratios (B_R).

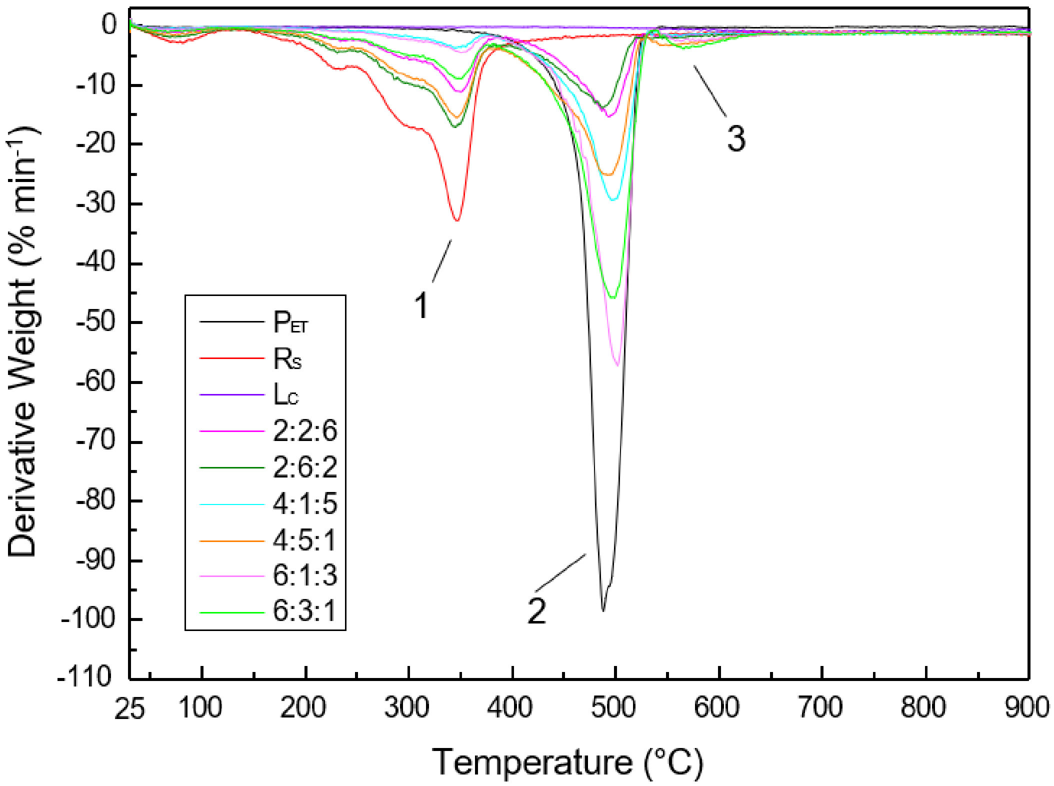

Figure 4.5: The DTG (weight % min^{-1} vs temperature) thermograms of individual samples of polyethylene terephthalate (P_{ET}), rice straw (R_S) and lignite coal (L_C), and those of their respective six blend ratios (B_R): 2:2:6, 2:6:2, 4:1:5, 4:5:1, 6:1:3 and 6:3:1.

On the basis of biomass's pyrolysis mechanism, the microgravity of the feedstock samples takes place before 200 °C temperature. The de-polymerization of feedstock biomass starts. As a result of this, some type of internal re-organization as well as the raw material's modification take place and followed with the release of the small molecular compounds. The literature shows that the thermal stability of the hemicellulose is lowest as compared to the thermal stability of cellulose and the lignin. The pyrolysis of hemicellulose takes place at temperatures ranging from 200 to 300 °C. The pyrolysis of cellulose takes place at the temperature ranging from 240 to 350 °C. And the pyrolysis of of lignin takes place at the end at the temperature ranging from 280 to 450 °C. Studies show that the hemicellulose is a type of a mixture of different polymerized monosaccharides. These polymerized monosaccharides include glucose, arabinose, mannose, galactose, and xylose etc. The degree of polymerization of hemicellulose is low. Its thermal stability is also lowest as compared to cellulose and lignin. The cellulose is difficult to thermally degrade as compared to hemicellulose because cellulose is the type of a D-glucosyl base. It is a base with macro-molecule compound having long and linear chain. Similarly, the crystal structure part of the cellulose is considered to be composed of microfibers that are in proper ordered form. This is why cellulose is more thermally stable than hemicellulose and cellulose is difficult to degrade thermally as compared to that of hemicellulose. The pyrolysis of polyethylene terephthalate takes place in the temperature range of 351.01-539 °C. Figure 4.5 shows that lignite coal has given a very small DTG thermogram as compared to that of rice straw and polyethylene terephthalate. While the studies have shown that the coal structure with its stationary phase is made up of mainly with the aromatic H/Cs. These aromatic hydrocarbons are polycyclic aromatic H/Cs. And they are linked with C-C bonds. These are much heat resistant. This is why the thermal decomposition of the lignite coal takes place at a higher temperature of 470.03 °C. So, the pyrolysis of L_C takes place at higher temperatures as compared to that of P_{ET} and R_S. L_C also has a lower rate of reaction overall. It also gives the large amount of residue char. On the other hand. the pyrolysis of polyethylene terephthalate shows a maximum weight loss rate. And its char residue is almost zero. Based on the TG and DTG graphs or curves, the weight loss process can be considered as the single-step process for the case of pyrolysis of the individual samples.

Figure 4.4 is showing the TGA weight loss % curves vs the temperature for the individual samples as well as for the six blend ratios. Figure 4.5 is showing that the rate of weight loss has been increased in case of the tri-pyrolysis of the blends that contain a higher ratio of R_S while the ratio of P_{ET} is same. Similar type of TGA profiles have been produced for the primary stage pyrolysis in case of the tri-pyrolysis of the blends that contain a fixed ratio of R_S (Figure 4.4). While carrying out tri-pyrolysis of blends when the B_R of P_{ET} is increased in the blends, it is observed that the rate of weight loss gets higher in the secondary stage of the pyrolysis. Also, it is observed that on increasing the ratio of P_{ET} in the blend results in decreasing the mass of residue as well. Figure 4.5 shows that there three distinct DTG peaks that are associated to tri-pyrolysis of blends. These three distinct weight loss DTG peaks of the blends in Figure 4.5 are associated with the largest peaks of the TG weight loss profiles for individual samples and blends in Figure 4.4.

Results shows that when the ratio of rice straw is increased in the blends, then the weight loss profiles obtained for the tri-pyrolysis of blends are quite similar in primary region as compared to the profile of individual rice straw pyrolysis (520 °C and 660 °C). When the ratio of rice straw is increased greater than 50 % in the blend, the results shows that it lowers the temperature of primary TGA weight loss. Results also show that the secondary profiles of the mass loss of the tri-pyrolysis blends are closer and comparable to the profile of individual P_{ET} pyrolysis as shown in Figure 4.4 for the case of the increased P_{ET} ratio in blends. Similarly, the results shows that the tri-pyrolysis of blends increases the reactivity of the process as compared to the individual sample pyrolysis and it can be seen from the graph also that the secondary peaks of mass loss are quite lower as compared to the individual P_{ET} pyrolysis (351 °C).

Following two relationships were applied for analyzing and studying the theoretical (calculated) and experimental TG and DTG thermograms:

$$M_{cal} = x_{P_{ET}} M_{P_{ET}} + x_{Rs} M_{Rs} + x_{Lc} M_{Lc} \tag{12}$$

$$(dM/dt)_{cal} = x_{P_{ET}} (dM/dt)_{P_{ET}} + x_{Rs} (dM/dt)_{Rs} + x_{Lc} (dM/dt)_{Lc} \tag{13}$$

Here:

M_{Cal} = total calculated weight loss (weight %).

c

x = ratio in blend for individual feed material polyethylene terephthalate (P_{ET}), rice straw (R_S) and lignite coal (L_C).

dM/dt = mass loss ratio (weight % min^{-1}).

The experimental and calculated TG and DTG thermograms of the six blend ratios that are under study in tri-pyrolysis have been shown below in Figure 4.6.

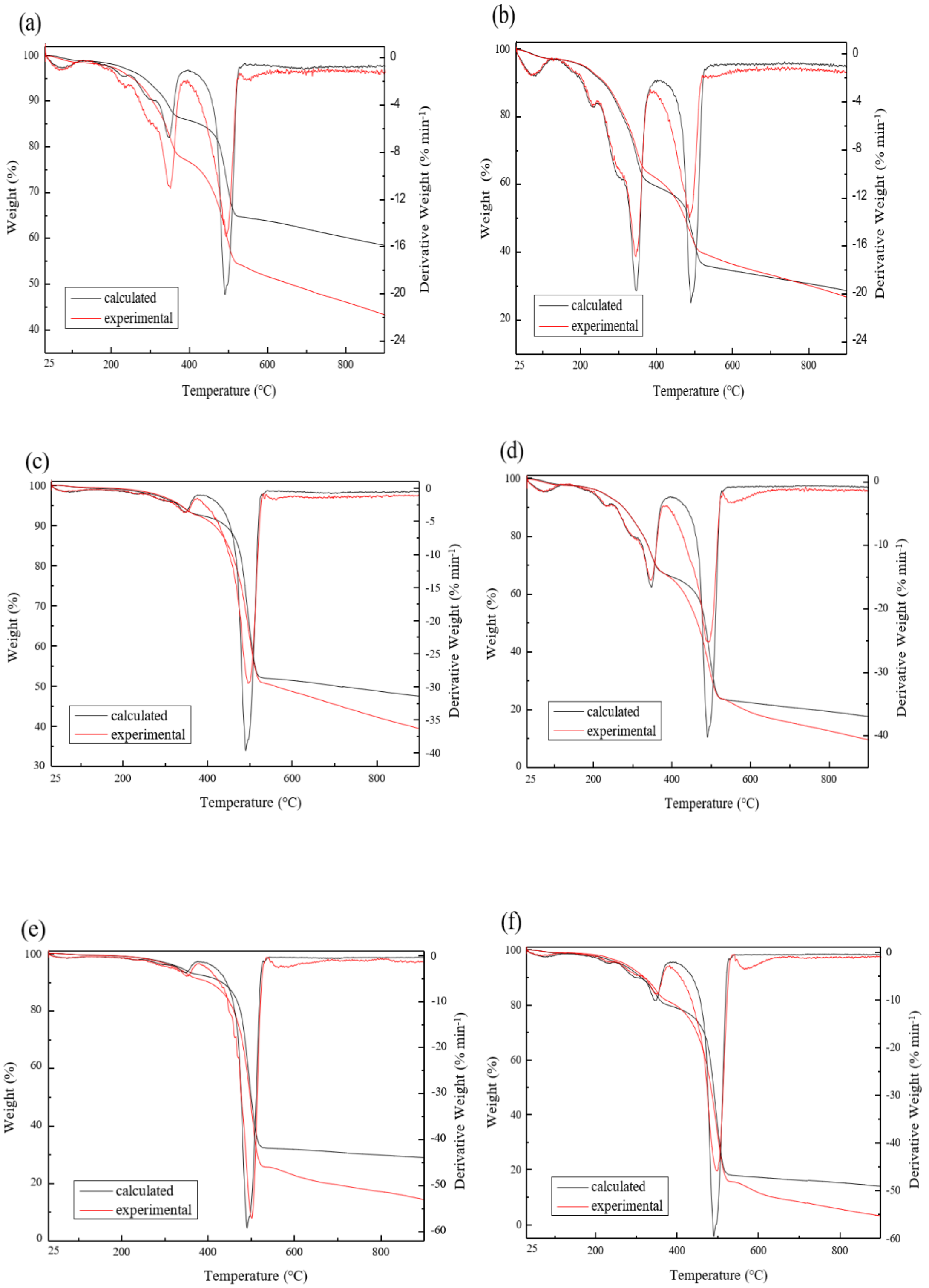

Figure 4.6: The experimental and calculated TG and DTG profiles of: (a) 2:2:6, (b) 2:6:2, (c) 4:1:5, (d) 4:5:1, (e) 6:1:3, (f) 6:3:1.

The results show that the tri-pyrolysis is a process which is a result of mutual interactions and influences of the particles of the sample materials blended in different blend ratios. On comparing the calculated and experimental curves, it can be seen that the temperature and the maximum reaction rate for the second stage of experimental curves is smaller. So, the blending has actually promoted the second stage reaction. The residue mass is also smaller for experimental curves as compared to calculated curves. The residual mass decreases in the presence of rice straw and polyethylene terephthalate in the blends. The mass loss rate for individual samples is also less than the tri-pyrolysis of blends. Most of the mass loss was completed before the temperature of 550 °C. The reaction rate and residue mass differences between the calculated curves and the experimental curves mainly observed after the temperature of 370 °C. Thus, it shows that the synergistic effects take place majorly at higher temperatures.

Table 4.4 shows the characteristic temperature and the other parameters of the individual sample pyrolysis as well as tri-pyrolysis of blends. It can be seen that the initial temperatures for pyrolysis of P_{ET}, *Rs*, and *Lc* are 351.01 °C, 124.21 °C, and 470.03 °C, respectively. As the reaction proceeds, the porous media play its role. The synergistic effect takes place in the porous media as the lignocellulosic substrates of rice straw turns into more porous. It is then followed by the interaction of the free radicals with each other during the process of degradation. The temperatures of the maximum reaction rates of blends are higher than that of individual P_{ET} (486.98 °C) except only for B_R = 2:6:2. This result is due to the presence of larger amounts of rice straw in this blend. The temperature of the initial pyrolysis gets lower due to the larger amount of rice straw in the blend. Thus, it can be concluded that addition of higher amounts of rice straw benefits the pyrolysis reaction. Meanwhile, the addition of higher amounts of P_{ET} in blends increases the maximum reaction rate of the blends. So, pyrolysis reaction becomes more intense on addition of polyethylene terephthalate. Similarly, the addition of both rice straw and polyethylene terephthalate decreases the residual amount of process specially the addition of polyethylene terephthalate. It can be seen that the residue mass of individual pyrolysis of polyethylene terephthalate is 0%, that of rice straw is 17.19% and that of lignite coal is 92.01%. Thus, the addition of polyethylene terephthalate in blends tends to get more complete reaction of pyrolysis. So, the amount of decrease in the wt % of residue is related to the amount of increase in wt % of P_{ET}.

Table 4.4: The characteristic temperature and other parameters of the individual sample pyrolysis and tri-pyrolysis of blends.

Sample	Initial Decomposition Temperature (°C)	Max. Reaction Rate (% min^{-1})			Max. Reaction Rate Temperature (°C)			Residual Mass (%)
P_{ET}	351.01	-98.30			486.98			0
R_S	124.21	-33.05			344.71			17.19
L_C	470.03	-2.27			688.13			92.01
		1st Peak	2nd Peak	3rd Peak	1st Peak	2nd Peak	3rd Peak	
B_R = 2:2:6	204.91	-10.94	-15.12	-1.85	350.65	493.71	544.71	43.52
B_R = 2:6:2	169.09	-16.85	-13.57	-1.99	343.50	485.91	533.81	27.02
B_R = 4:1:5	210.11	-3.60	-29.34	-1.63	349.65	495.92	553.75	40.00
B_R = 4:5:1	172.97	-15.45	-25.13	-3.19	345.07	491.74	549.32	9.69
B_R = 6:1:3	227.11	-4.27	-57.05	-2.48	349.44	500.75	568.17	15.21
B_R = 6:3:1	188.90	-8.62	-45.75	-3.64	347.43	496.05	564.71	3.36

4.2.1 Effect of P_{ET} on Yield

The results show that the maximum reaction rate increases on increasing the ratio of P_{ET} in the blends. Thus, the addition of polyethylene terephthalate in blends results in enhanced and increased pyrolysis reaction.

4.2.2 Effect of R_S on Yield

Results shows that the addition of rice straw in blends is useful and beneficial for the pyrolysis process. It is because of the fact that the addition of rice straw decreases the temperature required for initial pyrolysis decomposition.

4.2.3 Effect of L_C on Yield

The residual mass of lignite coal pyrolysis is 92.01% which is highest as compared to the residual mass of rice straw and polyethylene terephthalate. The residue mass of rice straw is 17.19%. The residual mass of polyethylene terephthalate is 0%. So, the addition of rice straw and polyethylene terephthalate in blends results in reduction of residue mass while the addition of lignite coal results in increase of residue mass.

4.3 Kinetic Analysis

From Eq. (4) by transferring and taking log on both sides, we get:

$$\ln\left(\frac{\beta G(a)}{T-To}\right) = lnA - E/RT \qquad (14)$$

where the terms β, A, E, R and T stands for the heating rate, pre-exponential factor, activation energy, universal gas constant, and sample temperature, respectively.

A common dynamic-mechanism function was used in this research study for the kinetic analysis of the pyrolysis process. The pre-exponential factor A and activation energy (E) were determined from the relationship of $\ln\left(\frac{\beta G(a)}{T-To}\right)$ vs 1/T. This study was carried out using a single heating rate method for dynamic analysis.

The following relation was used to study and analyze the calculated and experimental activation energies:

$$E_{cal}=X_{PET}\,E_{PET}+X_{Rs}\,E_{Rs}+X_{Lc}\,E_{Lc} \qquad (15)$$

Table 4.5 shows the kinetic analysis of the individual feedstock samples for pyrolysis as well as for the six blends for tri-pyrolysis process. Rice straw dominates the process in the primary stage of tri-pyrolysis of blends. The individual samples for pyrolysis need a higher final temperature of 900 °C for the completion of the pyrolysis process. Meanwhile the blends require a higher initial temperature of 203-266 °C. Table 4.5 also shows the details of the kinetic functions of the individual samples pyrolysis as well as for all the stages of blends tri-pyrolysis. Table 4.5 shows a clear difference between the kinetic mechanisms of the tri-pyrolysis blends and those of the individual feedstock sample. It shows the synergistic influence on the reaction mechanisms of pyrolysis for the case of blends. Results show that the activation energy of lignite coal is 76.06 KJ mol^{-1}. The activation energy of rice straw is 48.51 kJ mol^{-1}. While the activation energy of polyethylene terephthalate is 314.11 KJ mol^{-1}. Thus, the activation energy of rice straw is lowest as compared to that of polyethylene terephthalate and lignite coal. Polyethylene terephthalate has highest activation energy. Meanwhile the results also show that the activation energy of first stage of tri-pyrolysis of blends is almost similar to that of rice straw. The activation energy of plastic is greater that the rice straw due to the fact that there is a structural difference between plastic and rice straw. This is understood that why rice straw has lower activation energy than plastic. It is due to the difference in their structures. But what is the thing that have lowered the activation energy of the blends, it is required to be understood. It is due to the synergistic effects in case of blends.

The activation energies of the second stage of tri-pyrolysis of blends are between 40.20 and 125.01 KJ mol^{-1}. All these activation energies are also less than that of the polyethylene terephthalate which has activation energy of 314.11 KJ mol^{-1}. It shows that using blends or mixture of samples is useful and beneficial for pyrolysis process. After mixing of the three samples in the form of blends, the decomposition temperature of second stage gets decreased. The second stage is actually a joint action of the three samples materials blended. The addition of rice straw decreases the activation energy, and the addition of lignite coal and polyethylene terephthalate increases the activation energy of the blend. But still the activation energy of the second stage is less than that of the activation energy of polyethylene terephthalate. The activation energy of third stage of blends is negative. It is due to the result of multiple reactions superpositions. At, this stage, the reaction is exothermic. The calculated values of the activation energies are from 106.91 to 216.10 KJ mol^{-1}. From the results, it can be also noticed that the values of experimental activation energies are less than those of calculated values. It also shows that the pyrolysis becomes easier in case of the mixtures of samples. Finally, as a result of all the studies, the ideal blend ratio is 2:6:2.

Table 4.5: Kinetic analysis.

Sample	Temperature (°C)	E (kJ mol^{-1})	E_{cal} (kJ mol^{-1})	A (min^{-1})	Reaction Mechanisms	g(a)	r^2
P_{ET}	392.28-525.37	314.11		5.30 X 10^{19}	One-dimensional diffusion	a^2	0.9884
R_C	186.65-383.46	48.51		44.01	Three-dimensional diffusion	$[(1+a)^{1/3}-1]^2$	0.9930
L_C	483.39-900.6	76.06		10.91	Three-dimensional diffusion	$1-2/3a-(1-a)^{2/3}$	0.9921
B_R=2:2:6	252.11-376.07	64.72	118.06	5301	One-dim. Diffusion	a^2	0.9976
	392.88-496.89	111.94		7.50 X 10^6	Autocatalytic Reaction, dendrite nucleation	ln(a/1-a)	0.9969
	532.04-577.60	-10.75		0.015	n=3	$1-(1-a)^3$	1
B_R=2:6:2	253.62-362.89	54.16	106.91	678	One-dim. Diffusion	a^2	0.9928
	379.72-512.17	93.03		2.36 X 10^5	Autocatalytic Reaction, dendrite nucleation	ln(a/1-a)	0.9944
	512.17-575.44	-10.57		0.016	n=3	$1-(1-a)^3$	1
B_R=4:1:5	252.66-371.90	69.94	168.30	1031	One-dim. Diffusion	a^2	0.9978
	371.90-536.57	97.98		1.13 X 10^4	Three-dim. Diffusion	$[(1+a)^{1/3}-$	0.9660

	544.97-588.01	-10.89		0.015	n=3	1]^2 1-(1-a)^3	1
B_R=4:5:1	202.91-379.20	58.19	158.13	864	One-dim. Diffusion	a^2	0.9946
	379.20-529.35	40.20		2.04	Three-dim. Diffusion	[(1+a)$^{1/3}$-1]^2	0.9528
	533.75-619.59	-10.97		0.015	n=3	1-(1-a)^3	1
B_R=6:1:3	266.02-376.21	73.06	216.10	1420	One-dim. Diffusion	a^2	0.9983
	387.82-536.17	125.01		8.06 X 10^5	Three-dim. Diffusion	[(1+a)$^{1/3}$-1]^2	0.9568
	538.17-614.54	-10.93		0.015	n=3	1-(1-a)^3	1
B_R=6:3:1	207.21-379.27	63.54	210.41	715.51	One-dim. Diffusion	a^2	0.9976
	379.27-536.03	77.96		680.62	Three-dim. Diffusion	[(1+a)$^{1/3}$-1]^2	0.9519
	563.56-605.42	-10.99		0.015	n=3	1-(1-a)^3	1

4.4 Thermodynamic Analysis

Table 4.6 shows thermodynamic parameters that have been estimated and obtained from above kinetic data. These thermodynamic parameters include enthalpy change, Gibbs free energy change, and entropy change. These parameters were estimated using the kinetic data and Eq. (7-9).

The value of ΔH is highest for individual pyrolysis of P_{ET} which is 308.92 KJ mol^{-1}. While R_S has ΔH equal to 45.196 KJ mol^{-1} and L_C has ΔH equal to 69.881 KJ mol^{-1}. The values of ΔH for first and second peaks of tri-pyrolysis of blends are all positive values while the values of ΔH for all third peaks are negative values as can be seen in Table 4.6. The value of ΔS is only positive for individual sample pyrolysis of P_{ET} and rest all values are negative. The L_C has the highest ΔG as compared to all other samples and blends. Its value is 332.30 KJ mol^{-1}.

Table 4.6: Thermodynamic parameters obtained from kinetic data.

Sample	T (K)	Tm (K)	E (KJ/mol)	A (min^{-1})	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (KJ/mol k)
P_{ET}	624.16	760.13	314.11	5.30 x 10^{19}	308.92	243.78	0.086
R_S	397.36	617.86	48.51	44.01	45.196	202.76	-0.255
L_C	743.18	961.28	76.06	10.91	69.881	332.30	-0.273
B_R=2:2:6	478.06	623.8	64.72	5301	60.745	196.82	-0.218
		766.86	111.94	7.50 x 10^6	107.97	227.99	-0.156
		817.86	-10.75	0.015	-14.725	249.146	-0.323
B_R=2:6:2	442.59	616.65	54.16	678	50.48	194.88	-0.234
		759.06	93.03	2.36 x 10^5	89.35	229.2	-0.184
		806.96	-10.57	0.016	-14.25	245.08	-0.321
B_R=4:1:5	483.26	622.8	69.94	1031	65.92	210.32	-0.232
		769.07	97.98	1.13 x 10^4	93.96	255.92	-0.211
		826.9	-10.89	0.015	-14.91	252.17	-0.323
B_R=4:5:1	446.12	618.22	58.19	864	54.48	197.97	-0.232
		764.89	40.20	2.04	36.49	251.61	-0.281
		822.47	-10.97	0.015	-14.68	250.02	-0.322
B_R=6:1:3	500.26	622.59	73.06	1420	68.9	211.95	-0.230
		773.9	125.01	8.06 x 10^5	120.85	256.64	-0.175
		841.32	-10.93	0.015	-15.09	256.77	-0.323
B_R=6:3:1	462.05	620.58	63.54	715.5	59.7	205.02	-0.234
		769.2	77.96	680.6	74.12	253.8	-0.233

		837.86	-10.99	0.015	-14.83	179.04	-0.231

4.5 Synergistic Effects

Synergistic effects were studied and reviewed on the basis of the TGA results and kinetic data for analyzing the material particles' interactions in pyrolytic degradation of the blends. The study gave us some important results.

Studies have shown that when the three feedstock materials were blended and mixed for tri-pyrolysis degradation, some interactions were observed between the material particles of the three blended sample materials. These interactions were found to be much dominant as compared to the individual sample particles interactions. The study of these interactions is called the synergistic effects study. The results also show that these synergistic effects enhanced the conversion, yield and reaction rate of the thermochemical decomposition. Resulting in suggesting that the tri-pyrolysis of rice straw, polyethylene terephthalate and lignite coal is potentially better as compared to the individual feedstock pyrolysis.

The literature show that the product distribution, conversion, yield and quality is affected mainly by these factors: the initial pressure of inert N_2 gas, blend ratios, the pyrolysis temperature, and the use of additives in blends [109]. The initial nitrogen flow rate was kept constant 30mL/min here in this study for all individual samples as well as for all blend ratios. Similarly, no additive has been used in this study that may affect the conversion and yield. Thus, the conversion and reaction rate which enhanced in case of blend ratios as compared to the individual sample's pyrolysis, is just enhanced due to the synergistic effects and interactions found between the particles of three different blended materials.

Table 4.5 shows a clear difference between the kinetic mechanisms of the tri-pyrolysis blends and those of the individual feedstock sample. It shows the synergistic influence on the reaction mechanisms of pyrolysis for the case of blends. Results show that the activation energy of lignite coal is 76.06 KJ mol^{-1}. The activation energy of rice straw is 48.51 kJ mol^{-1}. While the activation energy of polyethylene terephthalate is 314.11 KJ mol^{-1}. Thus, the activation energy of rice straw is lowest as compared to that of polyethylene terephthalate and lignite coal. Polyethylene terephthalate has highest activation energy. Meanwhile the results also show that the activation energy of first stage of tri-pyrolysis of blends is almost similar to that of rice straw. The activation energy of plastic is greater that the rice straw due to the fact that there is a structural difference between plastic and rice straw. This is understood that why rice straw has lower activation energy than plastic. It is due to the difference in their structures. But what is the thing that have lowered the activation energy of the blends, it is required to be understood. It is due to the synergistic effects in case of blends.

The activation energies of the second stage of tri-pyrolysis of blends are between 40.20 and 125.01 KJ mol^{-1}. All these activation energies are also less than that of the polyethylene terephthalate which has activation energy of 314.11 KJ mol^{-1}. It shows that using blends or mixture of samples is useful and beneficial for pyrolysis process. After mixing of the three samples in the form of blends, the decomposition temperature of second stage gets decreased. The second stage is actually a joint action of the three samples materials blended. The addition of rice straw decreases the activation energy, and the addition of lignite coal and polyethylene terephthalate increases the activation energy of the blend. But still the activation energy of the second stage is less than that of the activation energy of polyethylene terephthalate. The activation energy of third stage of blends is negative. It is due to the result of multiple reactions superpositions. At, this stage, the reaction is exothermic. The calculated values of the activation energies are from 106.91 to 216.10 KJ mol^{-1}. From the results, it can be also noticed that the values of experimental activation energies are less than those of calculated values. It also shows that the pyrolysis becomes easier in case of the mixtures of samples. Finally, as a result of all the studies, the ideal blend ratio is 2:6:2.

CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATIONS

5.1 Conclusions

The results of this study show that pyrolytic degradation process is completed in three major stages as drying, devolatilization, and char formation stage. It can also be concluded that tri-pyrolysis is the potential method for production of biofuels as compared to the pyrolysis of individual feedstock. It is because the individual pyrolysis process requires higher activation energy as compared to tri-pyrolysis. Further, the results show that the tri-pyrolysis of lignite coal, rice straw, and polyethylene terephthalate is a complicated process. There are synergistic effects and interactions found between the three materials particles in blends. Similarly, the study of the synergistic effects show that the synergistic effects in case of blends enhance the conversion and product yields. Moreover, it is finally concluded:

- The results show that the maximum reaction rate increases on increasing the ratio of P_{ET} in the blends. Thus, the addition of polyethylene terephthalate in blends results in enhanced and increased pyrolysis reaction.
- Results show that the addition of rice straw in blends is useful and beneficial for the pyrolysis process. It is because of the fact that the addition of rice straw decreases the temperature required for initial pyrolysis decomposition.
- The residual mass of lignite coal pyrolysis is 92.01% which is highest as compared to the residual mass of rice straw and polyethylene terephthalate. The residue mass of rice straw is 17.19%. The residual mass of polyethylene terephthalate is 0%. So, the addition of rice straw and polyethylene terephthalate in blends results in reduction of residue mass while the addition of lignite coal results in increase of residue mass.

- On the basis of the results of profiles of TG and DTG and with respect to the kinetic data, we can also conclude that the ideal blend ratio for tri-pyrolysis is 2:6:2.

5.2 Future Recommendations

- The selection of feedstock is another big challenge. Earlier most of the research is being carried out using agricultural residues. Utilization of these residues for bio-fuels production may cause the shortage of animal food, so to overcome this, it is recommended to increase the cultivation of cereals crops, such as maize, corn, wheat, rice etc.
- The use of PET waste, its collection and shredding for production of biofuels is also a major challenge. Technology must be improved for fast and efficient shredding of PET plastic.
- In comparison with fossil fuels, bio-fuels production should be more focused in future due to the non-toxicity and environment friendly properties.
- The bio-fuels production cost in case of pyrolysis process is higher. More research work is recommended to optimize its production cost.
- It is necessary to ensure continued availability of crop residues before replacing fossil fuels with biofuels for use in machines engines in future.
- To improve bio-fuels shelf life, more research work in future is recommended.
- The lack of technology affects the production of biofuels on a large scale with comparative prices. Continuous supply of crop residues which are the main source of bio-fuels production is very necessary to control its price.
- Initially at low temperature, the pyrolysis process tends to form more solid biochar, due to which the gaseous and liquid bio-fuels amount decreases. It requires more study and enhancement of technology to improve the yields further.

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