Waste To Energy: Pyrolysis of Multilayered Plastic Packet For Hydrocarbon Fuel – Analysis of Thermodynamic And Thermal Degradation Behaviour

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Abstract- *This study investigates the thermal degradation and energy recovery potential of multilayered plastic (MLP) waste through pyrolysis, presenting an innovative approach to addressing the challenges of plastic waste management and energy sustainability. Comprehensive proximate and ultimate analyses revealed the material's high volatile matter (92.1%) and carbon content (82.5%), establishing its suitability for thermal decomposition. Pyrolysis was conducted in a controlled reactor, yielding three primary products: hydrocarbon fuel, char, and gaseous byproducts. Thermogravimetric analysis (TGA) delineated the material's degradation behavior into distinct phases: moisture evaporation (<150°C), volatile release (150–400°C), and fixed carbon decomposition (400–550°C). Thermodynamic analysis provided critical insights into energy parameters, including a gross calorific value (GCV) of 28.1 MJ/kg, with contributions from carbon (27.06 MJ/kg), hydrogen (14.91 MJ/kg), and sulfur (0.074 MJ/kg), culminating in a theoretical energy potential of 42.04 MJ/kg. The Gibbs free energy (ΔG = -28,187 kJ/kg) confirmed the spontaneity and energy efficiency of the pyrolysis process. This research highlights the viability of pyrolysis for converting MLP waste into high-value energy products, contributing to sustainable waste valorization and advancing the circular economy.*

I. INTRODUCTION

Plastic waste has become one of the most pressing environmental issues worldwide due to its significant volume, persistence in the environment, and far-reaching impacts on ecosystems and human health. Over the past century, plastics have transformed industries, providing convenient, durable, and inexpensive materials. However, their non-biodegradable nature means they can remain in the environment for hundreds, if not thousands, of years. In this overview, we'll explore the types, sources, and consequences of plastic waste, along with current efforts to manage it.

1.1 Overview of Plastic Waste

Plastic waste encompasses all discarded plastic products and materials, ranging from everyday items like bags, bottles, and packaging, to industrial and agricultural plastics, and more complex items like electronic and automotive parts. According to recent estimates, over 300 million tons of plastic are produced globally each year, and roughly half of that is designed for single-use purposes, discarded almost immediately after use.

1.2. Types of Plastic Waste

1.2.1 Single-Use Plastics

Single-use plastics are items intended for a short period of use before being discarded. This category includes plastic bags, straws, food wrappers, cutlery, and packaging. Single-use plastics are a major contributor to global plastic waste because they are widespread, inexpensive, and difficult to recycle effectively.

1.2.2 Packaging Waste

Plastic packaging makes up a substantial portion of plastic waste. It includes materials like bottles, wrappers, containers, and films used to protect and transport goods. While packaging offers many benefits, such as food preservation, it generates large volumes of waste because it's often not recyclable or is contaminated with food residues, making recycling inefficient or impossible.

1.2.3 Microplastics

Microplastics are tiny plastic particles less than 5mm in size, resulting from the breakdown of larger plastics or directly produced for applications in cosmetics, industrial processes, and textiles. Microplastics have been found in oceans, soil, air, and even in human bodies, as they are easily ingested by wildlife and can travel through food chains.

1.2.4 Multilayer Plastics (MLPs)

MLPs consist of multiple layers of different polymers bonded together, often with aluminum or other materials, to create a composite with specific properties. MLPs are used in food packaging, medical applications, and other areas where barriers to oxygen, moisture, and light are required. These plastics are very challenging to recycle due to their complex structure, leading most to end up in landfills or as environmental pollutants.

1.2.5 Non-Recyclable Plastics

Certain plastics, like polystyrene (used in Styrofoam), polyvinyl chloride (PVC), and specific plastic composites, are challenging to recycle due to technical limitations, high processing costs, or environmental concerns. These plastics often contribute to long-lasting environmental waste as they persist in landfills and ecosystems.

1.3. Sources of Plastic Waste

Plastic waste originates from a wide range of sectors:

Consumer Goods

The consumer goods sector contributes significantly to plastic waste, with items like packaging, bottles, bags, and containers. The convenience of disposable plastics has led to a culture of single-use products, creating a large volume of waste that is difficult to manage.

Industrial and Commercial Sectors

Industries generate plastic waste through manufacturing processes, packaging materials, and industrial components. These plastics can be large in scale and include items like plastic drums, pallets, and waste from packaging raw materials.

Agricultural Sector

Agricultural practices use various types of plastics for purposes such as greenhouse films, mulch films, irrigation systems, and silage bags. These materials, once used, become waste and often pose challenges in recycling due to contamination with soil and chemicals.

Medical and Healthcare Sector

Plastic waste in healthcare includes syringes, IV bags, gloves, and other single-use items designed to ensure safety and prevent contamination. Although essential, these items contribute to plastic waste because they are generally non-recyclable due to contamination risks.

1.4. Environmental Impact of Plastic Waste

Persistence and Pollution

Plastics do not decompose like organic materials, instead fragmenting into smaller pieces, known as microplastics, over time. These fragments contaminate land and water ecosystems, making their way into rivers, oceans, and marine life. Once in the ocean, plastics break down slowly, releasing toxic chemicals and polluting marine ecosystems.

Impact on Wildlife

Marine and terrestrial animals often mistake plastics for food or become entangled in them. Ingested plastics can block digestive tracts, reduce feeding, and lead to malnutrition, starvation, or death. Entanglement in plastic waste, such as fishing nets or plastic bags, can cause injuries or trap animals, often leading to drowning or death.

Human Health Risks

Plastic waste has begun to impact human health, primarily through microplastics entering the food chain. Studies have found microplastics in water, seafood, and other food sources, and researchers are still studying the potential health impacts. Additionally, certain chemicals used in plastics, like bisphenol A (BPA) and phthalates, can disrupt hormones and have been linked to reproductive and developmental health issues.

Greenhouse Gas Emissions

Plastic production is energy-intensive, relying heavily on fossil fuels, and releases significant amounts of greenhouse gases. Furthermore, when plastic waste is incinerated, it contributes to air pollution, releasing CO2, methane, and other harmful gases, exacerbating climate change.

1.5. Current Approaches to Plastic Waste Management

Efforts to manage plastic waste involve several strategies, from reducing consumption and improving recycling to developing alternative materials.

Recycling

Recycling is one of the main strategies for managing plastic waste. However, only about 9% of plastic is recycled globally. Many plastics cannot be recycled effectively due to contamination or lack of proper infrastructure. Advanced recycling methods, like chemical recycling, are being explored to break down complex plastics, but these are still limited in scope and scale.

Biodegradable and Compostable Plastics

In recent years, research has focused on developing biodegradable and compostable plastics derived from plant-based materials. These materials are designed to break down more easily, though they often require industrial composting facilities, which are not widely available. While these materials show promise, they cannot yet fully replace conventional plastics in terms of functionality and cost-effectiveness.

Extended Producer Responsibility (EPR)

EPR programs make manufacturers responsible for the entire lifecycle of their products, encouraging them to design more sustainable packaging and contribute to recycling costs. EPR is already implemented in several countries and incentivizes producers to create less wasteful and more recyclable products.

Waste-to-Energy (WtE)

Waste-to-energy involves incinerating plastic waste to generate energy, which reduces waste volume and provides an energy source. However, incineration releases toxic pollutants and greenhouse gases, and it’s often viewed as a last-resort option due to environmental concerns.

Reducing Plastic Use

Governments and organizations are increasingly promoting policies to reduce plastic use, particularly single-use items. Bans and restrictions on items like plastic bags, straws, and cutlery have been implemented in several countries, alongside consumer awareness campaigns that encourage reduced plastic use and alternative materials.

1.6 Multilayer plastic (MLP)

Multilayer plastic (MLP) waste refers to waste products made from multiple layers of different polymers (and sometimes including aluminum or other materials), bonded together to create specific properties. MLPs are commonly used in packaging, especially for food and beverages, due to their excellent barrier properties, which help preserve products by preventing oxygen, moisture, and light from penetrating.

1.6.1 Characteristics of Multilayer Plastics (MLPs)

Composition: MLPs typically combine several layers of materials, such as polyethylene (PE), polyethylene terephthalate (PET), aluminum, polypropylene (PP), and sometimes adhesives. The combination of layers provides strength, flexibility, and a superior barrier.

Properties: MLPs are lightweight, durable, moisture-resistant, and offer extended shelf life for products. However, the multiple layers make them difficult to separate, recycle, or process conventionally.

Applications: They are widely used in packaging for snacks, frozen foods, pet food, toiletries, pharmaceuticals, and liquid products like pouches for juices and condiments.

1.6.2 Challenges of Multilayer Plastic Waste

Recycling Difficulty:

Separating different layers requires specialized processes that are not available in standard recycling facilities. The layers, when bonded, cannot be recycled together in traditional recycling streams.

Only certain facilities with advanced sorting and separation technologies can handle MLP recycling, making it rare and costly.

Environmental Impact:

Due to recycling limitations, most MLPs end up in landfills, where they can take hundreds of years to decompose. MLPs contribute significantly to environmental pollution, especially in marine and terrestrial ecosystems, as they fragment into microplastics, causing harm to wildlife and entering food chains.

Low Market Value:

MLPs generally have low value in the recycling market because their separation and recycling are not cost-effective. They’re often landfilled or incinerated, adding to pollution and greenhouse gas emissions.

1.6.3. Current Solutions and Innovations for MLP Waste Management

Chemical Recycling:

Advanced methods like pyrolysis, depolymerization, or solvolysis can break down MLPs into their base components or convert them into fuels and chemicals. These methods, however, require significant energy and are not yet widespread.

Solvent-Based Processes:

Solvent-based technologies can selectively dissolve certain layers, allowing for partial recycling of MLPs. This approach is still under development and faces challenges in scalability.

Redesign and Material Innovation:

Some companies are exploring alternatives to MLPs, such as single-layer recyclable films or biodegradable materials. For example, using plant-based materials and compostable packaging as an eco-friendly alternative to traditional MLPs.

Collection and Recovery Initiatives:

Certain recycling programs and initiatives focus on collecting MLP waste for specialized processing, particularly in areas where MLP waste is prevalent. Extended Producer Responsibility (EPR) schemes are also encouraging manufacturers to manage the lifecycle of MLPs, promoting sustainable design and waste management.

1.7 objective

Potential conversion: To investigate the pyrolysis of multilayered plastic packets, specifically focusing on their potential conversion into hydrocarbon fuel feedstocks.

Thermal Degradation: To understand the thermal degradation behavior of multilayered plastics under controlled pyrolytic conditions

Temperature: To determine the optimal temperature ranges for hydrocarbon yield maximization.

Thermodynamic analysis: To conduct a comprehensive thermodynamic analysis of the process.

II. LITERATURE REVIEW

Krishnasamy Sivagami (2020), In this paper, the catalytic pyrolysis of different types of polyolefin and multilayer packaging based plastic wastes in the presence of commercial zeolite catalyst was studied in the batch pilot scale reactor. Different types of multi-layerplastics such as biaxial oriented polypropylene (BOPP), metalized biaxialoriented polypropylene layers (MET/BOPP), poly ethylene terepthalate (PET), metalized polyethylene-terepthalate (MET/PET), PET combined polyethylene (PET/PE) and mixed polyolefin plastic wastes obtained from the municipal corporation were pyrolyzed to determine the oil, gas and char distribution. BOPP based plastic waste exhibited higher oil yield and calorific value (65 – 70%, 45.14 KJ/g) compared to PET based MLPs (17.8%, 30 KJ/g) andlaminated metalized plastics (13%, 37 KJ/g). Modifying the feed composition by mixing of polyolefins-based waste plastics with PET based MLPs and BOPP/MET BOPP doubled the liquid yield and notably altered the physicochemical characterization of the resulted pyrolysis oil.

Aadhik Asokkumar (2016), The method and principal of the production / process of hydrocarbon fuels are discussed in this paper. The increased demand and high price for energy sources are driving efforts to convert organic compounds into useful hydrocarbon fuels. Although much of this work has focused on biomass, there are strong benefits to deriving fuels from waste plastic material. Waste plastic is abundant and its disposal creates large problems for the environment. Plastic does not break down in landfills, it is not easily recycled and degrades in quality during the recycling process, and it can produce waste ash, heavy metals, and potentially harmful gas emissions if incinerated at high temperatures. However, thermal processes can be used to convert plastics into hydrocarbon fuels such as gasoline, diesel, aviation / jet fuel, which have unlimited applications in airline industries, helicopter, heavy transportation, and electricity generation.

Azzah Amran (2018), This study look into the potential of value and wealth creation by transforming sewage sludge into new source of renewable energy. This study is using qualitative measures. The finding from this qualitative study reveals that, there is a potentiality of value and wealth creation by transforming sewage sludge into energy. Hopefully, this will contribute to green economy practices, which will eventually lead to sustainability of the environment.

Om Prakash Bamboriya (2022), This paper describes the thermal decomposition and determined the thermodynamics and kinetics for pyrolysis of soybean de-oiled cake (soya DOC). Authors analysed the physicochemical characteristics of biomass based on proximate, elemental, lignocellulosic balance, calorifc value, and FTIR results. The thermogravimetric data of soya DOC were obtained at 10, 20, and 30 °C min–1 heating rates in an inert system. Thermal analysis of soya DOC reveals that the signifcant mass loss occurred between 200 and 550 °C temperature ranges. The kinetic parameters (activation energy and pre-exponential factor) and thermodynamic parameters (changes in enthalpy, entropy and Gibb's free energy) were examined by Kissinger, KAS, OFW, and CR methods. Kissinger method gives Ea 121.05 kJ mol–1, while OFW and KAS give 162.33 and 151.88 kJ mol–1, respectively. Results reveal that the Ea depends on decomposition. For soya DOC, the pre-exponential factor is found between 4.12× 1012 and 6.39× 1013 min−1, and this range depends on heating rates and conversion. In order to assess the importance of the soya DOC as a pyrolysis feedstock, the activation energy of soya DOC is also compared with the other biomass and the results are found satisfactory. Simulation of soya DOC pyrolysis using data obtained from TGA analysis showed good agreement with experimental data.

Xue Ming (2019), This investigation focused on the thermal decomposition behavior, volatile release characteristics, and the pyrolytic product composition and distribution of two typical food waste components (pork and rice) via Thermogravimetric analyser coupled with Fourier Transform Infrared spectrometer and Pyrolyzer combined with a Gas Chromatograph and Mass Spectrometry. According to the pyrolysis experiments, two different pyrolysis stages occurred both in pork and rice, which were the volatilization of moisture and the main pyrolysis reaction. The gaseous products and typical functional groups of the released volatiles were detected by Infrared spectroscopy and mainly contained CO2, CO, small-molecule hydrocarbons, and oxygen-containing and nitrogen-containing functional groups. With the specific information from Pyrolyzer combined with a Gas Chromatograph and Mass Spectrometry, the pyrolytic products were classified into small-molecule gases, hydrocarbons, oxygenated compounds and nitrogencontaining compounds. The kinetic and thermodynamic results provided an important reference for future reactor design and the thermochemical treatment of mixed food waste.

Prakash Parthasarathy (2021), In this work, the sustainable valorisation of camel manure has been studied using thermogravimetric analysis. The gasification tests were performed from ambient conditions to 950 ◦C at 10, 20, and 50 ◦C/min under an O2 environment. The TGA data were applied to determine the kinetics of the O2 gasification. Single-heating rate models (Arrhenius and Coats-Redfern) and multi-heating rate models (Distributed activation energy, Friedman, Flynn-Wall-Ozawa, Starink, and Kissinger-Akahira-Sunose) were applied to estimate the kinetics of the process. Between the two single-heating rate models, the Coats-Redfern method fitted best with the experimental data. Among the multi-heating rate models, the Flynn-Wall-Ozawa model fitted best with the experimental results. The kinetic parameters-frequency factor, activation energy, and order of reaction were estimated using the FlynnWall-Ozawa model (the best-fitting model) and the estimated kinetic parameters were used to calculate the thermodynamic properties-Gibbs free energy, enthalpy, and entropy. The information on these kinetic and thermodynamic properties can be useful for the design of gasifiers and for optimising the O2 gasification operating conditions.

V. Kavan Kumar (2024), In order to design and optimize thermochemical systems for the production of bioenergy understanding the energy capacity of the pistachio shell and its kinetics of degradation is crucial. The Thermogravimetric analysis at diferent heating rates of biomass was studied along with thermodynamic study, primary characterizations like the composition of biomass, heating value and a reaction mechanism-assisted kinetic model. Nitrogen gas fow rate is used for thermogravimetric analysis (TGA), which is performed at 10, 15, 20 and 30 ℃/min diferent heating rates from room temperature to 900 ℃. The output also shows that maximal degradation took place between 180 and 430 °C. The various iso-conversional
models, such as Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), Starink and Friedman, are used to calculate kinetic and thermodynamic parameters, which give the average value of activation energy as 172.29, 170.47, 169.79, and 193.25 kJ/mol. The average values of Gibbs free energy for the FWO, KAS, Starink and Friedman techniques were found to be 176.49, 1176.54, 176.29, and 175.78 kJ/mol, respectively.

Rakesh Kumar (2022), In this research they examined the thermal degradation of pomegranate peel to determine its pyrolytic behavior for bio-energy generation. Initial characterizations (proximate analysis, ultimate analysis, biochemical analysis, and higher heating value) were performed before thermal deterioration to ensure that it was suitable for the pyrolysis process. Later, in a thermo-gravimetric analyzer with inert gas, thermo-gravimetric studies were carried out from ambient temperature to 1000 °C at three distinct heating rates (15, 20, and 25 °C/min). Thermo-gravimetric measurements revealed that the greatest devolatilization occurred between 200 and 540 °C. Four iso-conversional models (FWO, KAS, Tang, and Starink) were used for kinetic and thermodynamic analysis. The results revealed that the average activation energies were found 137.79, 149.63, 168.47, and 163.97 kJ/mol for FWO, KAS, Tang, and Starink model, respectively. The potential energy barrier (~4–8 kJ/mol) between activation energy and reaction enthalpy demonstrated favorable circumstances for product formation. Average Gibbs free energy change (ΔG) for pomegranate peel by using iso-conversional FWO, KAS, Tang, and Starink model was found to be 81.84, 145.54, 80.53, and 80.83 kJ/mol, respectively. Thus, kinetic and thermodynamic data demonstrated that pomegranate peel had sufcient bioenergy potential.

Saša Papuga (2015), This paper presents the results of investigation of the influence of temperature in the range of 450-525 °C, on the yield of the process of pyrolysis of waste plastics mixture, composed of 45% polypropylene, 35% low density polyethylene, and 25% high density polyethylene. Also, this paper presents results of the investigation of the effect of the reaction, at intervals of 30-90 minutes, on the yield of pyrolysis of the mentioned waste plastics mixture. Research was conducted in a fixed bed pilot reactor, which was developed for this purpose. The results of the research show that at a temperature of 500 °C, complete conversion of raw materials was achieved, for a period of 45 minutes, with a maximum yield of the pyrolysis oil of 32.80%, yield of the gaseous products of 65.75%, and the solid remains of 1.46%. A further increase of temperature increases the yield of gaseous products, at the expense of reducing the yield of pyrolysis oil. Obtained pyrolysis oil has a high calorific value of 45.96 MJ/kg and in this regard has potential applications as an alternative fuel.

Samy Yousef (2023), In this research pyrolysis process used to maximize polyethylene terephthalate (PET) nonwoven fabric waste and make it as a new source for benzoic acid extraction. The treatment was performed using a thermogravimetric analyzer (TGA) and released products were characterized using FTIR spectroscopy and gas chromatography–mass spectrometry (GC–MS). The pyrolysis kinetic and thermodynamic behavior of PET fabric was also studied and simulated using different linear and nonlinear models. The results show that the PET fabric is very rich in volatile matter (80 wt.%) and can completely degrade under 490 ◦C with a weight loss of 84%. Meanwhile, the generated vapor was rich in the carbonylic C=O functional group (FTIR), and the GC–MS analysis concluded that benzoic acid was the major compound with an abundance of 75% that was achieved at the lowest heating rate (5 ◦C/min). The linear kinetic results showed that PET samples had an activation energy in the ranges of 193–256 kJ/mol (linear models) and ~161 kJ/mol (nonlinear models). The thermodynamic parameters, including enthalpy, Gibbs free energy, and entropy, were estimated in the ranges of 149–250 kJ/mol, 153–232 kJ/mol, and 256–356 J/mol K, respectively. Accordingly,pyrolysis treatment can be used to extract benzoic acid from PET fabric waste with a 134% increase in the benzoic acid abundance that can be recovered from PET bottle plastic waste.

IV. SAMPLING AND ANALYSIS OF MLP FEEDSTOCKS

4.1 MLP sample

Shredded multilayered plastic of 10 kg is purchased from the recycling unit. Which is used for analysis of characteristics of MLP samples and pyrolyis process to obtain the hydrocarbon fuel.

4.2 Analysis of sample

4.2.1 Proximate analysis

Proximate analysis gives the gross composition of the biomass and hence it is relatively easy to measure. One can do this without any elaborate set up or expensive analytical equipment. Proximate analysis of a fuel provides the percentage of the material that burns in a gaseous state (volatile matter), in the solid state (fixed carbon), and the percentage of inorganic waste material (ash), and is therefore of fundamental importance for biomass energy use Proximate analysis gives the gross composition of the biomass and hence it is relatively easy to measure. One can do this without any elaborate set up or expensive analytical equipment. In this method we determine four things that are;

- **Determination of Moisture Content**
- **Determination of Volatile Matter**
- **Determination of Ash**
- **Determination of Fixed Carbon**

Determination of Moisture Content

The sample is heated in an electric hot oven at 108°C± 2°C for 1 to 1.5 hours. After heating it is taken out from oven and cooled in a desiccator and weighed.

% of moisture content = (Loss in weight) / (weight of sample) x 100

Determination of Volatile Matter

It is determine by heating a known weight of moisture content of sample in a covered platinum crucible at 950 ± 10°C for 7 minutes

100 x (M_2-M_3)

% of Volatile Matter = ---------------------- - M_o

(M_2-M_1)

Mo = % of Moisture in the sample

M1 = Weight of empty crucible with lid

M2 = Weight of crucible with lid and sample before ignition

M3 = Weight of crucible with lid and sample after ignition

Determination of ash

The sample is heated in air to 500°C in 30 minutes, from 500 to 815°C for a further 30 to 60 minutes and maintained at this temperature until constant in mass.

% of Ash content = (M_2-M_3)

------------ x 100

(M_2-M_1)

M1 = Weight of empty crucible with lid

M2 = Weight of crucible with lid and sample before ignition

M3 = Weight of crucible with lid and sample after ignition

Determination of Fixed Carbon

The fixed carbon content of is determined by subtracting the percentages of moisture, volatile matter and ash from the original mass of the sample.

% of Fixed Carbon = 100 – (% of moisture content + % of volatile matter + % of Ash)

Determination of Calorific Value

The Sample is burned in a calorimeter of known heat capacity. A known amount of fuel is kept in crucible supported over a ring, a fire Wire touching the sample of the fuel is then stretched across the electrode. The bomb is placed carefully in a Cu- Calorimeter containing water. After stirring the water temperature (t_1) is noted. The electrodes are then connected with battery and circuit. Thus combustion of fuel takes place and heat is liberated. Now stirring of water continued and the final of water temperature (t_2) is noted.

Bomb Calorimeter

H_S, kcal/kg = [(T) (E) – e_1- e_2 - e_3 - e_4]/g

H_s = Gross calorific value, kcal/kg

T = Corrected temperature, °C or °F

E = Energy equivalent

g = Weight of the sample, g

4.2.2 Ultimate analysis

Ultimate analysis tests produce more comprehensive results than the proximate analyses. Ultimate analysis tests to determine the elemental composition of the coal including carbon, hydrogen, nitrogen, sulphur, Ash and oxygen (by difference). This method is to determine each element through chemical analysis and express it as a percentage of the total mass of the original sample. Ultimate analysis tests produce more comprehensive results than the proximate analyses. In this method determine following things:

- **Determination of Carbon & Hydrogen**
- **Determination of Sulphur**
- **Determination of Nitrogen**
- **Determination of Ash**
- **Determination of Oxygen**

Determination of Carbon and Hydrogen

The weighed sample is taken in a combustion tube and is burnt in excess of pure oxygen. The carbon &

Hydrogen in a coal sample are converted into Carbon dioxide and Water Respectively.

The product of combustion CO_2 and H_2O are produced in KOH & $CaCl_2$ tubes of known weights respectively.

Combustion of Carbon:

$C + O_2 \rightarrow CO_2$

Combustion of Hydrogen:

$2H + 1/2\ O_2 \rightarrow H_2O$

Reactions

$$\mathbf{2KOH + CO_2 \rightarrow K_2CO_3 + H_2O}$$
$$\mathbf{CaCl_2 + 7H_2O \rightarrow CaCl_2.7H_2O}$$

% of Carbon = (Increase in wt. of KOH tube) / (wt. of sample) x 100

% of Hydrogen = (Increase in wt. of Cacl2 tube) / (wt. of sample) x 100

Determination of Sulphur

A known amount of sample is burnt completely in bomb calorimetry in presence of oxygen where sulphur converts into sulphates.

The % of Sulphur is determined by the washings of bomb calorimetry. The washings are treated with Barium Chloride solution which makes Barium Sulphate precipitate.

% of Sulphur = (wt. of precipitate x 32) / (wt. of sample) x 100

Determination of Nitrogen

Nitrogen present in sample can be estimated by Kjeldahl's method.

A known mass of the sample is heated with concentrated sulphuric acid in the presence of a catalyst to destroy the organic material and to convert the nitrogen into ammonium sulphate, from which ammonia, released by steam distillation in alkaline solution, is absorbed in boric acid solution and titrated directly with 0.05 N sulphuric acid.

Reactions

$$\mathbf{2N + 3H_2 + H_2SO_4 \rightarrow (NH_4)_2SO_4}$$

$$\mathbf{(NH_4)_2SO_4 + NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O}$$

$$\mathbf{NH_3 + HCl \rightarrow NH_4Cl}$$

$$\mathbf{\%\ of\ Nitrogen = \frac{1.4 \times N\ (V_1 - V_2)}{M}}$$

N = Normality of H_2SO_4,
V_1 = Titre value of sample,
V_2 = Titre value of blank,
M = Sample weight.

Determination Of ash

Ash content is determined by heating the residue left after the removal of volatile matter at 700 ± 20°C for half an hour without covering.

% of Ash = (weight of residue left) / (weight of sample) x 100
Determination of Oxygen

% of Oxygen = 100 – (% of Carbon + % of Hydrogen + % of Nitrogen + % of Sulphur + % of Ash)

4.3 Analysis of multilayer plastic (MLP) waste

S.No.	**PARAMETERS**	**UNITS**	**RESULTS**
I	**Proximate Analysis (as received basis)**		
1	Moisture Content	%	0.86
2	GCV	Kcal/kg	6703
3	Ash Content	%	4.01
4	Fixed Carbon	%	2.06
5	Volatile matter	%	92.1
II	**Ultimate Analysis (as received basis)**		
6.	Carbon	%	82.5
7.	Hydrogen	%	10.5
8.	Nitrogen	%	0.22

S.No.	PARAMETERS	UNITS	RESULTS
I	**Proximate Analysis (as received basis)**		
9.	Oxygen	%	0.97
10	Sulfur	%	0.80

Table 4.1 Characteristics report of Multilayered Plastic Waste

The analysis of multilayer plastic (MLP) waste shows promising results for its use in hydrocarbon fuel production through pyrolysis, a thermal degradation process in the absence of oxygen. Pyrolysis of MLP can yield a range of valuable hydrocarbons suitable for fuel production, making it a viable waste-to-energy option.

4.3.1. Proximate Analysis

Moisture Content

The low moisture content in MLP is advantageous as it reduces the energy required to evaporate water, making the pyrolysis process more energy-efficient. This also increases the yield of hydrocarbon products by focusing thermal energy on breaking down the plastic polymers rather than evaporating moisture.

Gross Calorific Value The high GCV of 6703 Kcal/kg indicates that MLP has substantial energy content, comparable to conventional fuels. This high energy value makes MLP an attractive feedstock for pyrolysis, as it suggests a strong potential for high-yield energy recovery in the form of hydrocarbon fuels.

Ash Content

A relatively low ash content in MLP is beneficial for the pyrolysis process, as it implies minimal residue that does not contribute to fuel production. Low ash content also helps reduce equipment fouling, minimizing maintenance costs and improving operational efficiency in pyrolysis units.

Fixed Carbon

Fixed carbon, representing the solid carbon residue post-combustion, is low in MLP, which aligns well with pyrolysis, as the aim is to maximize volatile hydrocarbons rather than solid residues. Low fixed carbon contributes to a higher yield of condensable hydrocarbon gases during pyrolysis.

Volatile Matter

High volatile matter indicates that MLP consists mostly of compounds that can vaporize under heat, favoring the pyrolysis process, which requires high volatiles for better fuel yield. This high volatility enables efficient breakdown of plastic polymers into smaller hydrocarbon chains, boosting liquid fuel and gas production.

4.3.2 Ultimate Analysis

Carbon

Carbon is the primary component in MLP and is essential for hydrocarbon fuel production. High carbon content translates into higher hydrocarbon yields, as it allows for efficient transformation of the plastic polymers into various liquid and gaseous hydrocarbons during pyrolysis.

Hydrogen

Hydrogen is critical for generating lighter hydrocarbon chains, contributing to the quality of pyrolysis oil. This high hydrogen content supports the formation of desirable light and medium-weight hydrocarbons, which are valuable for fuel applications.

Nitrogen

The low nitrogen content in MLP is beneficial as it minimizes the formation of nitrogen oxides (NOx) during pyrolysis, which are harmful pollutants. This low level contributes to a cleaner fuel output with fewer emissions.

Oxygen

Low oxygen content enhances the fuel quality, as high oxygen levels can lead to less stable compounds in pyrolysis oil. Low oxygen content in MLP makes it suitable for producing hydrocarbons with high energy density and good storage stability.

Sulfur

Moderate sulfur content could lead to sulfur oxides (SOx) emissions during combustion. While not ideal, the sulfur level can be managed with post-pyrolysis desulfurization processes to mitigate potential environmental impacts.

The analyzed MLP waste is efficient for hydrocarbon fuel production through pyrolysis due to its high carbon and hydrogen content, significant volatile matter, and low ash and moisture levels. These characteristics make MLP an excellent feedstock for obtaining liquid and gaseous hydrocarbon fuels. The high GCV supports an energy-efficient conversion process, and the low oxygen and nitrogen levels contribute to cleaner combustion of the resultant fuel. With adequate processing to address sulfur emissions, MLP-derived pyrolysis oil could be a viable alternative fuel source, potentially helping reduce plastic waste while providing sustainable energy.

V. PYROLYSIS OF MULTI LAYERED PLASTIC

Pyrolysis is a thermal decomposition process conducted in the absence of oxygen, where organic materials such as plastic are broken down into smaller molecules at high temperatures (typically between 300°C and 700°C). This process converts waste plastics into valuable products such as liquid fuels, syngas, and char. Pyrolysis has become an increasingly promising method for plastic waste management due to its potential to reduce plastic pollution and recover energy and materials from otherwise difficult-to-recycle plastics.

5.1 Pyrolysis of plastic

The pyrolysis of plastic waste generally involves the following steps:

Feedstock Preparation: The plastic waste is sorted, cleaned, and sometimes shredded into smaller pieces to ensure uniform heating in the reactor.

Heating and Decomposition: Plastic feedstock is heated in an oxygen-free environment in a reactor. The heat causes the long polymer chains in plastics to break down into smaller hydrocarbon molecules. This phase can be controlled to produce desired products based on temperature and residence time

- **Low Temperature (300–400°C):** Generally results in a higher yield of liquid oils.
- **Moderate Temperature (400–500°C):** Optimizes the production of a balanced mix of liquid and gas.
- **High Temperature (500–700°C):** Tends to favor gas production, including hydrogen and methane-rich syngas.

Condensation and Collection: The resulting vapors are then condensed to separate out the liquid hydrocarbon oils. The remaining non-condensable gases can be collected and used as fuel to sustain the pyrolysis process.

Product Collection: Three primary products are collected from the pyrolysis process:

- **Liquid Oil:** This can be refined and used as a fuel or chemical feedstock.
- **Syngas (Synthetic Gas)**: A mixture of gases (primarily methane, hydrogen, carbon monoxide) that can be used for heating or electricity generation.
- **Solid Char:** A carbon-rich residue that can be used as a solid fuel or as a soil amendment if it meets environmental safety standards.

5.2 Types of Pyrolysis Applied to Plastic Waste

The type of pyrolysis selected depends on the desired end products, available technology, and type of plastic waste:

Slow Pyrolysis: Operates at lower temperatures with longer residence times, yielding more solid char and some liquid products. This type is more suited to biomass and certain plastics with lower market value for the resulting gases.

Fast Pyrolysis: Involves higher temperatures (450–600°C) and short residence times, which maximizes the yield of liquid hydrocarbons. It is commonly used for plastics to produce a higher fraction of liquid fuels.

Flash Pyrolysis: Carried out at very high temperatures (>700°C) for very short residence times, typically to maximize gaseous products. This is more experimental in plastic waste applications but could be ideal for plastics with high energy content.

5.3 Applications of Pyrolysis in Plastic Waste Management

Plastic-to-Fuel Conversion: One of the most popular applications of pyrolysis is converting plastic waste into liquid fuels, which can serve as an alternative to traditional fossil fuels. This not only provides a potential energy source but also reduces plastic waste accumulation.

Chemical Feedstock Recovery: Pyrolysis offers an opportunity to recover valuable chemical feedstocks like aromatics, olefins, and waxes, which are essential building blocks in the petrochemical industry. These recovered materials can be used to manufacture new plastics and other industrial chemicals, contributing to a circular economy.

Energy Generation: The syngas produced in the pyrolysis of plastics can be used as a clean energy source. It can be burned directly for heat or used to power turbines for electricity generation. This can help in waste-to-energy facilities, especially in areas where managing plastic waste is challenging.

Char Utilization: Char, a byproduct of the pyrolysis process, can serve as a source of carbon for various industrial applications. It can be processed and used as an adsorbent material in water purification or as a soil additive (biochar) in agriculture if it meets quality standards.

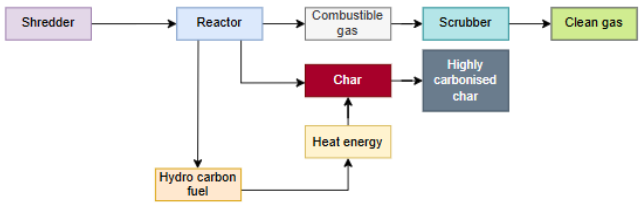
Processing Mixed and Hard-to-Recycle Plastics: Pyrolysis is particularly useful for processing mixed and multi-layered plastic waste, which are difficult to recycle through traditional mechanical means. Since pyrolysis relies on breaking down plastics into simpler molecules, it can handle various types of plastics, including polyethylene (PE), polypropylene (PP), and polystyrene (PS), as well as complex multi-layered structures like food packaging.

Environmental Impact Reduction: By converting plastic waste into usable products, pyrolysis offers a promising way to reduce the environmental footprint of plastic waste. This includes minimizing landfill waste, reducing greenhouse gas emissions from incineration, and decreasing pollution caused by plastics in natural ecosystems.

5.4 Pyrolysis Plant Process

The pyrolysis process for converting multilayer plastic (MLP) waste into hydrocarbon fuel involves several key phases to optimize the breakdown of the plastic polymers and recover valuable by-products. This specific pyrolysis design includes stages of incineration, oxidation, and an oxygen-free phase, all controlled at optimal temperatures to maximize the yield of hydrocarbon fuel, char, and combustible gases. The process also incorporates a scrubbing system for gas treatment and a self-sustaining energy recovery mechanism to produce highly carbonized char.

Process flow drawing



5.4.1 Pyrolysis Process Steps

1. Shredding for Homogenized MLP Waste

The MLP waste is shredded into uniform pieces of size 1mm to ensure consistent heating and decomposition during the pyrolysis process. Homogeneous feedstock size is crucial for achieving uniform reaction rates and improving the overall efficiency of the pyrolysis stages.

2.Pyrolysis reactor

A pyrolysis reactor is a specialized system engineered to thermally decompose organic feedstocks, such as plastics, biomass, or rubber, under oxygen-free or low-oxygen conditions. This controlled environment ensures the production of valuable outputs like pyrolytic oil, syngas, and solid char. The reactor is specifically designed for processing multilayered plastics and operates within a temperature range of 300°C to 600°C, depending on the nature of the feedstock. The heating rate is set at 10°C per minute, allowing for gradual thermal decomposition, and the material residence time within the reactor is approximately 1 hour, ensuring efficient breakdown of the feedstock. The system is designed to operate at a pressure of 2 bar, enhancing the process efficiency.

The reactor body is constructed from stainless steel (SS304), offering excellent thermal resistance and corrosion protection, while graphite-based seals and gaskets ensure leak-proof operation under high temperatures and pressures. The reactor employs an indirect electric furnace heating system, which ensures uniform heat distribution. Temperature control is achieved through a PID controller integrated with thermocouples, providing precise monitoring and regulation throughout the process. This reactor is a batch type system with a daily capacity of 1 ton, making it suitable for small-scale applications.

The output streams from the reactor include pyrolytic oil, which is a valuable hydrocarbon fuel; syngas, which can be utilized for heating or power generation; and solid char or residue, which may have further applications depending on the feedstock. To ensure safety, the reactor is equipped with an inert gas purge system to eliminate oxygen and maintain an inert atmosphere. Additional safety measures include a pressure relief valve to prevent over-pressurization and an emergency shut-off mechanism to mitigate risks of overheating or system failure.
The working principle of the pyrolysis reactor is based on following three phase

I. Incineration Phase (Feed-to-Air Ratio of 1:3)

In the first phase, shredded MLP waste is introduced into a reactor where incineration begins. A controlled air supply with a feed-to-air ratio of 1:3 is maintained, allowing partial combustion to initiate thermal breakdown of the polymers.

Optimum Temperature: Approximately 300–400°C. At this temperature range, the incineration phase initiates the breakdown of polymer bonds and preheats the material, preparing it for further decomposition in the oxidation and pyrolysis stages.

II. Oxidation Phase (Feed-to-Oxygen Ratio of 1:1)

In the oxidation phase, the feedstock is exposed to an oxygen supply with a feed-to-oxygen ratio of 1:1. This controlled oxidation aids in the thermal degradation of more complex bonds within the plastic polymers, releasing additional volatile gases and enhancing the energy yield.

Optimum Temperature: 400–500°C. This temperature is ideal for maximizing volatile release without fully combusting the material, thus preparing the feedstock for the oxygen-free pyrolysis stage.

III. Oxygen-Free Pyrolysis phase

The final phase occurs in the absence of oxygen to prevent combustion and focus on cracking long hydrocarbon chains into simpler hydrocarbons, yielding liquid fuel, char, and gas.

Optimum Temperature: 500–600°C. This high-temperature setting in an inert (oxygen-free) environment allows efficient conversion of the remaining feedstock into hydrocarbon liquids, gaseous products, and char without producing unwanted combustion by-products.

5.4.2 By-Products and Treatment Processes

Liquid Hydrocarbon Fuel:

The primary product, liquid hydrocarbon fuel, is collected as condensed vapor after the pyrolysis phase. This fuel can be directly used for heating or further refined for various industrial applications. Mass of the oil obtained is 658 g/kg.

Solid Char Residue:

The solid char by-product is rich in carbon content and can be further processed for additional energy applications. The heating process continues with energy supplied by the combustible gases, resulting in a highly carbonized char suitable for applications like activated carbon or biochar.

Combustible Gas:

Combustible gases produced during pyrolysis, such as methane, hydrogen, and other light hydrocarbons, are treated in a scrubbing system. The gas stream is scrubbed to remove dust and particulate matter, ensuring clean, dust-free gas suitable for energy recovery.

The cleaned gas can be utilized as a secondary fuel source, powering the pyrolysis system itself and minimizing external energy input, thereby making the process more self-sustaining and efficient.

5.4.3. Heat Recovery System

The hydrocarbon fuel produced in the pyrolysis process can be burned to generate heat energy. This heat energy is used to maintain optimal temperatures within the reactor, especially for further heating the solid char.

By applying additional heat to the char, a highly carbonized char product is obtained, with increased energy density and potential applications as a high-grade carbon source.

VI. RESULTS AND DISCUSSION

6.1 Thermodynamic study

To perform a thermodynamic study for multilayer plastic (MLP), we focus on calculating the following key thermodynamic properties:

6.1.1. Calorific Value (GCV)

Obtained value: 6703 kcal/kg

Conversion to Joules: 1 kcal=4184 J
GCV=6703×4184=28,076,752 J/kg (≈28.1 MJ/kg)

6.1.2. Heat of Combustion (Enthalpy Change, ΔH)

The heat released during combustion can be calculated as:

ΔH=GCV (MJ/kg)×mass of MLP (kg)
For 1 kg of MLP, ΔH=28.1 MJ

6.1.3. Elemental Contributions to Energy Release

Using the ultimate analysis, the energy contribution from each element can be estimated.

Carbon Contribution:

Combustion reaction: $C+O_2 \rightarrow CO_2$
Heat released: 32.8 MJ/kg
Energy from Carbon=82.5%×32.8=27.06 MJ

Hydrogen Contribution:

Combustion reaction: $2H_2+O_2 \rightarrow 2H_2O$
Heat released: 142 MJ/kg H
Energy from Hydrogen=10.5%×142=14.91 MJ/kg

Sulfur Contribution:

Combustion reaction: $S+O_2 \rightarrow SO_2$
Heat released: 9.3 MJ/kg S
Energy from Sulfur=0.80%×9.3=0.074 MJ/kg

6.1.4. Efficiency of Conversion

The overall energy output is primarily from carbon and hydrogen, with sulfur contributing minimally.

Summing these values:

Total Theoretical Energy=27.06+14.91+0.074=42.04 MJ/kg
This is higher than the GCV due to losses during combustion (e.g., heat dissipation, incomplete combustion).

6.1.5. Thermodynamic Feasibility (Gibbs Free Energy, ΔG)

To calculate ΔG for pyrolysis, use:
$\Delta G=\Delta H-T\Delta S$
Where:
ΔH: Enthalpy of reaction (GCV in J/kg)
T: Absolute temperature (in Kelvin)
ΔS: Entropy change during the reaction
Assume:
T=600 °C=873 K
Estimated ΔS=−0.1 kJ/(mol.K)
Approximation:
$\Delta G=(28.1\times103)-(873\times(-0.1))$
ΔG=28,187 kJ/kg (negative, indicating spontaneous reaction)

Parameter	**Value**
Gross Calorific Value (GCV)	**28.1 MJ/kg**
Energy from Carbon	**27.06 MJ/kg**
Energy from Hydrogen	**14.91 MJ/kg**
Energy from Sulfur	**0.074 MJ/kg**
Total Theoretical Energy	**42.04 MJ/kg**
Gibbs Free Energy (ΔG\Delta G)	**-28,187 kJ/kg** (spontaneous)

This study highlights the high energy potential of MLP and its feasibility for energy recovery through pyrolysis.

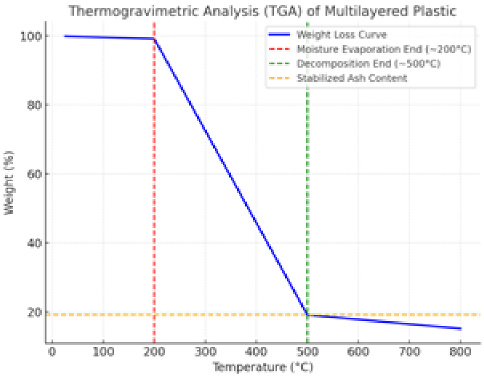
6.2. Thermal degradation Study

Thermal degradation analysis of multilayered plastic (MLP) involves studying the decomposition behavior of the material when exposed to increasing temperatures. Thermogravimetric Analysis (TGA) is a common method to evaluate this behavior, typically presented as a graph of weight loss (%) against temperature (°C or K).

6.1.1. Thermal Degradation Stages

Thermogravimetric degradation typically follows these stages:

1. Initial Stage (up to ~200°C): Evaporation of moisture, minor weight loss.
2. Major Degradation Stage (~200°C–500°C): Decomposition of volatile hydrocarbons, contributing to significant mass loss.
3. Final Stage (>500°C): Oxidation of fixed carbon and stabilization of residual ash content.



TGA Graph Analysis

Initial Region (25–200°C):The weight loss is minimal (~0.86%), attributed to the evaporation of moisture.

Major Decomposition Region (200–500°C):A steep decline (~80%) due to the release of volatile hydrocarbons.The high volatile matter (92.1%) aligns with this observation.

Final Stabilization Region (>500°C):The curve plateaus, reflecting residual ash (~4.01%) and fixed carbon oxidation.

5.5 Determination of Pyrolytic Oil Yield

The yield of pyrolytic oil can be calculated using the formula:
Oil Yield (%)= Mass of Oil Obtained (g) ×100
Mass of Feedstock (g)
Oil Yield (%) = (658 /1000) x 100
= 65.8 %

The pyrolytic oil yield calculated for the given process is 65.8%, indicating that 658 grams of oil were recovered from 1 kilogram of multilayered plastic feedstock. This result aligns well with typical yields reported for the pyrolysis of plastic materials, particularly multilayered plastics, which consist predominantly of hydrocarbons such as polyethylene (PE) and polypropylene (PP). These polymers are known for their high volatile matter content, making them ideal for thermal decomposition into liquid hydrocarbons.

The oil yield of 65.8% demonstrates an efficient conversion process, likely facilitated by favorable operating conditions, such as a well-controlled temperature range (300°C to 600°C), an adequate heating rate (10°C/min), and a suitable residence time (1 hour). The moderate operating pressure of 2 bar may have also contributed to the enhanced yield by promoting the breakdown of long-chain polymers into lower molecular weight hydrocarbons.

The remaining 34.2% of the feedstock mass consists of non-condensable gases (syngas) and solid char. These by-products are typical in pyrolysis and add value to the process:
Syngas: This gas fraction can be used as a source of energy for heating the reactor or for power generation, improving the overall energy efficiency of the system.

Char: The solid residue may have potential applications as a carbonaceous material or as a feedstock for further chemical processing.

The oil yield is highly influenced by the feedstock composition and process parameters. The high carbon (82.5%) and hydrogen (10.5%) content of the feedstock, as indicated in the ultimate analysis, likely contributed to the significant oil production. Additionally, the low ash content (4.01%) minimizes residue formation, further favoring liquid yield.This result underscores the effectiveness of the pyrolysis process for converting plastic waste into valuable pyrolytic oil, which can be used as a fuel or as a precursor for chemical synthesis. However, further optimization of process parameters and reactor design could potentially increase the oil yield and enhance the quality of the end products.

VII. CONCLUSION

The findings establish pyrolysis as a highly effective method for converting MLP waste into valuable products. Proximate and ultimate analyses validated the material's potential for thermal conversion due to its high energy content.The production of hydrocarbon fuel, char, and gases through pyrolysis not only addresses the environmental hazards of plastic waste but also creates a sustainable pathway for energy generation. Thermogravimetric analysis provided detailed insights into the degradation behavior, highlighting distinct thermal decomposition stages. Thermodynamic evaluation revealed critical energy parameters, with the gross calorific value reaching 28.1 MJ/kg and the theoretical energy potential totaling 42.04 MJ/kg. Gibbs free energy (-28,187 kJ/kg) indicated a spontaneous process, underscoring the efficiency of energy recovery. The pyrolytic oil yield calculated for the given process is 65.8%, indicating that 658 grams of oil were recovered from 1 kilogram of multilayered plastic feedstock. These results highlight the dual benefits of waste management and renewable energy generation, with future research aimed at optimizing process parameters for industrial applications.This work highlights the potential of MLP pyrolysis as a scalable solution to the global plastic waste crisis, with the added advantage of energy recovery.