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Kinetic and Thermodynamic Evaluation of Plastic Waste Degradation for Energy Recovery

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Abstract

Plastic consumption with effective recycling is essential for sustainable life-cycle management. In recent years, energy recovery and value-added product generation from plastic waste have gained increasing attention, with pyrolysis emerging as a promising thermochemical pathway for plastic degradation. This study investigates the thermokinetics of two waste plastic streams: mechanically recycled plastics, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polyethylene terephthalate (PET), and landfill-dumped mixed waste plastic (MWP) and multilayer plastic (MLP), to evaluate operational parameters for pyrolysis and hydrothermal liquefaction (HTL) to optimize their conversion into valuable products. Thermogravimetric analysis (TGA), conducted at a heating rate of 10 °C/min, revealed that HDPE exhibited the highest weight loss (98%) at a peak temperature of 494 °C with a degradation time of 13 minutes. PET has a low conversion rate (80.53%) than HDPE, LDPE, and PP, resulting in a larger residue. The Coats-Redfern model-fitting method, applied with various models, was used to calculate the kinetic triplet and thermodynamic properties. Among the tested models, F1 (First-order) and F2 (Second-order) reaction models were identified as the most suitable for recycled plastics, while D2 (two-dimensional diffusion) was found to be appropriate for dumped plastics. The activation energies of mechanically recycled plastics were estimated to range from 154 to 295 kJ/mol, whereas landfill-dumped plastics ranged from 117 to 171 kJ/mol. Analysis of degradation temperature, duration, and weight loss (%) obtained from TGA provided a reference point for determining the optimal operating parameters (reaction time and temperature) for pyrolysis, thereby minimizing solid residue and enhancing the efficiency of plastic conversion into oil and gases.

Keywords: Waste Plastic; TGA; Thermokinetics; Model-fitting; Pyrolysis

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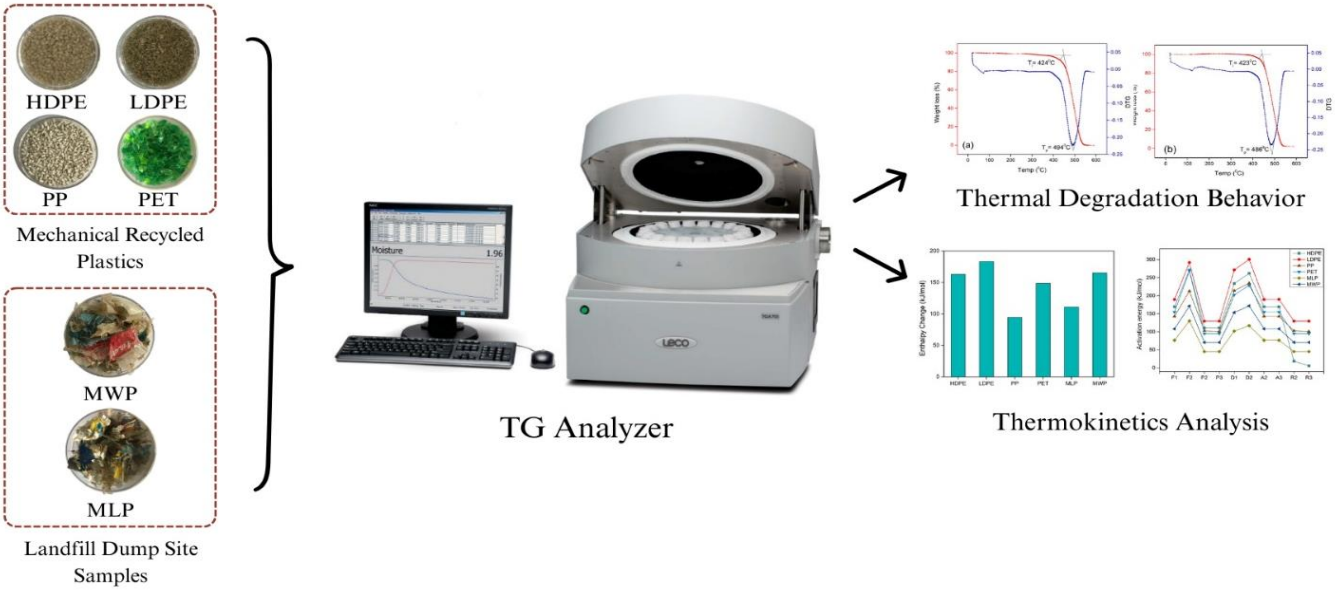

Graphical Abstract

1. Introduction:

Plastic products have become an unavoidable part of contemporary life, and are widely used in a vast array of industries, including packaging, automotive, construction, and electrical equipment, among many others, where the viable alternative is limited [1]. The majority of plastics are synthesized out of petroleum and natural gas, and their monomeric precursors are achieved through the refining and petrochemical industries. Approximately 360 million tons of fossil-based polymers are made globally every year [2]. A considerable proportion of this plastic, covering 76%, was relegated to landfills for disposal. Conversely, a lesser portion was subjected to incineration (12%), while only 9% of the overall plastic produced was processed through recycling. Moreover, around 3% of plastic waste is inadequately managed, leading to its infiltration into the environment or oceans, thereby presenting health hazards to both human populations and ecosystems [3]. The rapid depletion of natural resources, couple with the escalating issue of plastic pollution, has driven both academic research and industrial initiatives to focus on advancing the recycling and reuse of plastic waste. The circular economy seeks to minimize the environmental footprint of plastics by comprehensively addressing the complete life cycle of these materials. Recycling involves the transformation of diverse materials through appropriate processes to restore their economic value, avoiding the disposal of valuable resources, improving energy efficiency, and protecting human health and the environment [4]. Mechanical recycling utilizes melt-processing techniques, such as extrusion, to convert relatively homogeneous plastic waste into new products. However, processing mixed plastics poses challenges due to the poor compatibility and blending of polymers with differing viscosities. Additives can improve the recyclability of mixed plastics, but their effectiveness must be tailored to specific feedstocks. As a result, this method often leads to downcycling, producing materials of lower quality and reduced value [5, 6]. To address this issue, a recognized and effective recycling process was implemented to convert waste plastic into valuable chemicals. This process is known as pyrolysis, characterized by the thermal decomposition of materials in an inert environment. The development of an efficient industrial-scale pyrolysis process necessitates the identification of its kinetic and thermodynamic parameters to optimize the thermal behavior of plastic materials.

Silvarrey and Phan [7] studied the five polymers (HDPE, LDPE, PP, PS, and PET) using TGA over a temperature range of 30-700 °C. Their results showed that all polymers exhibited a similar single-stage degradation process. Aboulkas et al. [8] investigated the thermal decomposition behavior of HDPE, LDPE, and PP using the Coast-Redfern approach. Their findings indicated that the contracting sphere (R3) model described the best degradation mechanism for HDPE and LDPE, while the contracting cylinder (R2) model was more suitable for PP.

Kinetic data derived from TGA can be analyzed using two primary approaches: model-free and model-fitting methods. The model-free approach requires multiple heating rates to derive kinetic parameters at various degrees of conversion without assuming a specific reaction mechanism [9]. In contrast, the model-fitting approach applies theoretical kinetic models to a single TGA dataset to determine the activation energy (Ea) and pre-exponential factor (A), by fitting experimental data to algebraic functions that describe the relationship between reaction rate and conversion [10]. This method also provides insights into the possible reaction mechanism by selecting the best-fitting model. Numerous studies have utilized various TGA conditions differing in sample mass, heating rate, temperature range, and reaction atmosphere to investigate the pyrolysis behavior of plastics.

In this study, TGA was employed to evaluate the degradation behavior of waste plastic fractions. The Coast-Redfern model-fitting method was also applied to the TGA data to calculate the activation energy (Ea) and pre-exponential factor (A), as well as thermodynamic properties such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). The novelty of this study lies in its comprehensive investigation of the degradation behavior of waste plastic fractions sourced from two major streams: SME businesses using sorted plastics, including HDPE, LDPE, PP, and PET, and from landfill-dumped MWP and MLP. The focus of this study will be on determining the optimal operating parameters, such as temperature, reaction time, and percentage conversion, for pyrolysis and HTL processes. Additionally, the kinetic analysis plays a crucial role in elucidating pyrolysis behavior, providing a theoretical foundation for reactor design and process scale-up. This research aims to explore the potential of the pyrolysis or HTL process for producing oil rich in lighter hydrocarbon fractions from waste plastics.

2. Materials and Methods:

In this study, recycled plastic feedstocks including HDPE, LDPE, PP, and PET were obtained from nearby mechanical recycling facilities that extract materials from their associated waste sorting centers. The collected plastics were washed, dried, and size-reduced to produced pellets with particle sizes in the range of 2-3 mm. The MWP and MLP were collected from the Lakhodair landfill site located in Lahore, Pakistan, across eight distinct horizontal and vertical sectors. The collected materials were subsequently homogenized to form a representative sample for experimental analysis. The moisture content of plastic samples was determined and listed in Table 1.

Table 1: Percentage of moisture content in waste plastic materials

Materials	Moisture content (wt.%)
HDPE	1.12
LDPE	0.99
PP	0.98
PET	0.02
MWP	2.59
MLP	2.94

2.1. Experimental Setup and Procedure:

The thermal degradation of plastic waste samples under pyrolysis conditions was investigated using a LECO thermogravimetric analyzer (TGA-701). Each sample, mass 1 g, prepared as a pellet (2-3 mm), was placed in an empty crucible of the analyzer. Experiments were performed under a nitrogen atmosphere with a consistent flow rate of 3.5 L/min. The temperature was increased from ambient to 600 °C at a ramp rate of 10 °C/min, and the weight loss was monitored as a function of temperature and time. The calibration of the TGA to measure temperature and weight was achieved with certified reference standards based on the manufacturer's guidelines. Baseline stability was verified through blank runs prior to experimentation. The kinetic analysis was performed at a single heating rate of 10 °C/min, although multiple heating rates can improve the robustness of activation energy determination [11, 12]. Single-rate experiments at 10 °C/min are frequently adopted as a screening method to establish baseline kinetic trends, particularly in comparative studies of heterogeneous waste plastics [13]. Additionally, it enhances instrument sensitivity and reduces thermal lag and hysteresis effects that can occur at higher scan rates [14, 15].

2.2. Kinetic Study:

The DTG curve represented the rate of weight loss with temperature, serving as an indicator of the reactivity and thermo-kinetics breakdown reactions occurring in the samples. The Coats-Redfern method [16] incorporates

reaction order, power law, diffusivity, geometrical contraction, and nucleation models as depicted in Table 2, has been used to analyze the kinetic behavior of the plastic samples. The final kinetic equation for modeling the solid-state thermal decomposition process is derived from Eq. (1)[17]:

$$\frac{d\alpha}{dt} = f(T) * f(\alpha) \quad (1)$$

The parameter α, referred to as fraction conversion, was calculated using Eq. (2).

$$\alpha = m_i - m_t / m_i - m_f \quad (2)$$

Here, m_i and m_f represent the initial and final mass of a sample and m_t denotes the mass of the sample at any time.

$$f(T) = Ae^{-E_a/RT} \quad (3)$$

In this TGA analysis, the sample was subjected to heating at a constant rate under non-isothermal conditions. The conversion rate can be described by the following equations:

$$\frac{d\alpha}{dT} = \left(\frac{d\alpha}{dt}\right)\left(\frac{dt}{dT}\right) \quad (4)$$

Here, β= $\left(\frac{dT}{dt}\right)$ represents the constant heating rate, while $\frac{d\alpha}{dT}$ denotes the non-isothermal reaction rate.

After simplification Eq. (3) & Eq. (4) and putting into Eq. (1), the following equation (Eq. (5)) is formed.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (5)$$

A model-fitting approach particularly the Coats–Redfern method, is widely employed to estimate the kinetics of solid fuel reactions. Using various model within this method, the activation energy (E_a) and pre-exponential factor (A) can be determined. The integral form of non-isothermal rate law is expressed as (Eq. 6)[18].

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (6)$$

Rearranging the Eq. 5, Eq. 6 can be derived and expressed as:

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E_a/RT}\, dT \quad (7)$$

Here, $g(\alpha)$ represents the integral form of the reaction model. Since the right-hand side of the equation does not have a closed-form analytical solution, several simplifications have been proposed. Common formulations of $g(\alpha)$ are summarized in Table 1. The final form of Eq. 7 used for estimating the kinetic parameters is given as Eq. (8).

$$ln\left(\frac{g(\alpha)}{T^2}\right) = ln\left(\frac{(AR)}{(\beta E_a)}\right) X \left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad (8)$$

By plotting $ln\left(\frac{g(\alpha)}{T^2}\right)$ against 1/T, the slope and intercept of the linear fit are used to determine the activation energy (E_a), pre-exponential factor (A), and regression coefficient (R^2).

Table 2: Expression based on different reaction mechanisms for g(α) used in the Coats-Redfern method [17, 19]

Models	Mechanism	symbols	g (α)
Reaction order model	First order	F1	$-ln(1-\alpha)$
	Second order	F2	$(1-\alpha)^{-1} - 1$
Power law	Power law	P2	$\alpha^{1/2}$
	Power law	P3	$\alpha^{1/3}$
Diffusivity model	1-D diffusion	D1	α^2
	2-D diffusion	D2	$[(1-\alpha)\ln(1-\alpha)] + \alpha$
Geometrical Contraction model	Contracting Cylinder	R2	$[1-(1-\alpha)^{1/2}]$
	Contracting Sphere	R3	$[1-(1-\alpha)^{1/3}]$
Nucleation model	Avrami-Erofeev	A2	$[-\ln(1-\alpha)]^{1/2}$
	Avrami-Erofeev	A3	$[-\ln(1-\alpha)]^{1/3}$

2.3. Thermodynamic Study:

Thermogravimetric analysis (TGA) can be effectively used to determine thermodynamic properties such as change in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). The thermodynamic parameters are

calculated using kinetic data obtained through the model-fitting method, applying the equations reported in [20-22].

$$\Delta H = E_a - RT_m \quad (9)$$

$$\Delta G = E_a + RT_m \ln\left(\frac{K_b * T_m}{h * A}\right) \quad (10)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (11)$$

Here T_m (K) represents the maximum degradation temperature, K_b is the Boltzmann constant with a value of 1.381 × 10−23 J K^{-1}, and h is the Planck's constant, equal to 6.626 × 10^{-34} J s.

3. Results and Discussion:

3.1. Thermogravimetric Analysis (TGA):

Fig. 1 depicts the thermogravimetric (TG) and derivative thermogravimetry (DTG) curves of different plastic waste samples, including HDPE, LDPE, PP, PET, MLP, and MWP. Single-stage degradation of waste plastic samples was observed. The degradation temperature range, initial temperature (T_i), peak temperature (T_p), and weight loss (%) of various plastic samples are listed in Table 3. The HDPE, LDPE, and PP show similar trends in TGA/DTG curves that indicate the similarity in their molecular structures[23]. The degradation intervals of HDPE, LDPE, PP, PET, MWP and MLP are also listed in Table 3. TGA/DTG curves of MWP are comparable with HDPE, LDPE, PET, and PP. The TG/DTG curves of multi-layer plastics displayed a similar trend to those of PE (LDPE, HDPE) and PET.

The percentage of weight loss reflects the extent of decomposition or conversion of the polymer into gases, liquids (oils), and char during thermal degradation. A higher weight loss percentage suggests a greater conversion of plastic into volatile products (potentially valuable oils and gases) [24]. HDPE, LDPE, and PP have similar temperature ranges and peak temperatures, implying similar thermal stability and decomposition behavior. These polymers are primarily composed of carbon and hydrogen, which aid in their efficient thermal degradation [10]. HDPE (98.03%) and LDPE (96.51%) have the highest weight loss percentages, indicating that they break down almost completely under specified conditions. This suggests that HDPE and LDPE are excellent candidates for pyrolysis or HTL. Like HDPE and LDPE, PP (96.83%) has a high conversion rate, suggesting that it might produce a significant amount of valuable product during HTL, making it another viable candidate for thermal recycling. Several studies [25-27] have investigated the thermal decomposition of HDPE, LDPE, and PP under pyrolysis conditions, reporting that degradation occurs predominantly in a single mass-loss step. The decomposition process typically initiates around 327°C and is nearly complete by approximately 587°C with a material undergoing almost complete volatilization. PET has a significantly lower weight loss (80.53%) than HDPE, LDPE, and PP, indicating that PET may not fully convert into volatiles, resulting in a larger residue [28]. Girija et al. reported a similar degradation trend for PET, characterized by a single major decomposition peak and an overall weight loss of approximately 60% occurring around 440°C [29]. This is expected given that PET contains oxygenated functional groups (e.g., ester groups), which tend to create solid residues during breakdown [28, 30]. On the other hand, MLP (84.72%) is often made up of various polymer types, including barrier layers such as PET, and aluminum. The decreased weight loss compared to single polymers indicates incomplete conversion due to the material's complexity. MWP shows less weight loss (79.38%) due to low-grade quality and the heterogeneous composition of plastics in the combination is likely to produce more residue and lower the overall conversion efficiency[31].

The degradation time observed in TGA can serve as a baseline for estimating the minimum reaction time for pyrolysis and the HTL process. This degradation time is essential for determining the duration of exposure to high temperatures required to decompose a material into volatile substances (liquid and gas) with minimal solid residue. The time taken for degradation was similar for all materials, ranging from 12-15 minutes. However, each plastic's weight conversion (%) varied at their respective peak temperatures. For instance, HDPE undergoes nearly complete degradation (98%) in 13 min from 424-539℃ with a peak temperature of 494℃. This degradation temperature may be reduced due to enhanced reaction kinetics at subcritical and supercritical reactions conditions within HTL reactor. It is noted that the reaction time should begin at least from the initial temperature point provided by the TGA to get maximum conversion. Correlating the degradation temperature, time, and weight loss percentage obtained

from TGA offers a systematic approach to optimizing pyrolysis and the HTL processes.

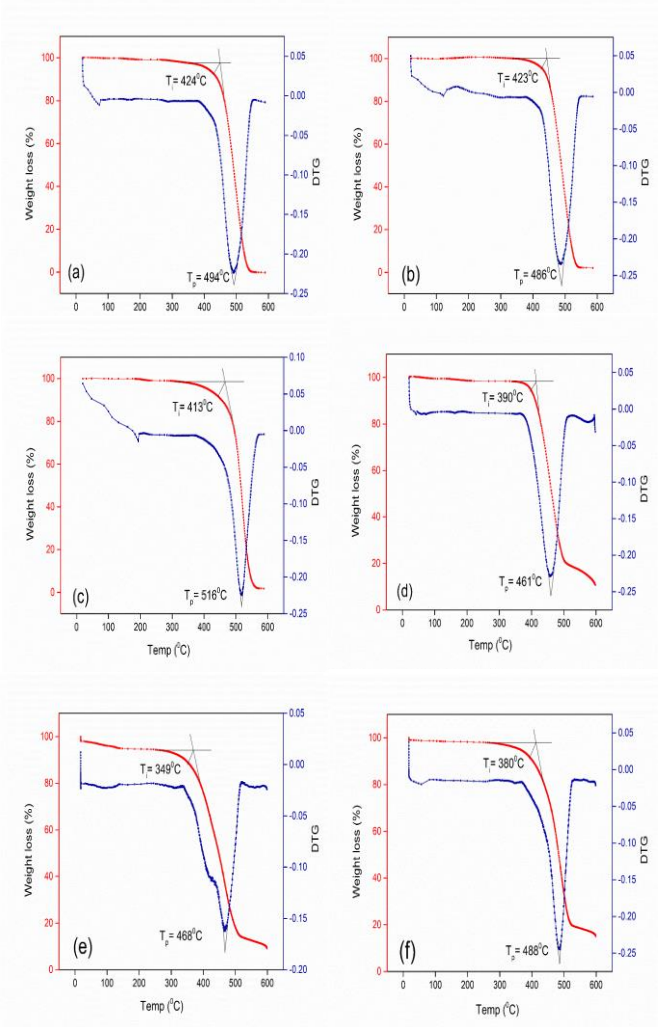

Figure 1: TG and DTG curves of different waste plastic samples (a) HDPE, (b) LDPE, (c) PP, (d) PET, (e) MLP, and (f) MWP

Table 3: Temperature ranges of degradation for different waste plastics.

Materials	Temperature Range (^{0}C)	Peak Temperature (^{0}C)	Degradation Time (min)	Weight loss (%)
HDPE	424-539	494	13	98.03
LDPE	423-535	486	12	96.51
PP	413-557	516	14	96.83
PET	390-513	461	12	80.53
MLP	349-509	468	15	84.72
MWP	380-519	488	13	79.35

3.2. Kinetic Analysis:

The kinetic parameters, including activation energy (E_a), regression coefficient (R^2), and pre-exponential factor (A), were determined using the Coats-Redfern method across various models given in Table 2. These parameters were evaluated for a single-stage degradation of waste plastic samples and are depicted in Fig. 2. The activation energy (E_a) for LDPE, HDPE, PP, PET, MWP, and MLP ranged from 295–117 kJ/mol. Regression coefficients (R^2) varied between 0.768 and 0.998, while pre-exponential factors (A) spanned 6.6E-04 to 3.2E+14 min^{-1}. Each material exhibited distinct kinetic parameters, highlighting variations in degradation behavior. Activation energy values are inherently influenced by parameters such as heating rate, feedstock characteristics, and experimental conditions; consequently, the reported values are strictly applicable to the specific experimental conditions employed in this study [10].

For HDPE and LDPE, model F2 exhibit higher regression coefficient (R^2 > 0.991), with activation energy around 269 kJ/mol for HDPE and 295 kJ/mol for LDPE as depicted in Fig 2. The first-order (F1) and second-order (F2) reactions have been widely reported in the literature as appropriate for describing the thermal degradation behavior of HDPE and LDPE, which is consistent with the findings of this study. Moreover, the corresponding activation energy values generally fall within the range of 230-290 kJ/mol [32-34]. LDPE typically has a lower activation energy for thermal deterioration because it has greater branching, resulting in more amorphous areas [35]. HDPE, on the other hand, has a more linear structure and a higher degree of crystallinity, which often means that heat degradation will need a larger activation energy[36, 37]. The presence of stabilizers or additives in LDPE samples can increase their thermal stability and activation energy [38, 39]. The residue obtained from TGA indicates that the impurity level in LDPE (4%) is greater than in HDPE (2%), suggesting the presence of additives and stabilizers (mainly CaCO3) introduced during their utilization and recycling processes [40, 41]. For PP, the D2 model was identified as the most suitable with an activation energy of 213.68 kJ/mol based on the regression coefficient (0.987). The presence of a methyl group along PP's backbone introduces Steric hindrance, making the polymer chains less densely packed and reducing the material's crystallinity, which lowers the activation energy required for thermal breakdown[42]. For PET, the model F1 was found to be the most suitable with an activation energy of 154.61 kJ/mol and

a higher regression coefficient (0.998). The rigidity and thermal stability of PET are attributed to its chain, which is composed of benzene rings. PET has a semi-crystalline structure, with regions of high crystallinity that provide thermal resistance and are harder to decompose than the amorphous regions, contributing to the higher activation energy [43]. Das and Tiwari [44] employed an iso-conversional method to evaluate the pyrolysis kinetics of PET and reported activation energy values in the range of 197-217 kJ/mol. Variations in PET feedstock composition, including the presence of additives, impurities, and contaminations, can significantly influence pyrolysis behavior and, consequently, the estimated activation energy [45]. For MLP and MWP, the D2 model was determined to be the most suitable, estimating an activation energy of 117.04 kJ/mol and 171.87 kJ/mol, respectively. The activation energy can be affected by the presence of additives, fillers, or metalized layers (e.g., aluminum), which can act as catalysts or inhibitors, changing the degradation pathway and, in turn, the activation energy.

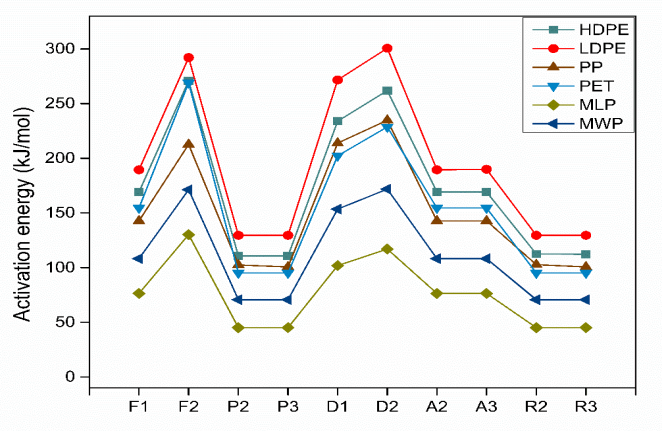

Figure 2: The activation energy of different waste plastics for various models

3.3. Thermodynamic Analysis:

The average value of enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) of most fitted models for reported samples can be found in Fig. 3. ΔH represents the difference in energy level between reactant and product. According to the Coats-Redfern method, the enthalpy change in HDPE (162kj/mol) was marginally lower than that of LDPE (183 kJ/mol), attributed to the intricate reactions in LDPE demanding more external energy. The ΔH (165 kJ/mol) observed for MWP was analogous to that of HDPE and LDPE, suggesting a significant presence of these polymers within the MWP composition. ΔS exhibited negative values for all the samples, indicating that the disorder resulting from bond breaking in products was less than in the primary reactants. Consequently, the time required to form the activated complex increases due to the reduced reactivity of the reactants[46]. LDPE demonstrated a more negative value of ΔS (-0.36) than other samples, implying the presence of an organized breakdown structure in an active state[47]. ΔG provides a full evaluation of the flow of heat and change in disorder, with a larger value of Gibbs free energy indicating that a reaction is less favorable and vice versa[46]. The positive ΔG and ΔH readings, as well as the negative ΔS, indicate that the reactions are not spontaneous under the specific temperature considered; however, spontaneity may change with temperature due to the temperature dependence of ΔG [48, 49]. PP has less thermal stability than other olefins (LDPE, HDPE) with ΔH (94.12 kJ/mol) and ΔG (277.36 kJ/mol), and ΔS (-0.232) suggesting a lesser degree of ordering during degradation, likely due to its less crystalline structure. PET demonstrates robust thermal resistance, as evidenced by its stable ΔG of 388.50 kJ/mol, high ΔH of 148.51 kJ/mol, and significant negative ΔS of -0.327. Its backbone's benzene rings, which improve crystalline structure and stiffness, aid in its stability. MLP exhibits considerable thermal stability, with an ΔH of 110.88 kJ/mol, ΔG of 308.63 kJ/mol, and ΔS of -0.266.

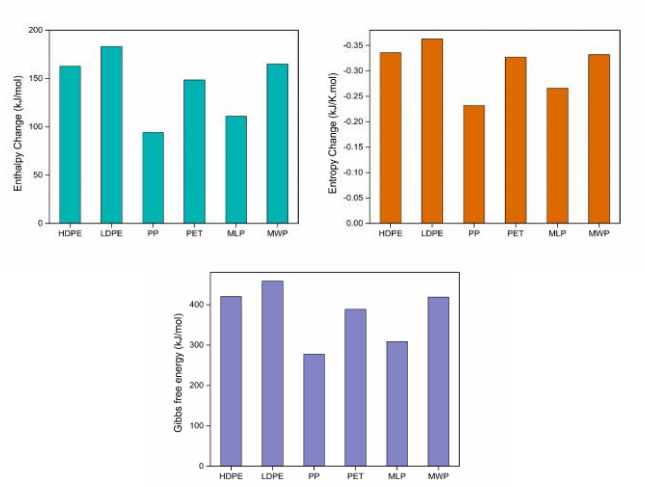

Figure 3: Thermodynamic values of different waste plastic samples

The kinetic and thermodynamic parameters reported in this study were obtained from single-run TGA experiments conducted at a fixed heating rate (10

°C/min). This approach is widely adopted in thermokinetic screening studies, as reliable activation energy values can be obtained through model fitting when high linear regression coefficients are achieved, and consistent degradation trends are observed across samples [19, 50]. In present work, regression coefficient (R^2) exceeding 0.98 indicates good agreement between experimental data and applied kinetic models. Nevertheless, the absence of replicate runs and statistical uncertainty analysis is acknowledge as a limitation, and future studies will incorporate multiple heating rates and replicate measurement to enable uncertainly quantification and improve the robustness of kinetic and thermodynamic evaluations.

4. Conclusions:

This experimental study presented thermal degrading behavior and kinetics using the Coats-Redfern approach with the integration of different models in the thermogravimeter analyzer. These findings on % conversion, reaction time, and temperature from TGA combined with kinetic analysis set a benchmark for identifying the onset reaction parameters of pyrolysis and HTL. The major findings are summarized as follows:

- A conversion range of 80-98 % was observed for PET, HDPE, LDPE, and PP, while a range of 79-84% was observed for MWP and MLP in TGA. The lower conversion percentage observed for PET is due to the presence of the oxygenated functional group, whereas the heterogeneous nature and low-grade quality of MWP and MLP account for their lower conversion ranges.
- The thermokinetic analysis exhibited that the suitable reaction models for HDPE, LDPE, and PET were reaction order and nucleation, with activation energies of 169 kJ/mol, 189 kJ/mol, and 154.61 kJ/mol, respectively. For MWP and MLP, the diffusivity model was determined to be the most suitable, with activation energies of 171.87 kJ/mol and 117.04 kJ/mol, respectively. For PP, the power law and geometrical contraction models were identified as the most suitable with an activation energy of 102.68 kJ/mol.
- The thermodynamic parameters ΔH, ΔS, and ΔG provide insights into the energy properties and practicality of thermal degradation. HDPE and LDPE showed ΔH values of 183–162 kJ/mol, while MWP's ΔH (165 kJ/mol) indicated a composition like these polymers. PP had a lower ΔH (94.12 kJ/mol) and ΔS (-0.232), suggesting less ordering during degradation. PET exhibited robust thermal resistance due to its benzene ring structure, with high ΔG (388.50 kJ/mol) and ΔH (148.51 kJ/mol). MLP demonstrated significant thermal stability, with ΔH (110.88 kJ/mol), ΔG (308.63 kJ/mol), and ΔS (-0.266).
- This study represents laboratory-scale foundational research using TGA. The kinetic and thermodynamic insights gained from TGA give a fundamental understanding of plastic waste degradation behavior and aid in the development of optimum operating settings. Further validation at pilot and industrial sizes, supported by techno-economic and environmental studies, is necessary to take the technique to practical use.

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Data Availability The datasets used or analyzed in the paper are available from the corresponding author on reasonable request.

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