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KINETICS OF THE PYROLYSIS OF HIGH-DENSITY POLYETHYLENE, LOW-DENSITY POLYETHYLENE, STYROFOAM AND THEIR BLENDS

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Abstract

The pyrolysis characteristics of High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE), Styrofoam (STF), and their blends were investigated to compare the process of the pure components with those of the blends. Thermogravimetric analysis (TGA) was employed to monitor the mass loss of the plastic samples during heating, providing critical insights into their thermal degradation behaviour. The pyrolysis kinetics were further examined using a multi-step integral method to determine the reactivities and activation energies of the materials. The results revealed that the pyrolysis processes of individual plastics could be characterized by a single reaction in the main decomposition zone. In contrast, the pyrolysis of binary (LDPE-HDPE, LDPE-STF, HDPE-STF) and tertiary blends (LDPE-HDPE-STF) exhibited two and three distinct reactions, respectively. Consequently, the decomposition of pure plastics follows a one-step mechanism, while the blends undergo multi-step mechanisms. Plastic pyrolysis is a crucial method for converting waste plastics into fuel-like substances. Hence, the term "fuels" highlights the potential of the resulting pyrolyzed products to serve as alternative energy sources. The results also showed variations in peak temperatures and decomposition intensities across different blends, significantly influencing the individual plastic materials' reactivities and activation energies. The activation energies for LDPE, HDPE, and STF ranged from 126.22 to 134.52 kJ/mol, while those for the blends were between 129.12 and 299.99 kJ/mol. Determining reactivities and activation energies is essential for understanding the efficiency and energy requirements of the pyrolysis process, helping optimize conditions for maximum fuel yield.

Keywords: Pyrolysis Kinetics; Plastic waste; Activation energy; TGA Analysis; LDPE-HDPE-STF

1. INTRODUCTION

The increase in human population growth and technological advancement has led to a drastic increase in energy demand. Globally, fossil fuels such as crude oil, natural gas, and coal constitute the principal source of a substantial portion of energy supply. This source of energy has been reported to be gradually depleting in the last few decades (IEA 2021). For the sustainability of economic growth, it is essential to use fossil fuels efficiently and cost-effectively. Plastics, derived from petroleum, are widely used due to their low cost, lightweight, ease of processing, and versatility, greatly enhancing the quality of life. However, the growing volume of plastic waste presents significant environmental challenges, making effective waste management crucial for long-term sustainability. Plastics are generally classified into industrial or municipal waste, each requiring different management strategies and these two categories require different management strategies (Brebu *et al.*, 2010; Panda et *al.,* 2010; Al-Salem *et al.,* 2009; Luo *et al.,* 1999). Traditional methods for managing municipal solid waste (MSW), such as landfilling and incineration, are still widely practised. Still, they are costly, and landfill space is becoming increasingly scarce (Paradela *et al*., 2009). Therefore, finding more efficient and sustainable disposal solutions is critical.

Plastic waste presents a considerable environmental challenge owing to its non-biodegradable characteristics, resulting in prolonged accumulation in landfills and contamination of oceans and ecosystems. This persistent waste problem exacerbates issues such as soil and water contamination, threatens marine and wildlife, and contributes to greenhouse gas emissions when incinerated, underscoring the urgent need for sustainable waste management solutions (Jambeck *et al.,* 2015). There is an urgent need to adopt alternative techniques to address pressing environmental challenges. The literature identifies four essential clean technology methods: pyrolysis and gasification, composting and anaerobic digestion, waste-to-energy, and material recycling, all of which offer sustainable solutions for waste management and environmental conservation (Singer *et al.,* 1999; Awasthi *et al.,* 2019). Among these clean technologies, converting plastic waste to energy, mainly through pyrolysis, holds significant promise. Pyrolysis effectively transforms plastic refuse into useful fuels or valuable chemicals for the petrochemical industry. This process is advantageous because it reduces the volume of plastic waste and produces high-value products such as fuels and feedstocks for further chemical applications. Numerous researchers have investigated the thermal degradation of polymers, with a focus on polyolefins like polyethylene (PE), polypropylene (PP), and polystyrene (PS), due to their cracking-yielding products with desirable properties for subsequent use in energy and chemical production (Brebu *et al*., 2010; Panda *et al.,* 2010; Al-Salem *et al.,* 2009; Luo *et al.,* 1999). A description of the thermal degradation of individual plastics has been thoroughly documented, highlighting various decomposition techniques, mechanisms, and kinetic data. This extensive literature underscores the importance of understanding these processes to optimize pyrolysis and other clean technologies, ensuring more efficient conversion of plastic waste into valuable products (Paradela *et al., 2009*). Descriptions of reactions during the decomposition of plastic wastes are complicated because of their complex nature. As a result, in many works of literature on thermal decomposition of polymers, authors usually focused on single polymers such as PP, PS, and polyvinyl chloride (PVC). The literature reports a review of the kinetic parameters (Westerhout *et al.,* 1997) and analysis methods. The paper discusses the conditions under which pyrolysis is most effective, such as temperature and catalyst types, and reviews the resulting products, including fuels and chemicals. The review highlights the advantages of pyrolysis, such as reducing plastic waste and producing valuable by-products. Most studies have utilized Thermogravimetric Analysis (TGA) to assess the kinetic parameters involved in plastic pyrolysis. This technique is commonly applied using empirical kinetics, often modelled as a single reaction, to better understand the decomposition behaviour and optimize the process for efficient energy and material recovery (Otero *et al*., 2008; Aboulkas *et al*., 2009; Encinara *et al.,* 2008). A parallel reaction model (Pantoleontes *et al*., 2009; Lin *et al.,* 2001; Al-Salem *et al*., 2010) has recently been employed in TGA experiments of pyrolysis. Encinar *et al*. (2008) used TGA to determine the pyrolysis kinetics of six plastic materials. The effects of process variables such as nitrogen (N_2) flow rate, initial sample mass to reactor, temperature, and heating rate were investigated. The activation energy of plastic materials was determined using the kinetic model derived from the single reaction model. Previously, Miskolczi *et al*. (2004) investigate the thermal degradation and kinetic parameters for individual plastic materials High-Density Polyethylene, Low-Density Polyethylene, Polypropylene, Polystyrene, and Polyvinyl Chloride (HDPE, LDPE, PP, PS, and PVC), as well as overall kinetic parameters for binary and multicomponent mixtures, using a single reaction model. Yang *et al.* (2001) used a single reaction curve-fitting method to determine the kinetic parameters of six different polymeric materials: HDPE, LDPE, PS, PP, PVC, and PET. This method measured the degradation behaviour and then differentially used a single reaction to fit the differential thermogram. Sinfronio *et al.* (2005) investigated non-isothermal decomposition using various kinetic methods, including the Flynn-Wall-Ozawa method, the Van Krevelen method, the Horowitz-Metzger method, the Coats-Redfern method, the Madhusudanan method, and the Vyazovkin method. The Coats-Redfern method was discovered to best describe the decomposition reaction. There are limited studies in the literature on the degradation of mixtures of plastic wastes, such as HPDE and PS, PP and PS (Pielichowski *et al.,* 2022). Some studies on the decomposition behaviour of plastic mixtures have also been investigated to provide insight into the physical properties of the plastic material (Paul *et al*., 2000). The studies on the degradation behaviour of the binary blends include polypropylene (PP) and polyethylene (PE) PP–PE, polypropylene, and polyurethane (PU) PP-PU. Some researchers have reported no interaction between PE and PS blends during degradation. Others reported a considerable degree of synergistic effect using reactor pyrolysis. The miscibility of the constituents in polymer blends influences their decomposition behaviour. Miscible blends typically have lower thermal stability than immiscible blends. To measure the weight loss of the different plastic waste and their mixture, TGA experiments were used in a non-isothermal condition with a balance. The kinetic parameters for the pyrolysis reaction of plastic waste were determined by applying a multi-step integral method to TGA experiment data. The multi-step integral method is preferred for pyrolysis research because it provides more precise, complex, and multi-stage degradation modelling. It captures sequential and overlapping reactions, giving better insights into activation energies and reaction mechanisms. It is especially useful for optimizing the pyrolysis of mixed materials, such as plastic blends.

This study addresses significant research gaps by investigating the pyrolysis kinetics of HDPE, LDPE, Styrofoam, and their blends—areas that have been relatively underexplored in existing literature. While many studies focus on the pyrolysis of individual plastics, they frequently overlook the kinetic behaviour of plastic blends. Additionally, this research contributes to sustainable waste management by enhancing pyrolysis processes for mixed plastic waste, commonly encountered in real-world applications.

2.0 Material and Method

2.1 Materials

The plastic waste samples used in this study were collected from both domestic and industrial activities. The plastics used were HDPE, LDPE, and Styrofoam (STF).

2.2 Methodology

The following steps were undertaken to obtain and prepare these samples:

2.2.1 Sample Types

Samples of HDPE and LDPE were obtained from used packaging materials collected from local recycling centres and industrial waste streams. These included empty bottles, containers, and plastic bags.

In addition, STF samples were obtained from used STF such as takeaway containers. They were collected from commercial establishments such as restaurants and fast-food outlets. These containers were explicitly chosen for their everyday use and relevance to waste management studies.

2.2.2 Collection Process

The HDPE and LDPE were collected from designated recycling bins and waste collection sites, while the STF was gathered from commercial waste disposal units. This plastic waste was manually sorted and cleaned in containers to avoid contamination.

2.2.3 Classification and Preparation of Samples

The plastics were classified based on their type and intended use upon collection, which involved separating HDPE, LDPE, and STF into distinct groups to ensure accurate analysis and experimentation.

The classified samples were subsequently cleaned after being classified. First, they are subjected to a cleaning by removing any residues, labels, and contaminants. This step also involved washing the plastics with water and a mild detergent, rinsing, and air drying.

After cleaning, the plastics were mechanically shredded into smaller pieces to facilitate uniformity in the pyrolysis process. This step was crucial for ensuring consistent sample size and effective processing.

2.2.4 Preparation for Experimentation

The cleaned and size-reduced plastic samples were then prepared for the pyrolysis experiments. To ensure even pyrolysis, the HDPE, LDPE, and STF plastic samples were thoroughly air-dried before being shredded into small, uniform particles less than 75 mm in size. Then, blended samples of LDPE_HDPE, LDPE_STF, and HDPE_STF in the ratio of 1:1 (by weight) were mixed in this study. For the LDPE_HDPE_STF, the ratio of 1:1:1 was used.

The prepared samples were stored in airtight containers to prevent contamination. The samples are then ready for pyrolysis testing. Blend homogeneity was achieved by mixing plastic waste samples in a mortar and pestle until a uniform mixture was obtained, ensuring consistent composition and allowing for even thermal degradation during pyrolysis. A non-isothermal TGA test was conducted using a Perkin Elmer Thermogravimetric Analyzer (TGA-4000) for all plastic samples. The samples were clean, dry, and prepared in small, uniform pieces. Before testing, the instrument was calibrated for baseline, mass, and temperature accuracy. Approximately 10 mg of each sample was accurately weighed and loaded onto a platinum sample pan and then placed in the furnace chamber. The system was flushed with oxygen gas at a flow rate of 20 mL/min, while the temperature was ramped at a rate of 10°C/min, spanning a range from 30°C to 900°C. The test was initiated, allowing the TGA to heat the sample while monitoring real-time weight loss. Data collected during the test were used to analyze thermal stability, decomposition stages, and kinetic parameters. After the test, the furnace was left to cool, the sample was extracted, and the pan was cleaned in preparation for the next experiment.

2.3 Kinetic modeling

The pyrolysis of solid material can be defined as the thermal breakdown of a solid substance (Hu *et al.*, 2007):

Solid →Char + Volatiles

The rate of decomposition of solid material can be represented as (Khawam *et al.*, 2006):

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E}{RT}\right)}f(\alpha) \qquad (1)$$

Here, α represents the conversion factor, A denotes the pre-exponential (frequency) factor, E is the activation energy, T refers to the absolute temperature, R is the gas constant, and f(α) corresponds to the reaction model.

Gravimetrically, α is defined by:

$$\alpha = \frac{mo-mt}{mo-mf} \qquad (2)$$

Here, m_0 represents the initial mass of the sample, m_t is the mass at temperature T, and m_x is the final mass after pyrolysis. Numerous researchers have adopted a first-order reaction model to describe the pyrolysis process of solid fuels (Vasile *et al.*, 2010; Aboulkas *et al.*, 2009], Thus, the pyrolysis reaction equation for waste plastic is reformulated as Eq. (3):

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E}{RT}\right)}(1-\alpha) \qquad (3)$$

Under non-isothermal conditions where the sample is heated at a constant rate, rearranging and integrating Eq. (3) results in

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right]\left(1-\frac{2RT}{E}\right)] - \frac{E}{RT} \qquad (4)$$

where β = dT/dt represents the heating rate. It has been demonstrated that for the majority of values of E within the pyrolysis temperature range, E/RT >> 1. Therefore, the expression ln[(AR/βE) × (1−2RT/E)] in Eq. (4) can be considered a constant, leading to:

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

The graph of [-ln(1–α)/T²] against 1/T produces a straight line with a slope of -E/R. From this slope and the intercept, the activation energy E and the pre-exponential factor A can be calculated, respectively.
Note: First-order reaction models assume that the reaction rate depends linearly on the concentration of one reactant, which may not fully capture the interactions and dynamics in a blend of multiple polymers.

3.0 Result and Discussion

3.1 Thermal degradation of individual material

The pyrolysis processes of the materials are marked by three stages of degradation, with the majority of decomposition occurring in the second stage, as illustrated in Fig. 1. During degradation, depolymerization takes place as the end of the polymer chain detaches, generating low-activity free radicals. Fig. 1 presents the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the pyrolysis of LDPE, corresponding to a heating rate of 10 °C min⁻¹. From the mass loss curve for the pyrolysis of LDPE, it can be noted that about 6% of residues tend to remain at 876 °C. This aligns with findings by (Ketov *et al.,* 2022) , which indicated that the mass loss curve for low-density polyethylene (LDPE) shows approximately 6% of residues at a temperature of 876 K. The initial mass loss occurring between 30 and 350 °C is associated with the removal of moisture from the sample. Devolatilization occurs between 350 and 470 °C, marking the primary decomposition zone and an active stage of pyrolysis. Beyond 470 °C, mass loss slows down until reaching 876 °C, as the plastic materials stabilize and become more resistant to degradation. The temperature range for devolatilization of LDPE is notably narrow, spanning from 350 °C to 450 °C, likely due to the uniformity of the plastic material found in this type of HDP waste. Fig. 2 illustrates the DTG curves for various plastic wastes. The weight loss patterns for LDPE, HDPE, and STF are nearly identical, suggesting that they share similar pyrolysis characteristics, which can be attributed to the comparable chemical bonds present in their molecular structures. The decomposition of HDPE takes place at temperatures ranging from 412 to 450 °C (see Figure 2 and Table 1), while LDPE decomposes at 462 to 520 °C. The decomposition temperature range for STF is lower (280 to 430 °C) and wider than that of both LDPE and HDPE. This finding aligns with observations made by(Dubdub & Al-Yaari, 2020), who noted significant variations in the thermal decomposition of polyethylene based on its different forms, including high-density polyethylene (HDPE), low-density polyethylene (LDPE), and other materials like Styrene-Butadiene Rubber (STF). LDPE showed the highest peak temperature of 520 °C, with a decomposition intensity of -40.163 wt/K, where "wt/K" refers to weight loss per unit temperature increase in this thermal analysis.
This was followed by HDPE, which had a peak temperature of 460 °C and a decomposition intensity of -33.384 wt/K. In contrast, STF exhibited the lowest peak temperature of 380 °C and a decomposition intensity of -23.912 wt/K. The peak temperatures and corresponding decomposition intensities for LDPE, HDPE, and STF are 508.56 °C (-39.118 wt/K), 438.37 °C (-32.65 wt/K), and 390.51 °C (-23.331 wt/K), respectively. Based on the peak temperatures, the stability of the plastic materials can be inferred, decreasing in the following order: LDPE < HDPE < STF. Table 1, the R1, R2, and R3 are the blends' first, second, and third-order reactions, respectively.

3.2 Degradation of mixture

When plastic materials are mixed, pyrolysis usually shows two or more devolatilization stages, unlike the single main stage seen when the plastics are pyrolyzed alone. The intensity of decomposition differs based on the types of materials in the blend and their respective proportions. Fig. 3 depicts the TG and DTG curves for the HDPE-LDPE mixture.
The initial decomposition stage in the HDPE-LDPE mixture is attributed to the breakdown of HDPE, while the second stage is influenced by the presence of LDPE. The first peak corresponds to the melting of HDPE, which begins at 350 °C and continues up to 470 °C, while the second peak corresponds to the melting of LDPE, which occurs at the temperature range of 460–530 °C. The two peak temperatures in the HDPE-LDPE mixture show a decomposition intensity of -6.14 wt/K and -20.05 wt/K, which corresponds to the appearance of the peak temperatures of the HDPE and LDPE in the mixture. The pyrolysis characteristic of the separate plastic materials appears also in the mix. Fig. 4 illustrate the TG and DTG curves for the LDPE-STF mixture. The first decomposition stage in the LDPE-STF mixture is attributed to the decomposition of STF, and the second decomposition stage is affected by LDPE.

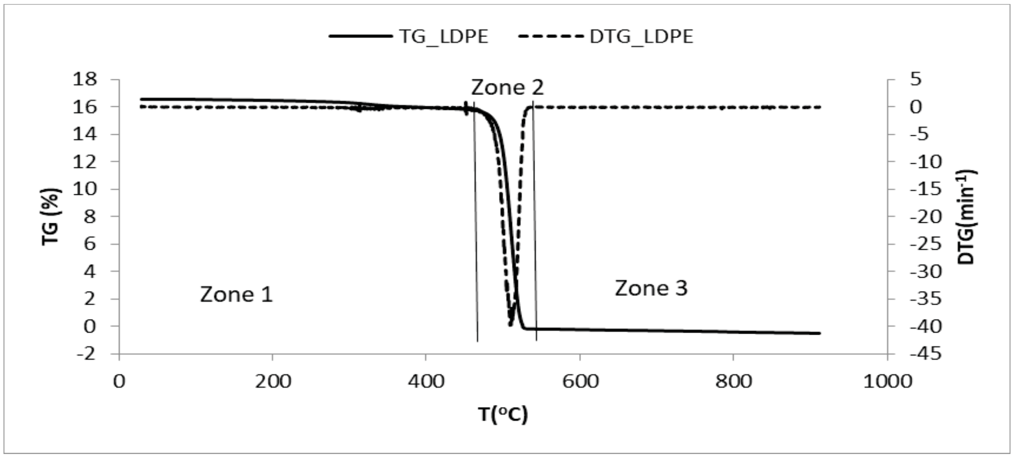

Figure 1: Pyrolysis TG and DTG curves for LDPE.

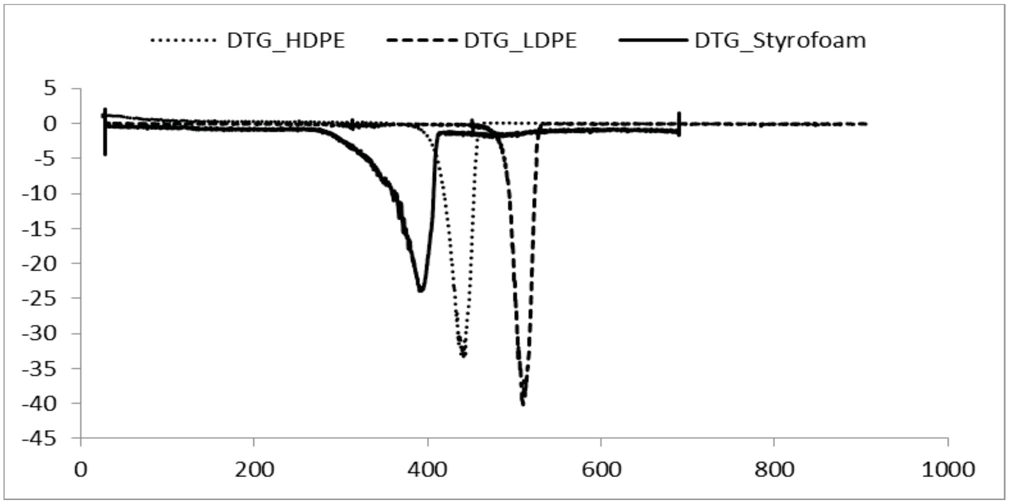

Figure 2: Pyrolysis DTG curves of HDPE, LDPE, and STF.

Table 1: Decomposition characteristic of the pure samples and their blend

Material	Temperature interval (*°C*)	Peak temperature (*°C*)	Decomposition intensity (wt/K)
LDPE	468.22-503.34(R1)	508.56	-39.118
HDPE	387.23-458.12(R1)	438.37	-32.65
STF	269.67-402.87(R1)	390.51	-23.331
LDPE-HDPE	389.12-461.84(R1) 461.65-524.94(R2)	438.22 499.77	-16.14 -19.805
HDPE-STF	288.15-431.33(R1) 380.58-490.87(R2)	322.12 423.22	-15.54 -18.65
LDPE-STF	291.01-392.12(R1) 392.99-573.44(R2)	359.32 508.4	-11.878 -20.437
LDPE-HDPE-STF	290.15-370.65(R1) 370.78-463.33(R2) 463.44-530.56(R3)	356.98 448.35 508.88	-7.989 -11.7756 -20.437

The first peak corresponds to the melting of STF, which begins at 268 *°C* and continues up to 365 *°C,* while the second peak corresponds to the melting of LDPE, which occurs at the temperature range of 460-530 *°C*. The two peak temperatures in the LDPE-STF mixture show decomposition intensity of -11.878 wt/K and -20.437 wt/K, corresponding to the appearance of the peak temperatures of the STF and LDPE in the mixture. The pyrolysis characteristic of the separate plastic materials appears also in the mixture. Relatively, the LDPE-HDPE-STF mixture thermographs exhibited three stages contrary to the two stages exhibited by LDPE-HDPE and LDPE-STF mixtures. Figure 5 shows the TG and DTG curves for the LDPE-HDPE-STF mixture. The DTG curves of the LDPE-HDPE-STF mixture have three notable weight loss peaks attributed to the synergistic effect of the component in the mixture, respectively. The first and the second peaks in Table 1 correspond to the melting of STF and HDPE at 268–365 *°C* and 350–470 *°C,* respectively. The third peak corresponds to LDPE melting at 460–530 *°C*. The decomposition intensity of -7.989 wt/K, -11.775 wt/K, and -20.437 wt/K (corresponding to STF, HDPE, and LDPE) are observed in the decreasing order of magnitude from the DTG curve in Fig. 5. At the peak temperatures of DTG curves, the rate of weight loss attained its maximum.

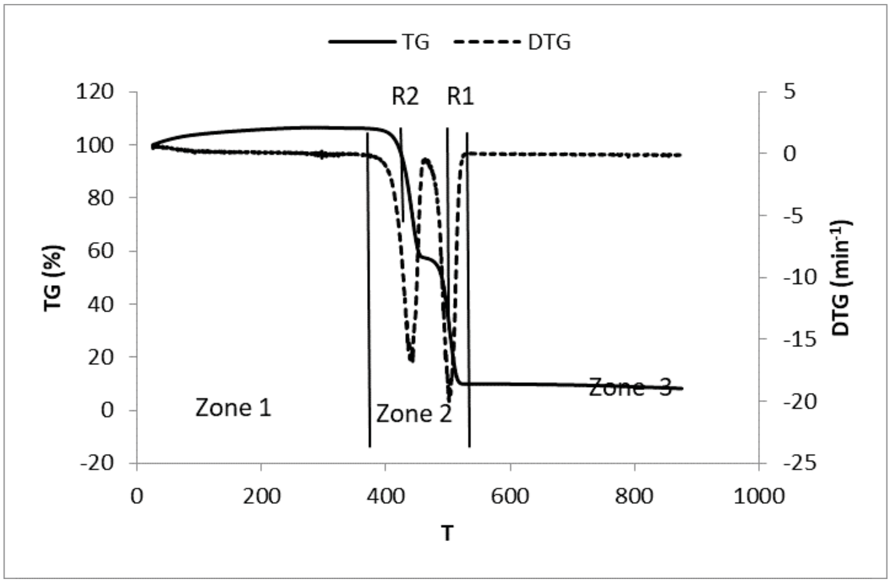

Figure 3: Pyrolysis TG and DTG curves of HDPE-LDPE blend.

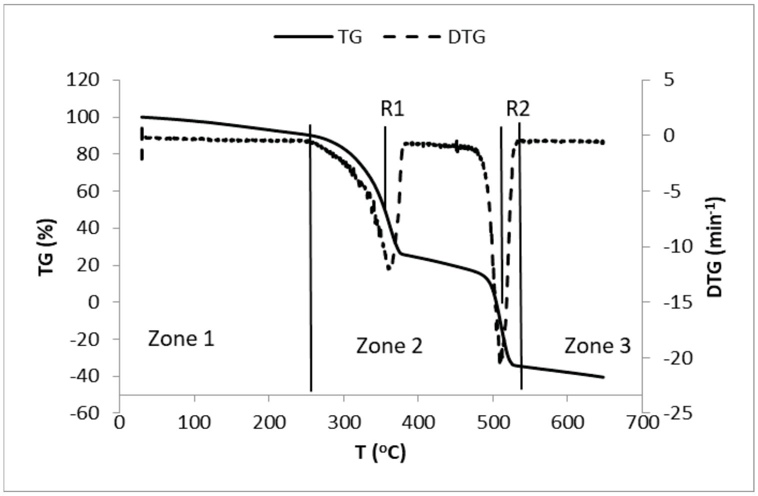

Figure 4: Pyrolysis TG and DTG curves of LDPE-STF blend.

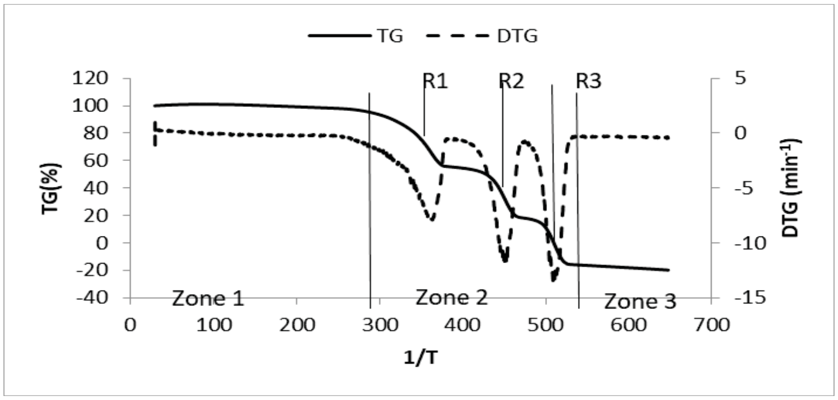

Figure 5: Pyrolysis TG and DTG curves of HDPE-LDPE-STF blend.

3.3 Kinetic Analysis

The TGA data used to calculate the kinetic parameters focused exclusively on Zone 2 for each type of plastic waste. In contrast, the mixed plastics depicted in Figs. 6, 7, and 8 show the plot of ln [g(α)/T²] versus 1/T for pyrolysis, calculated using both single-step and multi-step integral methods. Table 2 summarizes the degradation temperature range, fractional conversion, activation energy, pre-exponential factor, and R² values for both the individual materials and the blends. In the pyrolysis of pure samples, a single reaction is observed in the main decomposition zone (see Figure 1). In contrast, the co-pyrolysis of blends results in multiple reactions within the main decomposition zone, as illustrated in Figures 4 and 5 for LDPE-STF and LDPE-HDPE-STF, respectively. Consequently, the kinetic plot of ln $[g(\alpha)/T^2]$ versus 1/T of LDPE was described by a single reaction (R1) mechanism, as shown in Fig. 6. The kinetic plot of ln $[g(\alpha)/T^2]$ versus 1/T of LDPE-STF and LDPE-HDPE-STF was described by two reactions (R1 and R2) and three reactions (R1, R2, and R3) mechanism as shown in Fig. 7 and 8 respectively.

The kinetic parameters from the pure plastic wastes presented in Table 2 indicate that LDPE is more reactive than HDPE and STF, with a higher *E* value of 134.52 kJ/mol and higher pre-exponential factors. STF has the highest conversion with activation energy, with no residue remaining at the end of the experiment. Vasile *et al*. (2010) obtained activation energies for the plastic decomposition range of 130 and 195kJ/mol with a first-order reaction rate. Fritsky *et al*. (1994) reported an activation energy of 184 kJ/mol. However, Chan et al. (1997) found higher activation energy for polyethylene (324 kJ/mol). It can be concluded that these authors show that activation energy is strongly dependent on the calculation method, experimental facilities, and procedures.

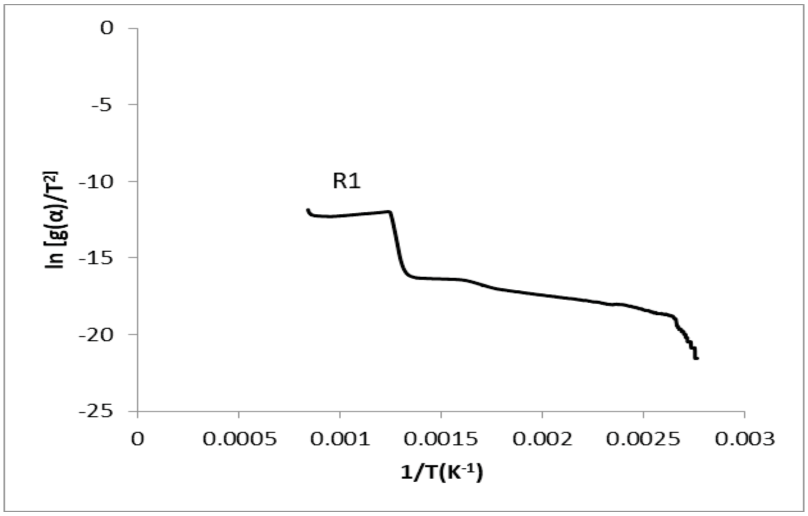

Figure 6: Plot of ln$[g(\alpha)/T^2]/(1/T)$ for HDPE pyrolysis calculated by the one-step integral method.

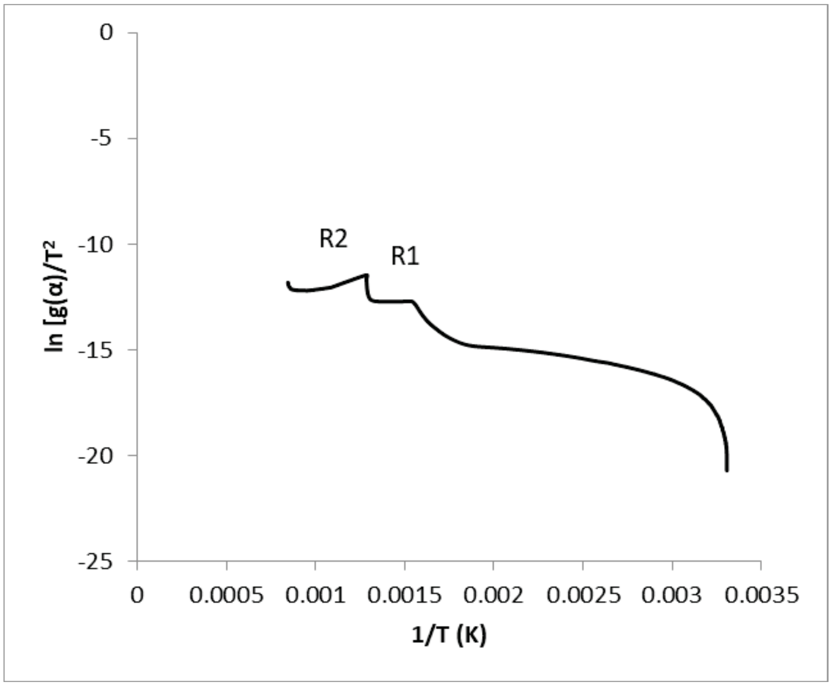

Figure 7: Plot of ln[g(α)/T^2]/(1/T) for LDPE-STF pyrolysis calculated by the one-step integral method.

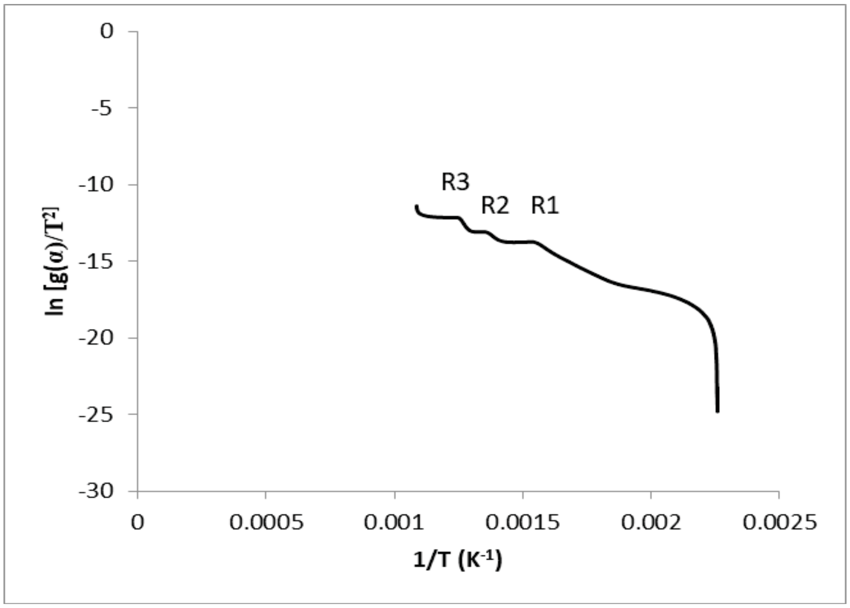

Figure 8: Plot of ln[g(α)/T^2]/(1/T) for LDPE-HDPE-STF pyrolysis calculated by the one-step integral method.

Fig. 9 below shows the plots from the multi-step integral method for various LDPE, HDPE, and STF blends. According to the activation energy values listed in Table 2, the temperature and activation energy required for the decomposition of the LDPE-HDPE blend are higher than those for the LDPE-STF blend (see Fig. 10). STF exhibits the lowest activation energy, which is evident in the pyrolysis reactivity of its blend. We employed three first-order reactions to characterize the co-pyrolysis of LDPE-HDPE-STF (as depicted in Fig. 11), with activation energies of 162 kJ/mol for R1, 187 kJ/mol for R2, and 299.99 kJ/mol for R3. At the main decomposition zone of the non-isothermal TGA process, it is intrinsic to note that the high-temperature degradation leads to high fractional conversion. This trend shows that the kinetic control mechanism is adequate to drive the decomposition faster. The wide variability in the activation energy between reaction R1 (162 kJ/mol) and R3 (299.99 kJ/mol) in the multi-step method hinged on the complex reactivity of the blend (Opiecka *et al*., 2012).

The LDPE-HDPE-STF blend shows peak temperatures at different degradation temperatures. The peak temperatures in the LDPE-HDPE-STF blend show a slight deviation when compared with the peak temperatures of pure STF, HDPE, and LDPE, respectively. However, the change is more significant when the decomposition intensity of the LDPE-HDPESTF blend is compared with that of pure samples. It is known that peak temperature is directly related to plastic structure. Therefore, the small change in plastic structure emanating from slight variations in peak temperatures strongly affects decomposition intensities. Notably, the conversion rates for all the blends exceed 15%, indicating that the bulk of the decomposition takes place at elevated temperatures. The prospect of the decomposition towards high fractional conversion is raised at high temperatures. The conversion achieved for the plastic materials is comparable to that reported by Zhou *et al*. (2009). Activation energy plays a crucial role in determining the thermogravimetric pyrolysis mechanism of any material. Chemical reactions with high activation energy necessitate elevated temperatures or extended reaction times (Zhou *et al*., 2009). The differences in activation energy revealed that a blend of different polymeric materials has pyrolysis reactivity at different temperature regimes. Oyedun *et al*. (2014) noted that polyethylene undergoes single-stage degradation and that its thermal decomposition requires higher temperatures due to its complex structure. The activation energies obtained ranged from 126.22 to 134.52 kJ/mol for LDPE, HDPE, and STF, and from 129.12 to 299.99 kJ/mol for the blend. Williams *et al*. (1999) investigated the thermal degradation of polystyrene and polypropylene, finding that the thermal decomposition of the blend was greater than the total decomposition of the individual components. The activation energy values between 162.12 and 299.99 kJ/mol obtained from LDPE-HDPE-STF blends were within the 160 to 320 kJ/mol polyethylene values reported by Costa *et al.* (2007). However, other studies have reported activation energy values reaching as high as 498 kJ/mol. The differences in activation energy may be due to variations in polymer chain length, degree of crystallinity, and intermolecular forces present within the polymers. In blends, the interaction between various polymers can alter their thermal stability, leading to an increase in the energy required for degradation (Zein *et al.,* 2022).

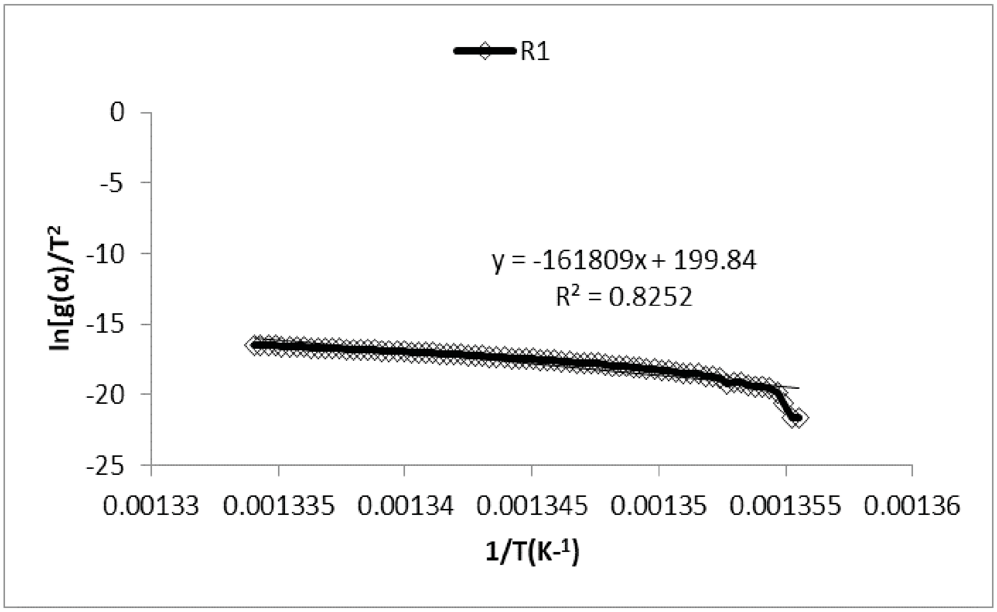

Figure 9: Plot of ln[g(α)/T^2]/(1/T) for LDPE pyrolysis calculated by the multi-step integral method.

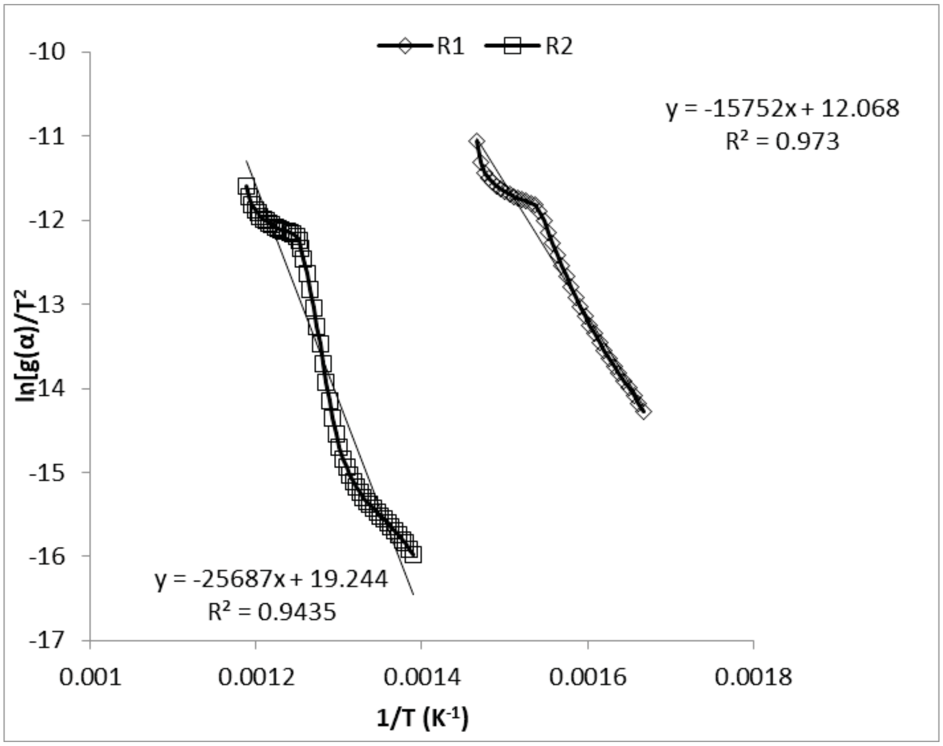

Figure 10: Plot of ln[g(α)/T^2]/(1/T) for LDPE-STF pyrolysis calculated by multi-step integral method.

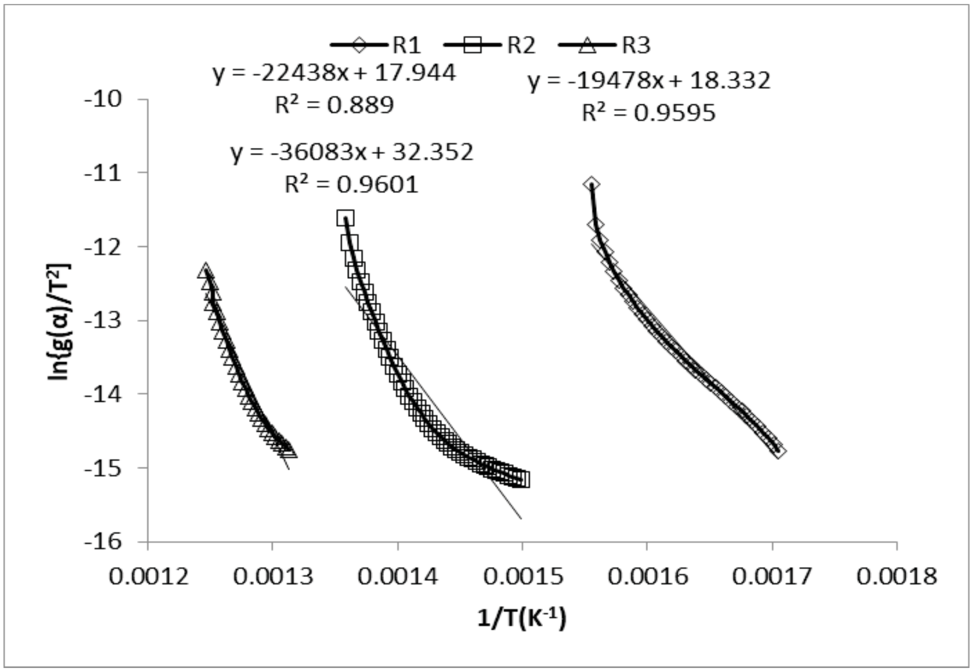

Figure 11: Plot of ln[g(α)/T^2]/(1/T) for LDPE-HDPE-STF pyrolysis calculated by the multi-step integral method.

Table 2: Kinetic parameters for pyrolysis of LDP, HDP, STF, and their blend

Reaction	**Temperature range (°C)**	**Conversion**	***Ea* (kJ/mol)**	**A (min^{-1})**	***R^2***
LDPE	468.22-503.34(R1)	50	134.52	5.9E+25	0.9425
HDPE	387.23-458.12(R1)	47	131.34	4.74E+22	0.959
STF	269.67-402.87(R1)	16	126.22	5.5E+8	0.9756
LDPE-HDPE	389.12-461.84(R1) 461.65-524.94(R2)	40 35	373.22	5.9E+25	0.9425
HDPE-STF	288.15-431.33	22	129.12		
	380.58.-490.87.76	34	206.11		
LDPE-STF	291.01-392.12	24	130.162		
	392.99-573.44	37	213.561		
LDPE-HDPE-STF	290.15-370.65(R1) 370.78-463.33(R2) 463.44-530.56(R3)	19 44 58	162.12 187.32 299.99	-----	0.9102

4.0 Conclusion

A thorough examination of the decomposition of individual plastic wastes (LDPE, HDPE, and STF) and their blends during pyrolysis was conducted using TGA. The results from the thermogravimetric analysis suggest that the pyrolysis of the blend can be represented as a multi-stage process, exhibiting distinct pyrolysis characteristics based on the components of the blends. Consequently, the decomposition of the blends was described by a multi-step mechanism.

The result obtained shows some variations in the peak temperatures and decomposition intensities. These variations significantly impact each plastic material's reactivities and activation energies in the blend. The wide variation in activation energies of the blend hinged on the complex multi-step pyrolysis mechanisms. This trend shows that the kinetic control mechanism for the degradation of the blends was more significant than the combined degradation of the isolated components. The findings underscore the need for tailored pyrolysis strategies for plastic waste mixtures, as the kinetic control mechanisms for blends are more complex than those for individual components. Understanding these multi-step degradation processes can lead to improved optimization of pyrolysis conditions, enhancing the efficiency of waste-to-energy technologies. Moreover, it significantly contributes to more effective and sustainable management of mixed plastic waste, potentially reducing environmental impact and improving resource recovery from plastic waste. However, future research could investigate how varying operational parameters such as temperature, pressure, and heating rates affect the multi-step degradation processes of different plastic blends or examine a broader range of plastic types and blends to generalize the findings and develop more comprehensive models for various plastic waste mixtures.

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