



# Thermogravimetric Analysis of Biomass-Plastic Co-Pyrolysis: Characterization and Evaluation

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## ABSTRACT

Renewable biomass has emerged as a paramount energy source capable of undergoing multifaceted transformations into various forms of fuel, encompassing liquid, solid, and gaseous states, facilitated by an array of processes. The extraction of high-value materials from biomass necessitates meticulous equipment design and the implementation of diverse methodologies, with pyrolysis emerging as a prominent avenue in this regard. The engineering of apparatuses pertinent to this process mandates a comprehensive understanding of reaction kinetics. In this study, an investigation into agricultural residues generated in Iran was conducted, identifying bagasse as the preferred biomass material, while LDPE and PET polymers were chosen to represent plastic waste. The kinetics of pyrolysis reactions involving LDPE, PET, and their amalgamation with bagasse were scrutinized. Through the execution of heat-weighted experiments, combined with the exploration of kinetic models for the pyrolysis reactions of LDPE, PET, and their blends with bagasse, a novel kinetic model was introduced, drawing from both single and multiple independent reaction frameworks. Comparative analysis of the outcomes derived from the proposed model for LDPE, PET, bagasse blends, as well as LDPE and PET, against laboratory results yielded coefficients of determination of 0.9937, 0.9875, 0.9883, and 0.9909, respectively. This finding underscores a robust concurrence between the prognosticated model outcomes and empirical laboratory data, affirming the efficacy of the developed kinetic model.

**Keywords:** Pyrolysis, Kinetic modeling, Thermogravimetric analysis (TGA), Plastic, Biomass.

## Introduction

In recent years, the amount of agricultural waste worldwide has been rapidly increasing, consequently garnering more attention to the environmental drawbacks and issues arising from agricultural waste. Therefore, appropriate methods for managing agricultural waste must be employed. The surge in agricultural waste production can be attributed to various factors, including the intensification of agricultural practices, the expansion of agricultural land, and shifts in consumption patterns [1]. As agricultural activities expand to meet the needs of a growing global population, the associated waste generated poses significant environmental challenges. These challenges

encompass soil degradation, water contamination, greenhouse gas emissions, and biodiversity loss, underscoring the urgent need for effective waste management strategies. Moreover, the disposal of agricultural waste often entails additional costs and logistical complexities, further highlighting the necessity for adopting efficient and sustainable waste management practices [2]. Consequently, the exploration of viable approaches to mitigate the environmental impact of agricultural waste is imperative, with a focus on reducing waste generation, promoting recycling and reuse, and implementing environmentally friendly disposal methods [3]. By addressing these challenges, agricultural waste management practices can contribute to the



preservation of ecosystems, the conservation of natural resources, and the advancement of sustainable development objectives at both local and global levels [1]. Despite these challenges, the increasing development of renewable energy sources, particularly biomass resources, appears vital [2, 3]. Biomass stands out as the only renewable energy source that can be converted into various forms of fuels (biofuels), including liquid, solid, and gas, and possesses promising flexibility in production and marketing [2]. It is estimated that biomass could account for between 15 to 50 percent of the world's primary energy sources by 2050. Furthermore, biomass, recognized as one of the largest sustainable energy sources globally, harbors numerous alternative energy resources available in various forms across the world. Due to its accessibility and myriad economic and environmental benefits, biomass can be utilized as a substitute for conventional fossil fuels. After coal, oil, and gas, biomass is acknowledged as the fourth-largest energy system, currently supplying approximately 14% of the world's annual energy consumption. Consequently, the development and utilization of biomass have attracted global attention [2, 4]. The remarkable growth in energy consumption will ultimately lead to increased greenhouse gas emissions and environmental issues [5, 6]. Presently, more than 80% of the total energy consumed worldwide is derived from fossil fuels, raising serious concerns regarding environmental and health issues [5, 7].

### Methodology

The bagasse sample was obtained from the Khuzestan province (Karooon Agriculture and Industry Company). One of the prerequisites before identifying the raw material and biomass pyrolysis is reducing the moisture content of the biomass to below 10 percent. Excessive moisture content in biomass has adverse effects on the pyrolysis process, including the need for additional heat to evaporate the moisture and heat to raise steam to the required pyrolysis temperature. The amount of energy required to heat the biomass to the pyrolysis temperature and evaporate its products is estimated to be approximately 2 megajoules per kilogram. The energy required for the pyrolysis of raw materials with moisture content exceeding 10 percent increases.

In order to reduce the moisture content to less than 10 percent, these materials were air-dried for several days and then, according to the AOAC Official Method 934.01 standard [8], the bagasse sample was placed in an oven with a maximum temperature of 70 degrees Celsius and a maximum pressure of 50 millimeters of mercury

until the sample reached a constant weight, at which point it was heated. The bagasse sample, after drying, was crushed to a mesh size of less than 35 using a Planetary Ball-Mill apparatus. The Planetary Ball-Mill apparatus is illustrated in Figure 1.

Plastic waste comprises various types of polymers such as Polyethylene Terephthalate (PET), High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE), Polyvinyl Chloride (PVC), Polypropylene (PP), Polystyrene (PS), Polycarbonate (PC), Polyacrylate (PA), and so forth. Although each of these plastics possesses a different chemical structure with varying amounts of carbon, oxygen, and hydrogen, they share common characteristics including low volatility, high viscosity, relatively high calorific value, and very low moisture and ash content [9]. For the procurement of raw materials for the experiments, PET was obtained from Tondgouyan Petrochemical Company, and LDPE was acquired from Laleh Petrochemical Company. The polymers were cryogenically milled using a CryoMill apparatus manufactured by Retsch, Germany, under liquid nitrogen to achieve a mesh size of less than 50.

Thermogravimetric analysis refers to the decomposition of a substance concerning its weight with respect to time and temperature. Essentially, thermogravimetric analysis evaluates the weight loss at a specific temperature and time, serving as a fundamental study for the activation process. This process aids in determining the pyrolysis temperature range. The TGA experiment was conducted using a TA Instrument 2960 apparatus manufactured in the United States. The experimental conditions for TGA are as follows:

1. The temperature range of the experiment ranges from room temperature to 850°C.
2. The desired heating rate is 20°C/min.
3. Four sample experiments were conducted, including PET Mesh 50 with index P5, LDPE Mesh 50 with index L5, a mixture of bagasse Mesh 35 + LDPE Mesh 50 with index BL5, and a mixture of bagasse Mesh 35 + PET Mesh 50 with index BP5.
4. For each sample experiment, TGA was conducted at a heating rate of 20°C/min with nitrogen gas.
5. The nitrogen gas flow rate during the experiment ranged from 60 to 65 ml/min.

### Experimental temperature conditions:

Initially, each sample was subjected to room temperature up to 105°C at a heating rate of 10°C/min for 15 minutes. Subsequently, each sample was tested from 105°C to 850°C at a heating rate of 20 °C/min

under a nitrogen gas atmosphere with a purity of 99.9999% at a flow rate of 60-65 ml/min.

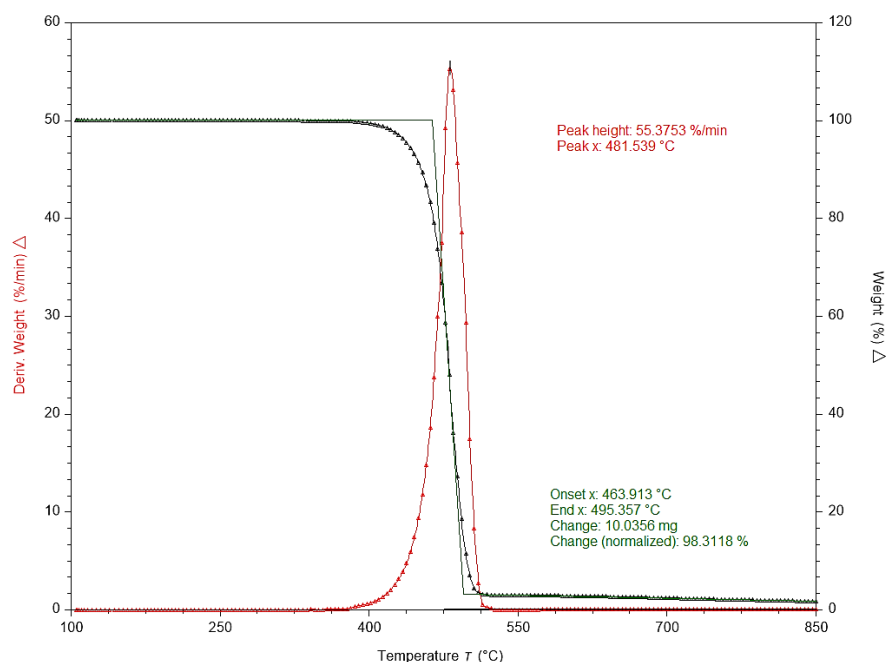
## Results And Discussion

The thermogravimetric analysis (TGA) conducted on low-density polyethylene (LDPE), polyethylene

terephthalate (PET), and their respective mixtures with bagasse which will be discussed.

## Thermal analysis of Low-Density Polyethylene (LDPE) or lightweight polyethylene.

The results of the TGA experiment for pure LDPE are illustrated in Figure 1.



**Fig. 1.** Output curve from the TGA device software for LDPE at a heating rate of 20°C/min.

To investigate the reaction conditions of polymers based on laboratory results, a single-step reaction assumption has been utilized. Accordingly:

Table 1 presents the results of modeling the laboratory experimental data based on the Sestak-Berggren equation (Equation (1)) for LDPE.

$$f(\alpha) = (1 - \alpha)^n \alpha^m \quad (1)$$

**Table 1.** The result obtained from modeling the Sestak-Berggren equation for LDPE.

m	n	Ln(cA) (1/s)	E <sub>a</sub> (kJ/mol)
0	1.04	49.5	335.8

As you are aware, the Master plot method is a suitable approach for determining mechanism-dependent parameters in decomposition reactions. In this method, by plotting various kinetic models and experimental data graphs, comparisons can be made between them, enabling the selection of the best-fitting model to the laboratory data. This facilitates a comprehensive understanding of the reaction kinetics

and aids in accurately characterizing the reaction mechanism. Additionally, the Master plot technique allows for the extrapolation of reaction parameters, providing insights into the behavior of the reaction under different conditions. Overall, employing the Master plot method enhances the precision and reliability of kinetic analyses in decomposition reactions, thereby contributing to advancements in reaction mechanism elucidation and process optimization.

As depicted in Figure 2, the conformity between the data model and the F1 kinetic model is strikingly evident. Employing the Levenberg-Marquardt method for fitting the model to the data and the Petzold-Hindmarsh routine for solving the model, implemented within a C++ framework, and underscored a meticulous computational approach. The benchmark data for comparison were derived from laboratory DTG experiments, ensuring a robust evaluation. The outcomes of modeling utilizing the F1 equation, deemed the most suitable proposed formulation, were meticulously computed. Subsequent analysis revealed a notable concurrence when juxtaposed with the laboratory-derived results, as delineated in Table 2.

Furthermore, this robust computational framework underscores the meticulous calibration of theoretical models against empirical data, thus providing a robust foundation for elucidating the kinetic mechanisms governing the pyrolysis process. The utilization of advanced computational algorithms not only enhances

the precision of model fitting but also facilitates a deeper understanding of the underlying chemical reactions and reaction kinetics. Such insights are crucial for refining theoretical models, thereby advancing the predictive capabilities of pyrolysis models and their applicability in real-world scenarios.

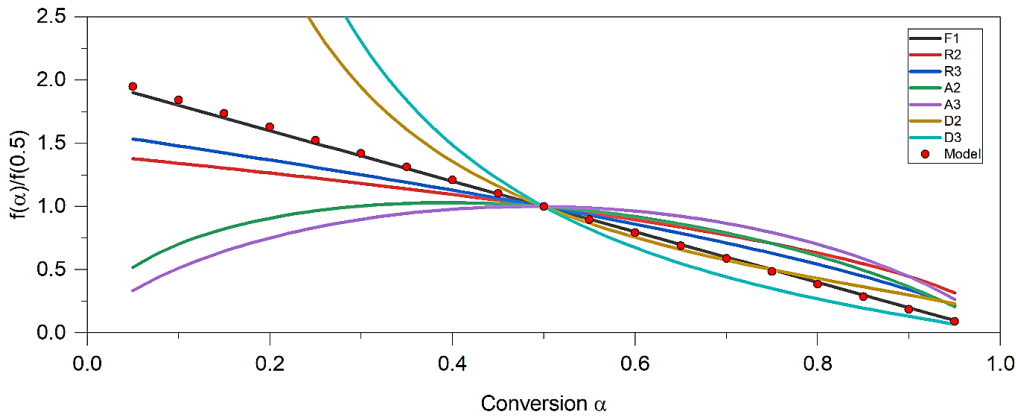


Fig. 2. Comparative curve with other models for LDPE.

**Table 2.** Results obtained from modeling LDPE data using the F1 equation.

LDPE, F1 Model			
R <sup>2</sup>	Residual standard error	(kJ/mol) <i>E<sub>a</sub></i>	lnA
0.9937	0.0001703	350.00000	51.85102

0.9937	0.0001703	350.00000	51.85102
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**Thermal analysis of polyethylene terephthalate.**

The results of the TGA experiment for pure PET are illustrated in Figure 3.

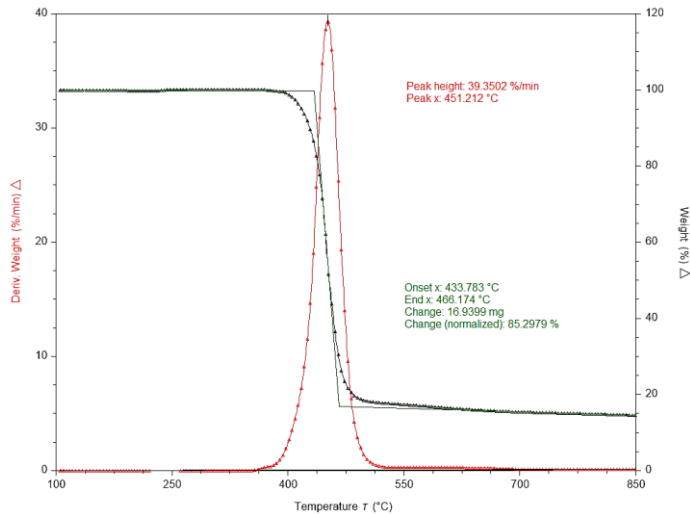
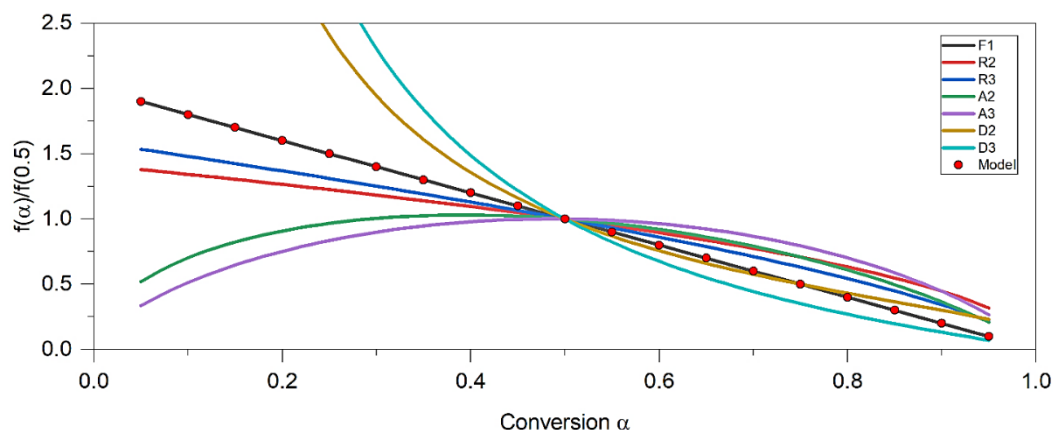


Fig. 3. depicts the output curve from the TGA device software for PET with a heating rate of 20°C/min.

Table 3 presents the results obtained from modeling for PET.

**Table 3.** The result of modeling using the Sestak-Berggren equation for PET.

m	n	Ln(cA) (1/s)	E <sub>a</sub> (kJ/mol)
0.0	1.0	37.8	254.1



**Fig. 4.** Comparative curve with other models for PET.

As depicted in Figure 4, a significant concordance is evident between the data and the F1 kinetic model. In this section, akin to the preceding segment, the fitting of the model to the data was achieved through the Levenberg-Marquardt method, while the Petzold-Hindmarsh routine was employed for solving the model equations. The software implementation was executed in the C++ programming language. The target dataset for comparison encompassed the DTG laboratory data. Subsequently, the outcomes derived from modeling using the F1 equation, deemed the most optimal form, were meticulously computed. These results exhibit a commendable alignment with the findings presented in Table 4, consolidating the robustness and efficacy of the proposed modeling approach. Such congruence underscores the reliability and validity of the derived

kinetic model in elucidating the thermal decomposition behavior of the PET polymer under investigation.

**Table 4.** Results obtained from modeling PET data using the F1 equation.

PET, F1 Model			
R <sup>2</sup>	Residual standard error	(kJ/mol) E <sub>a</sub>	lnA
0.9875	0.0001898	264.0329	39.7795

#### Thermal analysis of a mixture containing 50% LDPE and 50% bagasse

The results of the TGA experiment for the 50% LDPE and 50% bagasse mixture are depicted in Figure 5.

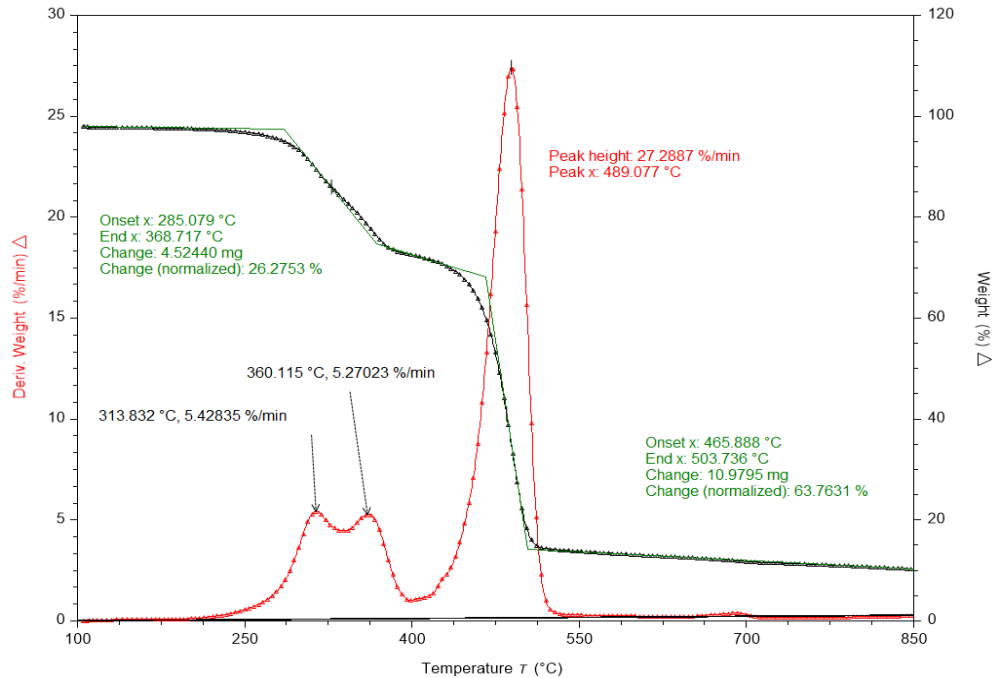


Fig. 5. Output curve from the TGA instrument software for the 50% LDPE and 50% bagasse mixture with a heating rate of 20°C/min.

Given the explanations in Chapter Two, it is not feasible to utilize previous methods to obtain kinetic parameters and select an appropriate model due to the increased complexity resulting from the combination of two different substances. Therefore, based on this premise, the extended Prout–Tompkins equation (ePT) has been employed for the curve obtained from the bagasse and LDPE mixture experiment, considering a two-step independent non-dependent reaction [10]. The results of modeling the laboratory data, compared to the DTG data as the target data, are as follows: the value of  $q$  in all equations has been considered as 0.999.

$$f(\alpha) = (1 - \alpha)^n \cdot [1 - q \cdot (1 - \alpha)]^m \quad (2)$$

$$\frac{d\alpha_m}{dt} = c \cdot k_1 \cdot f(\alpha)_1 + (1 - c) \cdot k_2 \cdot f(\alpha)_2 \quad (3)$$

In the above equation, the value of  $k$  represents the reaction rate constant, and  $c$  denotes the reaction impact coefficient of the first reaction compared to the second. These values will be optimized based on the laboratory data, and the optimal values will be obtained. The results obtained are listed in Table 5.

Similar to the previous section, here, for the curve obtained from the Bagasse and PET mixture experiment, the extended Prout-Tompkins equation (ePT) has been utilized, considering a two-step independent reaction. The results obtained from modeling the laboratory data by comparing DTG data as the target data are as follows: the value of  $q$  in all equations has been considered as 999/0, as mentioned in Table 6.

The thermogravimetric analysis (TGA) conducted on low-density polyethylene (LDPE), polyethylene terephthalate (PET), and their respective mixtures with bagasse has yielded profound insights into the thermal degradation behavior of these materials. LDPE demonstrates a unimodal decomposition profile, wherein approximately 98.3% of its initial mass undergoes degradation in a single stage. This thermal decomposition reaches its apex at 481.5°C, coinciding with the temperature at which LDPE exhibits its maximum decomposition rate, recorded at 55.4 %/min. Furthermore, the activation energy for LDPE is calculated to be 350 KJ/mol, underscoring the energetic threshold required for its thermal degradation processes.

Similarly, PET showcases a unimodal decomposition pattern, with around 85.3% of its initial mass succumbing to degradation in a singular phase. Notably, PET attains its peak decomposition rate at 451.2°C, with a corresponding rate of 39.4 %/min. The activation

energy for PET is determined to be 264.0329 KJ/mol, elucidating the energy barrier associated with its thermal decomposition.

The inclusion of bagasse as a co-component in LDPE and PET mixtures introduces a more intricate decomposition behavior, characterized by biphasic degradation stages. In both LDPE and PET mixtures, the initial decomposition stage accounts for approximately 26.3% to 27.5% of the initial mass, followed by a subsequent stage involving 63.8% to 67.1% of the sample mass. Notably, the DTG curves for these mixtures exhibit triphasic decomposition patterns, with distinct peaks observed at varying temperatures. The highest decomposition rates for LDPE and bagasse mixture and PET and bagasse mixture are recorded at 489.1°C and 445.0°C, respectively, indicating the synergistic effects between the polymer matrix and lignocellulosic component.

The comprehensive understanding of the thermal decomposition characteristics and reaction kinetics of LDPE, PET, and their mixtures with bagasse provides crucial insights for various applications in industries ranging from packaging to renewable energy systems. These findings contribute significantly to the advancement of eco-friendly materials science and engineering practices, paving the way for the development of sustainable materials and technologies

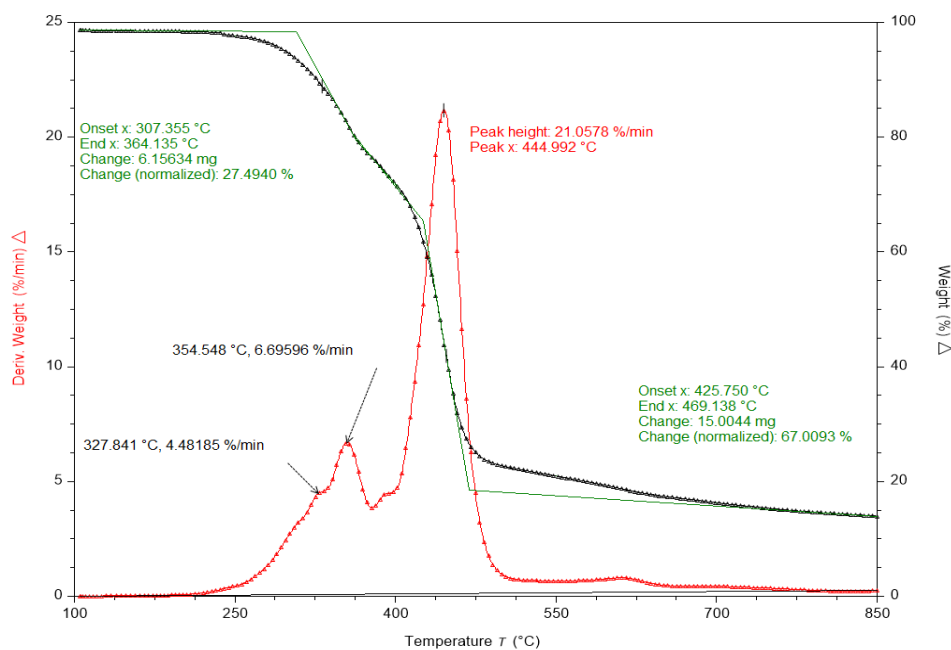
tailored to meet the challenges of a rapidly evolving global landscape.

**Table 5.** Results of modeling for 50% LDPE and 50% Bagasse mixture.

LDEP+Bagasse (1:1)									
R <sup>2</sup>	Residual standard error	c	m <sub>2</sub>	m <sub>1</sub>	n <sub>2</sub>	n <sub>1</sub>	E <sub>a</sub> (kJ/mol)		lnA <sub>1</sub>
							E <sub>a2</sub>	E <sub>a1</sub>	
0.9883	0.0001149	3.407 e-01	5.589 e-01	-e5.595 e-01	9.881 e-01	1.067 e+00	1.567 e+02	1.218 e+02	2.110 e+01
									1.878 e+01

#### Thermal analysis of a mixture containing 50% PET and 50% bagasse

The results of the TGA experiment for the 50% PET and 50% Bagasse mixture are depicted in Figure 6.



**Fig. 6.** The output curve from the TGA device software for the 50% PET and 50% Bagasse mixture with a heating rate of 20°C/min

**Table 6.** Results of modeling for the mixture of 50% PET and 50% Bagasse.

PET+Bagasse (1:1)									
R <sup>2</sup>	Residual standard error	c	m <sub>2</sub>	m <sub>1</sub>	n <sub>2</sub>	n <sub>1</sub>	E <sub>a</sub>		lnA <sub>2</sub>
							E <sub>a2</sub>	E <sub>a1</sub>	
							(kJ/mol)		lnA <sub>1</sub>
0.9909	9.686 e-05	5.138 e-01	3.015 e-01	2.705 e-01	3.000 e+00	1.184 e+00	9.018 e+01	2.105 e+02	1.317 e+01
									3.146 e+01

## Conclusion

The results of this study can be categorized into two parts: experimental and kinetic modeling. Initially, the investigation focused on the pyrolysis behavior, the interaction between materials, and the kinetic of the pyrolysis process using thermogravimetric analysis. A model representing the kinetics of these reactions was developed.

## Results obtained from thermogravimetric analysis

- Thermal decomposition of LDPE occurs in a single stage. In this single stage, approximately 98.3% of the initial sample mass, equivalent to 10.0356 mg, decomposes.

- Based on the DTG curve related to LDPE, it can be observed that it exhibits a peak at 481.5°C. At this temperature, the maximum thermal decomposition rate for LDPE occurs, reaching a maximum rate of 55.4 %/min. additionally, the activation energy of LDPE is calculated as 350 KJ/mol.

- Thermal decomposition of PET also occurs in a single stage. In this single stage, around 85.3% of the initial sample mass, equivalent to 16.9399 mg, decomposes.

- Examining the DTG curve associated with PET reveals a peak occurring at 451.2°C, representing the temperature of maximum thermal decomposition rate for PET. The maximum decomposition rate is 39.4 %/min, and the activation energy of PET is calculated as 264.0329 KJ/mol.

- The thermal decomposition of LDPE and bagasse mixture (1:1) occurs in two stages. In the first stage, approximately 26.3% of the initial sample mass, equivalent to 4.52440 mg, decomposes, while in the second stage, around 63.8% of the initial sample mass, equivalent to 10.9795 mg, decomposes.

- Analyzing the DTG curve related to the LDPE and bagasse mixture (1:1) reveals three peaks occurring at temperatures of 313.8°C, 360.1°C, and 489.1°C. The temperature of 489.1°C corresponds to the highest thermal decomposition rate for the LDPE and bagasse mixture (1:1).

- The thermal decomposition of PET and bagasse mixture (1:1) occurs in two stages. In the first stage, approximately 27.5% of the initial sample mass, equivalent to 6.15634 mg, decomposes, while in the second stage, around 67.1% of the initial sample mass, equivalent to 15.0044 mg, decomposes.

- The DTG curve associated with the PET and bagasse mixture (1:1) displays three peaks occurring at temperatures of 327.8°C, 354.5°C, and 445.0°C. The temperature of 445.0°C corresponds to the highest thermal decomposition rate for the PET and bagasse mixture (1:1).

Based on the comprehensive thermogravimetric analysis (TGA) conducted on low-density polyethylene (LDPE), polyethylene terephthalate (PET), and their respective mixtures with bagasse (at a 1:1 ratio), several significant findings have emerged, elucidating the thermal decomposition behavior of these materials. Notably, LDPE undergoes a singular decomposition stage, during which an overwhelming majority of its initial mass, approximately 98.3%, is lost. This decomposition manifests a peak at 481.5°C, indicative of the temperature at which LDPE experiences its maximum decomposition rate, attaining a notable 55.4 %/min. Additionally, the activation energy calculated for LDPE stands at 350 KJ/mol, highlighting the energy threshold required for its thermal decomposition processes.

In contrast, PET similarly demonstrates a unimodal decomposition profile, wherein approximately 85.3% of its initial mass is lost in a single stage. The peak decomposition rate for PET occurs at 451.2°C, reaching 39.4 %/min, with an associated activation energy of 264.0329 KJ/mol. These distinctive characteristics delineate the thermally induced degradation pathways of LDPE and PET, underscoring their disparate molecular structures and inherent thermal stability.

The introduction of bagasse as a co-component in LDPE and PET mixtures engenders multifaceted

decomposition behaviors, manifesting in two distinct stages. In both LDPE and PET mixtures, the initial decomposition stage accounts for approximately 27.5% to 26.3% of the initial mass, followed by a subsequent stage encompassing 67.1% to 63.8% of the sample mass. The DTG curves for these mixtures exhibit triphasic decomposition patterns, revealing peaks at varying temperatures, reflective of the complex interplay between LDPE or PET and bagasse constituents.

Of particular interest is the emergence of the highest decomposition rates observed at 489.1°C for LDPE and bagasse mixture, and at 445.0°C for PET and bagasse mixture, indicative of the intricate synergistic effects between the polymer matrix and the lignocellulosic component. These findings underscore the importance of understanding the thermomechanical properties of polymer-biomass composites, as they hold significant implications for their processing, utilization, and potential valorization within the realm of sustainable materials science and engineering.

In conclusion, the elucidation of the thermal decomposition characteristics of LDPE, PET, and their mixtures with bagasse through TGA analysis provides invaluable insights into their thermal stability, degradation kinetics, and potential applications in various industrial sectors, ranging from packaging to renewable energy systems. These findings lay a solid foundation for further research endeavors aimed at optimizing the thermal performance and sustainability of polymer-biomass composites, thereby contributing to the advancement of eco-friendly materials and technologies.

### Recommendations for Future Work

1. Conducting experiments at higher temperature rates for the mixtures of agricultural materials and polymers, coupled with the development of a comprehensive model for such blends, constitutes a promising avenue for future investigation. This would entail exploring a wider range of temperature regimes to comprehensively capture the thermal degradation behavior of these complex systems. Additionally, the establishment of a robust mathematical framework would facilitate a deeper understanding of the interplay between the constituent components, thereby enabling more accurate predictions of their thermal responses under diverse processing conditions.

2. Investigating the TG curve behavior of agricultural material-polymer blends and examining the influence of varying blend compositions on their reaction kinetics represent crucial endeavors for

advancing the current understanding of these hybrid materials. A systematic exploration of the TG curves across different blend compositions would elucidate the intricate relationships between the degree of blending and the corresponding reaction rates, shedding light on the optimal formulation parameters for achieving desired thermal performance characteristics.

3. A comparative analysis between the reaction rates obtained from laboratory pyrolysis experiments of bagasse-polymer mixtures and the thermogravimetric analysis results holds significant potential for validating the predictive capabilities of the developed models. By juxtaposing experimental data with theoretical predictions, discrepancies and nuances in the thermal degradation mechanisms can be discerned, thereby refining and calibrating the predictive models to enhance their accuracy and reliability.

4. The development of alternative kinetic modeling approaches for estimating the production rates of pyrolysis products and their subsequent comparison with the developed methodologies for multi-component mixtures represents a frontier for advancing the field of thermal degradation kinetics. By exploring diverse kinetic models tailored to the specific intricacies of polymer-biomass blends, a more nuanced understanding of the underlying reaction mechanisms can be attained, paving the way for enhanced predictive capabilities and informed decision-making in the design and optimization of thermal conversion processes.

In essence, the proposed avenues for future research endeavor to deepen our understanding of the thermal behavior and reaction kinetics of polymer-agricultural material mixtures, with the ultimate goal of advancing sustainable materials science and engineering practices. Through meticulous experimentation, theoretical modeling, and interdisciplinary collaboration, these endeavors aim to foster innovation and propel the development of eco-friendly materials and technologies for a more sustainable future.

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