# Kinetic Studies of Effects of Heat on PET Plastics: TGA, DTA, XRD and DSC Analysis

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*Authors' contributions*

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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## ABSTRACT

In this work, the effects of heat on plastic waste (PET plastic bottles) were investigated. During thermogravimetric analysis, the kinetics of the PET pyrolysis was studied using a combination of model-fitting and model-free methods. About 12mg of the grinded PET sample was weighed into the ceramic crucible and then heated from temperature of 30 °C to 950 °C at two heating rates of 10°C/min and 20°C /min. Thermogravimetric analysis indicated that the decomposition of plastic waste in a Nitrogen atmosphere can be divided into three stages: the minor loss stage (100°C), the major loss stage (450–520°C) and the stable loss stage (500–900°C). The corresponding weight loss at two different heating rates of 10°C/min and 20°C /min were determined to of 70% and 77.7% respectively. Based on $R^2$ (regression coefficient) values, heating rate of 20°C/min gave the values (0.9279) for the model free method employed (KAS model). When compared to the model fitting, 0.75[th] order of reaction gave the closest $R^2$ value (0.9643) which also translated to a very close Activation energies of 264 KJ/mol and 255 KJ/mol respectively. All in all, it can be deduced that the activation energy of PET pyrolysis falls within 250 – 280 KJ/mol based on this study. Also, X-Ray

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Diffraction and Differential Scanning Calorimetry analysis were carried out. The narrow and high nature of the XRD peaks depicted that the sample is crystalline. And lastly, DSC analysis investigated the heat flowing in and out of the PET sample. The exodermal (where cold re-crystallization occurred) and endothermal (where melting occur) peaks were recorded as 165$^o$C and 138$^o$C respectively. It is recommended that other model-free and model-fitting methods should be invested in further research in order to generate a wide range of data for kinetics of PET.

## 1. INTRODUCTION

"Plastic has played a vital role in enhancing human living standards for more than 50 years. It is important for the innovation of many products across a range of industries, including packaging, electronics, automotive, healthcare, and construction. Because of the world population's rapid growth, there is a greater demand for commodity plastics, and this has made global production of plastic reach about 299 million tons in 2013, which has increased by 4% over 2012. The continuous rise in plastic demand and its production led to an increase in waste accumulation every year. According to 2013 statistics, the US produced 33 million tons of plastic waste, and in Europe, 25 million tons of plastic entered the waste stream in 2012" [1].

"In most cases, landfills or incinerators have been used to dispose of plastic waste. Landfilling plastic waste is not a solution, mainly because it is more difficult to find sites that are technically suitable for constructing landfills due to the local population's resistance. Incineration of plastic waste to produce heat may be possible for disposing of plastic, but its organic content would be destroyed and converted only into carbon dioxide and water. Additionally, depending on its nature, combustion may produce toxins such as light hydrocarbons, nitrous and sulfur oxides, dust, dioxins, and other substances that have a severe negative impact on the environment" [2]. Goals number 7 (Affordable and Clean Energy), 11 (Sustainable Cities and Communities) and 12 (Responsible Consumption and Production) of the UN Sustainable Development Goal [3] are being addressed in this research. Plastic is a non-biodegradable polymer and therefore, studying the kinetics involved in its pyrolysis helps to optimize the process.

"Models provide insights into how particular polymers are transformed into smaller molecules and then reassembled into new materials. This kind of modeling involves data on broad kinetic processes and detailed data on specific, sometimes microscopic reactions" [4]. "There are two significant types of kinetic modeling methods: model-fitting and model-free, which are employed for the study of the decomposition of solids. Model-fitting methods are frequently used because they directly determine the kinetic parameters and reveal information about the reaction mechanisms. Different reaction models have been proposed, and kinetic parameters can be determined based on these models. The model-free method enables the kinetic parameters to be calculated as a function of the degree of conversion while making no prior assumptions about the reaction model. Different model-free methods, such as the Friedman, the Flynn-Wall-Ozawa (FWO), the Kissinger-Akahira-Sunose (KAS), and the Tang methods, have been proposed and used for the kinetic study of solid materials" [5].

## 2. METHODOLOGY

### 2.1 Materials

The measurement of the kinetic parameters during the pyrolysis of plastic waste was carried out using materials like waste plastic drink bottles (PET sample), reagents like Nitrogen and Potassium Bromide. The instruments used during the analysis are analytical weighing balance, Fourier Transform Infrared Spectrophotometer, Differential Scanning Calorimeter, X-Ray Diffractometer, Thermogravimetric Analyzer.

### 2.2 Sample Preparation

The PET sample (plastic drink bottles) was gathered from the Tanke Community dumping site in Ilorin. Then the sample was washed with deionized water to prevent ion contamination from ordinary or distilled water. The washed sample was then dried and finally crushed down into small particles using plastic granulator and sieved in the range of less than 100 μm to obtain

homogenous sample and to avoid mass and heat transfer limitations during the kinetic modelling and pyrolysis tests.

## 2.3 Spectroscopic Analysis of PET Sample

### 2.3.1 Thermogravimetric analysis (TGA)

Approximately 12.257 mg of the plastic sample (PET) was placed on the ceramic crucibles and heated from 30 °C to 950 °C under a Nitrogen gas flow of 50 mL/min. The tests were repeated at different heating rates of 10 °C/min and 20 °C/min. The sample weight and temperature changes during the thermal process were recorded to obtain the TG and derivative thermogravimetric (DTG) profiles

### 2.3.2 Differential scanning calorimetry

After the differential scanning calorimeter (heat flux Chip-DSC 1) was calibrated, 3 mg of the plastic sample was weighed using an analytical balance. The weighed sample was introduced gently into the DSC pan and covered securely. The sample pan was then loaded into the DSC instrument, and the heating rate was set at 20°C/min. Then, the heat flow as a function of temperature was measured and recorded. The result obtained was used to prepare and analyze the DSC curve.

### 2.3.3 X-ray diffractometry

2 mg of the powdered plastic sample (PET) was mounted on a sample holder. The XRD measurement was started, and the diffraction angles (2θ) over the range of 5° - 80° were scanned. The recording of the XRD pattern and identification of the crystalline phases present in the plastic sample were carried out. Lastly, the changes in the XRD pattern, such as peak shifting or intensity variations, during pyrolysis were monitored.

### 2.3.4 Kinetic modeling

Kinetic models consist of mathematical tools that give better understanding of mechanisms of a reaction. The model-fitting method and the model-free method are the two main approaches used to study the breakdown of solids. Model-fitting techniques are frequently used because they can directly determine the kinetic parameters and provide details on potential reaction mechanisms. The model fitting (Coats-Redfern model) and the model-free (Kissinger-Akhaira-Sunose model) methods used in this study is summarized in Table 1.

## 3. RESULTS AND DISCUSSION

### 3.1 DSC Analysis of PET

Differential Scanning Calorimetry (DSC) analysis measures physical and chemical changes within a material in response to temperature. It gives information about the change in heat capacity. The Figures below (Fig. 3a, 3b and 3c) show different peaks corresponding to the physical changes or phase transitions of the PET plastic. Fig. 3a and 3b are curves showing the variations of heat flow with temperature and time respectively. The area under the curve corresponds to the enthalpies of transition.

From Fig. 1a, the glass temperature (Tg) of the PET is around 131.5°C. This temperature is where transition of the sample (PET plastic) from a hard, glassy material to a soft, rubbery material occur. Pure PETs are thought to have glass temperature between the range of 75°C to 85°C. However, the higher glass temperature recorded for the PET sample in this experiment may be due to increased chemical cross linking or presence of polar groups. The endothermic temperature which is equivalent to the melting temperature of the PET was observed at around temperature of 138°C as seen from Fig. 1b. The melting of the PET occurred at around 9mins after the heating commenced and it is the point of the lowest heat flow as seen in Fig. 1c. This value is in agreement with that reported by Focus (2018) which was 240°C. This melting temperature describes the crystallinity of the PET sample. There are also less strong endothermal peaks observed around 245°C and 262°C. These less strong peaks are reported in K. Chen *et al.* (2021) work, to be due to the lamella structure and thickness, caused by different crystallization processes such as the primary and secondary crystallization.

The exothermal peak shows the cold crystallization temperature of the PET at around 165°C as seen in Fig. 3b. This occurred at around 4mins as seen Fig. 3c and it is the point of highest heat flow. The area under the exothermal peak if estimated, would give the heat of cold crystallization. This heat is the amount of energy released as the PET sample cooled and re-crystallized.

**Table 1. Kinetic model equations**

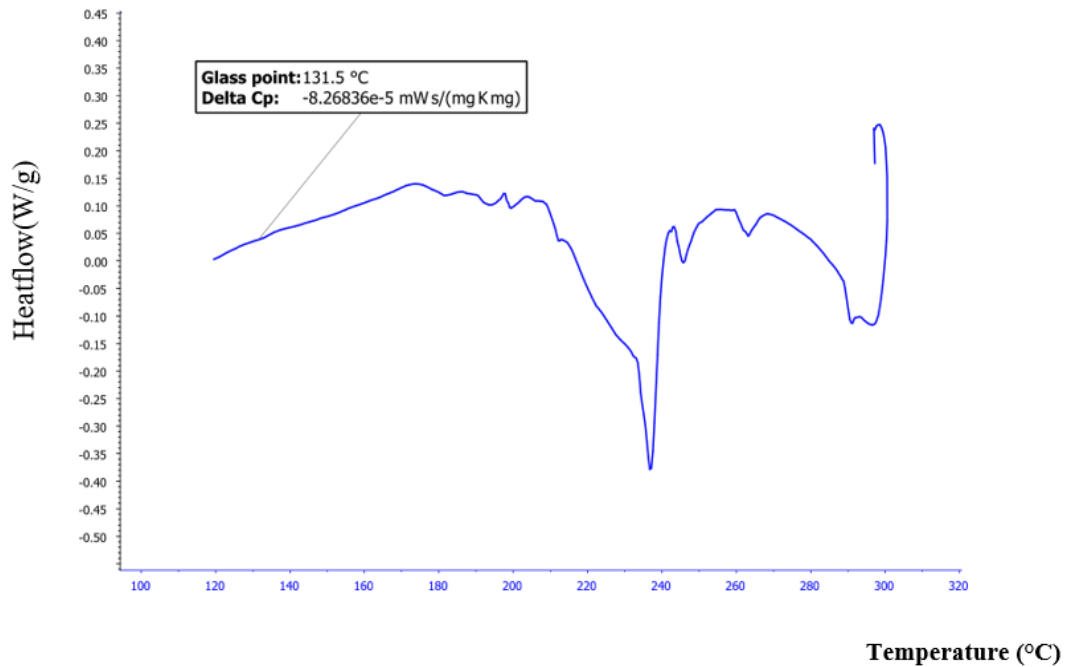| Techniques | Kinetic models | Equations |
|---|---|---|
| Model-Fitting | Coats-Redfern (CR), 1964 | $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT$ |
| Model-Free | Kissinger-Akahira-Sunose (KAS), 1971 | $\ln\frac{\beta}{T^2} = \ln\frac{AR}{E_a g(\alpha)} - \frac{E_a}{RT}$ |



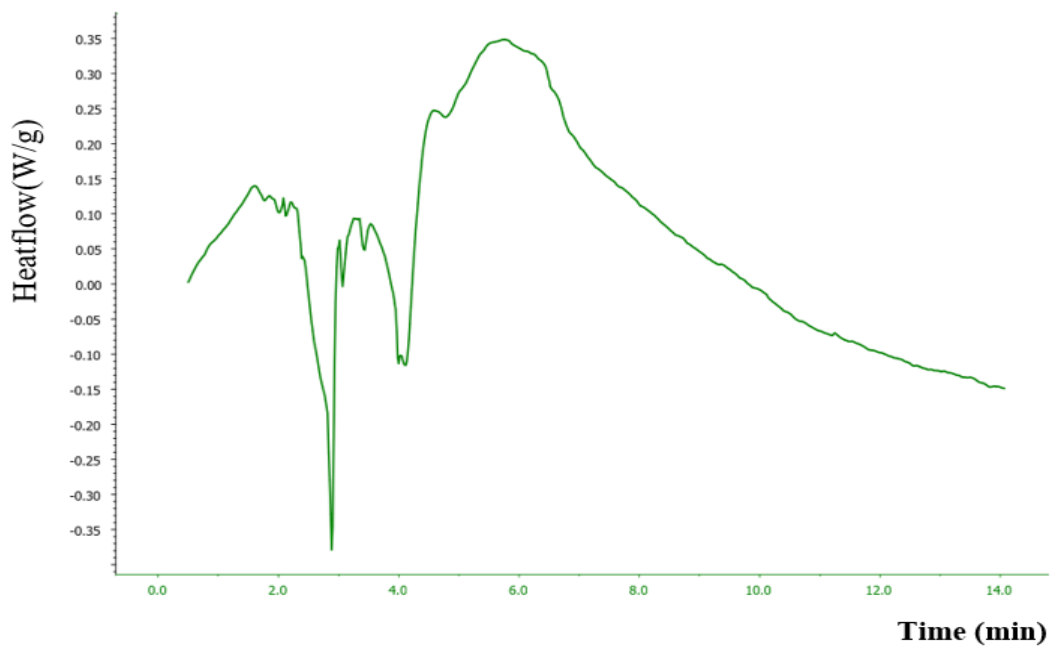**Fig. 1a. Thermograph of heat flow against temperature**
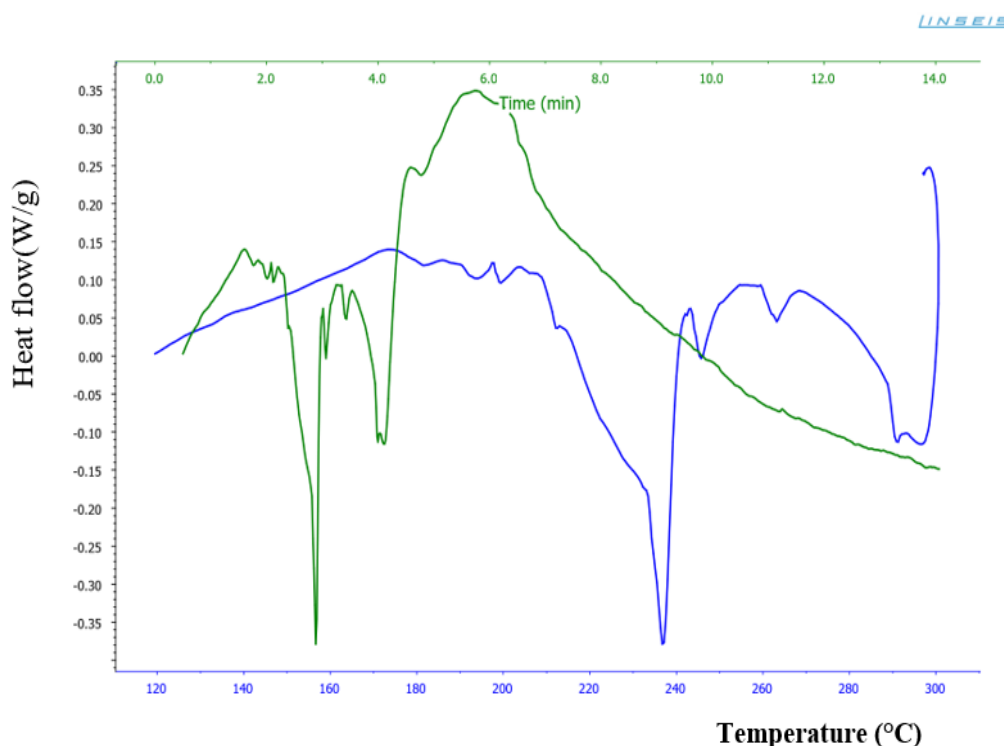


**Fig. 1b. Thermograph of heat flow against time**

**Fig. 1c. Thermograph of heat flow against time and temperature**

## 3.2 XRD Analysis of PET

According to Libretexts [6] X-ray diffraction is a common technique that determine a sample's composition or crystalline structure. It sends x-ray beams through the sample and the X-ray beams are chosen because their wavelength is similar to the spacing between atoms in the sample.  So, the angle of diffraction will be affected by the spacing of the atoms in the molecule, as opposed to using much larger wavelengths, which would be unaltered by the spacing between atoms. Fig. 2 is the X-ray diffractogram of the PET sample and it is the plot of intensity of the intensity of the signal for various angles of diffraction at their respective two theta positions.

The thinner nature of the Peaks in the Fig. 2 shows that the PET sample is crystalline. This is in agreement with the report made in Libretexts [6] that a thinner peak corresponds to a bigger crystal. The peak at 2θ corresponding to about $17^o$ (17 degree) shows that there is more concentration of crystals at the region. This means that the greater the intensity of the peak, the greater the amounts of crystals. The numbers 111, 200, 220, 311 and 222 are called Miller indices (hkl) and they describe the orientation of

crystalline planes in a material. Therefore, the XRD diffractogram of PET in Fig. 2 with peaks at 111, 200, 220, 311, and 222 indicates the presence of different crystallographic planes within the PET crystal lattice, providing valuable information about the PET's crystalline structure and orientation.

## 3.3 Kinetic Studies Using TGA DATA

### 3.3.1 TGA and DTA analysis

"In general, a thermogravimetric analysis (TGA) is used to study mass decomposition and kinetics over the pyrolysis of the solid materials including coal and plastic. It plays a role in the determination of mass decomposition of the material linear to time and temperature. The kinetic parameters of this reaction are obtained by applying the Arrhenius law equation" [7]. The knowledge of the kinetics of the thermal decomposition of the plastic waste feedstock is essential for further design of the pyrolysis systems and their conversion mechanisms.

"The weight loss curve (TG) (Fig. 3.a and b) shows the loss of mass with temperature from 30 to 900°C at 10°C/min and 20°C/min heating rate respectively for all plastics types used in this study (PET). The plot shows that PET exhibits

similar temperature behavior and have same shape of the decomposition curves with other plastic types. TGA curves can be broken down into three parts. First part shows dehydration (moisture evaporation), second part shows the maximum devolatilization which is the active stage and the third part is continuous slight devolatilization which usually have higher percentage of solid residue. The DTG curve (Fig. 3a and b) is the first derivation of the TG curve and it shows the mass change per time along the temperature program.

For PET plastic waste in this analysis, the maximum degradation was achieved within 450–520$^o$C (Fig. 3a and b) with single step decomposition. Single step decomposition indicates the presence of carbon-carbon bond that promotes the random scission mechanism with an increase in temperature" [8].

"PET has a cyclic structure, and its maximum weight loss degradation under the thermal condition involves both random chain and end-chain scission which enhances the process" [8]. The initial decomposition started at 100 °C and reached its maximum decomposition point of 77.4% at 884°C (Fig. 3a). "From literature, it can be observed that PET did not fully decomposes which agrees with this study however, slight

variation may be due additives added in the preparation of the polymer. The optimum temperature for conversion of PET plastic waste into liquid via pyrolysis is 480°C this is because additional increase of temperature from 500°C to 700°C resulted in 0.6% weight loss. Similar phenomenon can be observed in the DTG curve (Fig. 4) where an endothermal peak is attributed to the decomposition of PET plastic. Although previous studies reported that PET starts to decompose at temperatures varying from 190, 252 and 400$^o$C which is dependent on the polymer grade and experimental set-up" [8]. "In PET thermal degradation process, the initial step is the scission of the chain of the ester linkage either through random scission at the ester linkages or through chain ends leading to a reduction in molecular weight and an increase in carboxyl end-groups" [9]. At 500$^o$C the sample has lost 65.6% of its initial weight. The maximum degradation for PET was 70%. Saha and Ghoshal, [10] studied "the pyrolysis kinetics of two PET samples under non-isothermal conditions and it was reported that both samples exhibited 70-80% weight loss between 380-515$^o$C; this was attributed to the slower heating rates used in their study (10, 15 and 25$^o$C min-1). The DTG indicates a single step reaction with melting peak at 474$^o$C. The optimum temperature for pyrolysis is 474$^o$C".
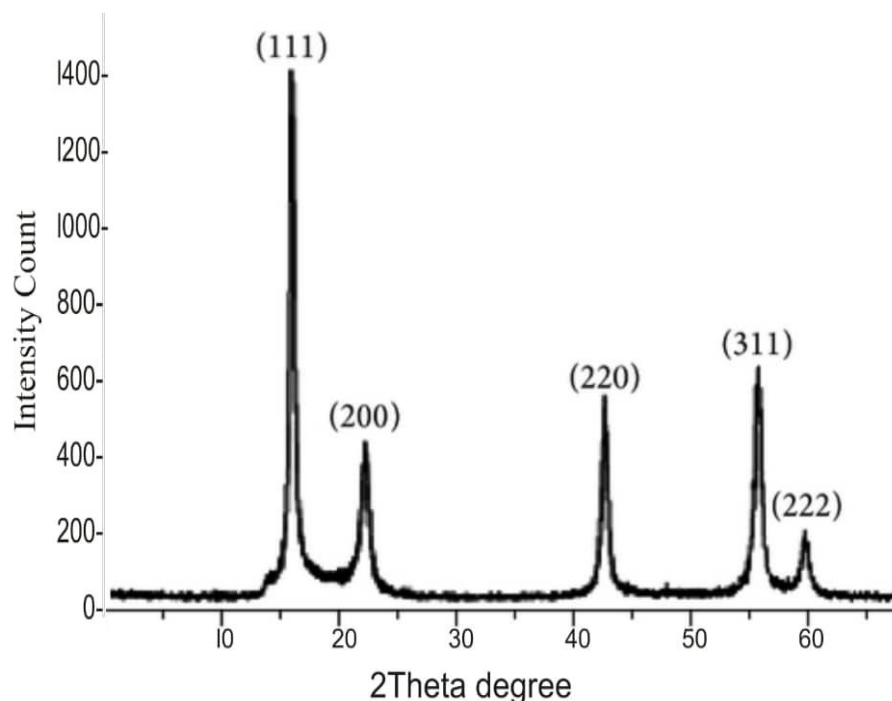


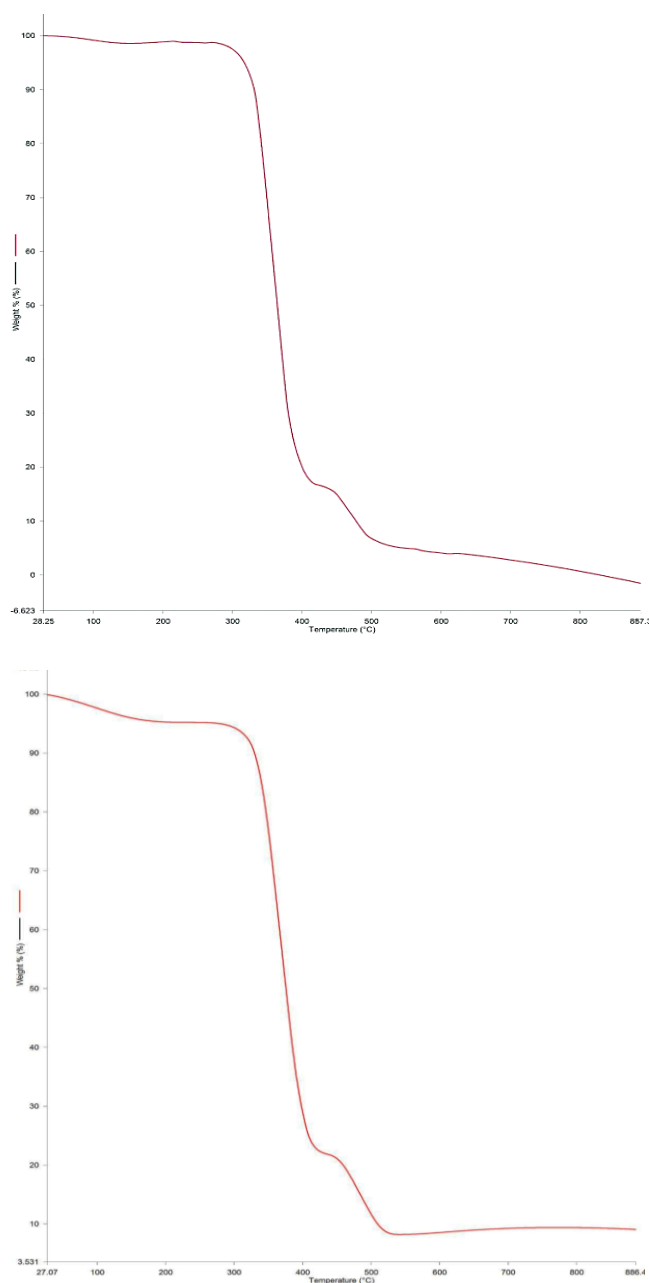**Fig. 2. X-Ray Diffractogram of PET**

**Fig. 3. TGA of PET at heating rate of (a) 10 °C/min from 30°C to 900°C (b) 20°C/min from 30°C to 900°C**

### 3.3.2 Kinetic parameters using model free and model fitting methods

In this study, one model free method (KAS model) was compared with one model fitting method (Coats and Redfern model) using assumed reactions orders of n = 0.25, 0.5, 0.75 and 1 investing TGA data from both heating rates considered. Fig. 6a, 5b. are the KAS model free at 10°C/min, CR model fitting at nth orders (0.25, 0.5, 0.75 and 1) at 10°C/min, KAS model free at

20°C/min and CR model fitting at nth orders (0.25, 0.5, 0.75 and 1) at 20°C/min. The slope of each plot was utilized in calculating the activation energy corresponding to that model.

Table 2 compares calculated Activation Energies from the models in Fig. 5–6. Based on $R^2$ (regression coefficient) values, heating rate of 20°C/min gave the values (0.9279) for the model free method employed (KAS model). When compared to the model fitting, 0.75th order of

reaction gave the closest $R^2$ value (0.9643) which also translated to a very close Activation energies of 264 KJ/mol and 255 KJ/mol respectively.

All in all, it can be deduced that the activation energy of PET pyrolysis falls within 250 – 280 KJ/mol based on this study.
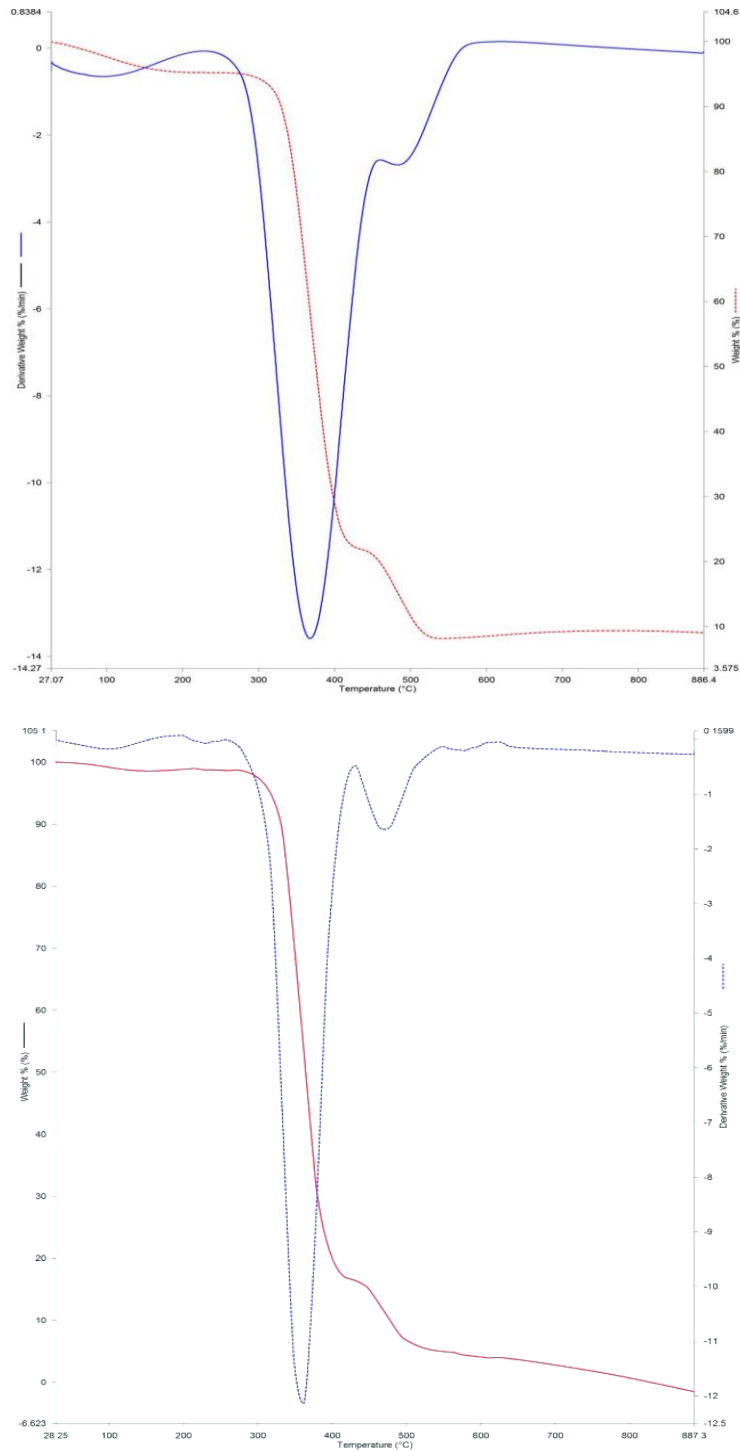


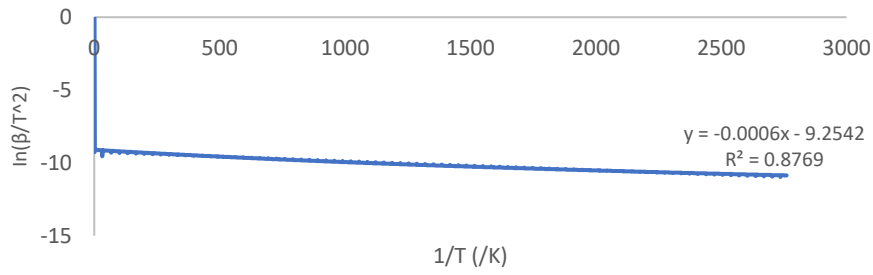**Fig. 4. DTG of PET at heating rate of (a) 10 °C/min from 30°C to 900°C (b) 20°C/min from 30°C to 900 °C**
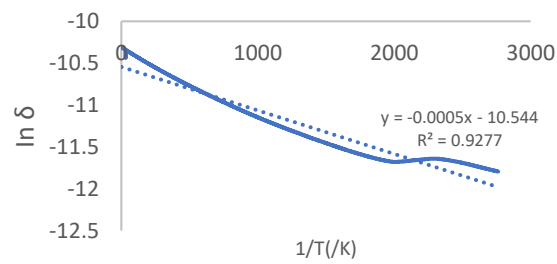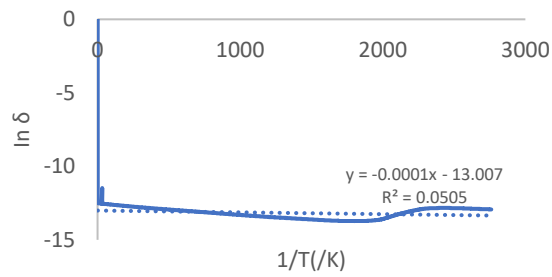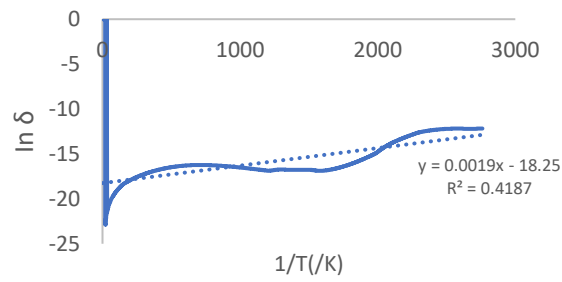
**Fig. 5a. KAS model free of PET at 10°C/min**
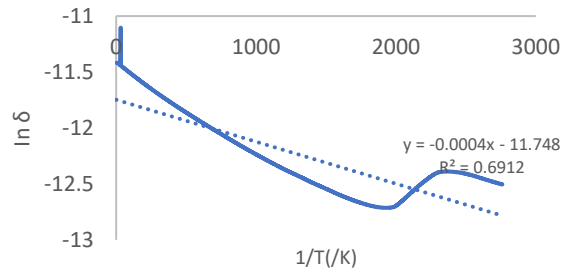
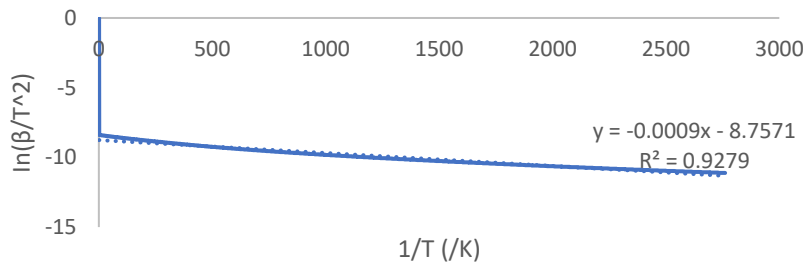**Fig. 5b. CR Model fitting of PET at 10 °C /min for n = 0.25, 0.5, 0.75 and 1**
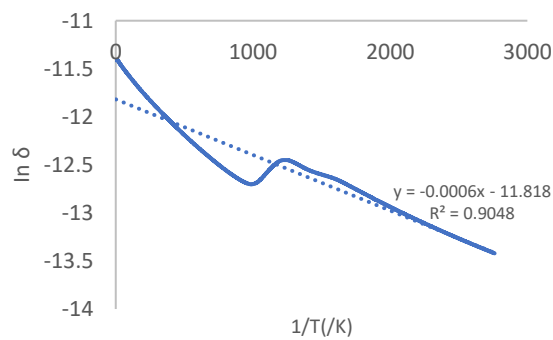


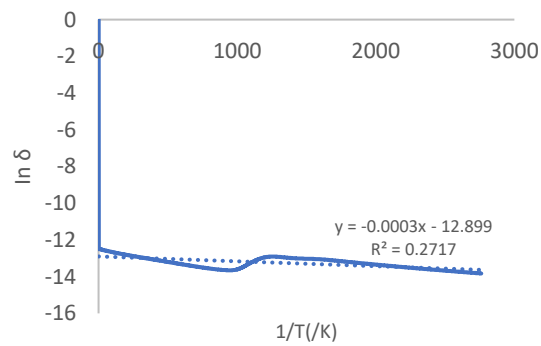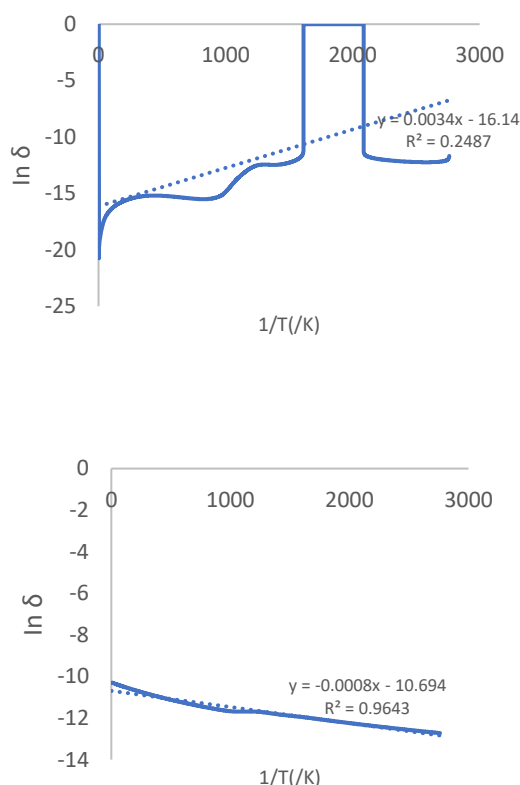**Fig. 6a. KAS model-free of PET at 20°C/min**

**Fig. 6b. CR Model-fitting of PET at 20 °C /min for n = 0.25, 0.5, 0.75 and 1**

**Table 2. KAS and CR Model Kinetic Parameters of Pyrolysis of PET plastic**

| Model | Heating Rate (°C/min) | Assumed order (n) | $R^2$ – value | Calculated Activation Energies (KJ/mol) |
|---|---|---|---|---|
| Model Free (KAS Model) | 10 | - | 0.8769 | 276.80 |
| | 20 | - | 0.9279 | 264.30 |
| Model Fitting (CR Model) | 10 | 0.25 | 0.0505 | 453.2 |
| | | 0.5 | 0.6912 | 352.0 |
| | | 0.75 | 0.9277 | 275.3 |
| | | 1 | 0.4187 | 108.3 |
| | 20 | 0.25 | 0.2717 | 500.2 |
| | | 0.5 | 0.9048 | 250.1 |
| | | 0.75 | 0.9643 | 255.0 |
| | | 1 | 0.2487 | 589.2 |

## 4. CONCLUSIONS

In this research, the kinetics studies of effects of heat on the PET sample was carried out. The TG analysis revealed that the decomposition process can be divided into three stages with corresponding weight losses of 2.80–3.02%, 77.4% and 0.6%, respectively. The maximum peak temperatures were observed at 423, 433 for two heating rates in the second stage. Based on the TG analysis, the activation energy and linear correlation coefficient ($R^2$) were determined at different conversion rates using one model-free method (KAS model) and one model-fitting method (CR model). Based on $R^2$ (regression coefficient) values, heating rate of 20 °C/min gave the values (0.9279) for the model free method employed (KAS model). When compared to the model fitting, 0.75th order of reaction gave the closest $R^2$ value (0.9643)

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which also translated to a very close Activation energies of 264 KJ/mol and 255 KJ/mol respectively. All in all, it can be deduced that the activation energy of PET pyrolysis falls within 250 – 280 KJ/mol based on this study. To also investigate the structure, composition and thermal behavior of the PET sample, X-Ray Diffraction and Differential Scanning Calorimetry analysis were carried out. PET being an organic polymer. The narrow and high nature of the XRD peaks depicted that the sample is crystalline. And lastly, DSC analysis investigated the heat flowing in and out of the PET sample. The exodermal (where cold re-crystallization occurred) and endothermal (where melting occur) peaks were recorded as 165 $^o$C and 138 $^o$C respectively.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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