emissions monitoring

Ahmed I. Osman a,b*, Charlie Farrell c,d, Ala'a H. Al-Muhtaseb e, Ahmed S. Al-Fatesh f, John Harrison c, David W. Rooney a

a School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9 5AG, Northern Ireland, UK.

b Chemistry Department, Faculty of Science, South Valley University, Qena 83523 – Egypt.

c South West College, Cookstown, Co. Tyrone, BT80 8DN, Northern Ireland, UK.

d School of Mechanical and Aerospace Engineering, Queen’s University Belfast, Belfast BT9 5AH, Northern Ireland, UK.

e Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman.

f Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia.

Corresponding Author: Ahmed Osman

Email: aosmanahmed01@qub.ac.uk

Address: School of Chemistry and Chemical Engineering, Queen’s University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, United Kingdom

Fax: +44 2890 97 4687

Tel.: +44 2890 97 4412
Abstract

Background:
Recycling the ever-increasing plastic waste has become an urgent global concern. One of the most convenient methods for plastic recycling is pyrolysis, owing to its environmentally friendly nature and its intrinsic properties. Understanding the pyrolysis process and the degradation mechanism is crucial for scale-up and reactor design. Therefore, we studied kinetic modelling of the pyrolysis process for one of the most common plastics, polyethylene terephthalate (PET). The focus was to better understand and predict PET pyrolysis when transitioning to a low carbon economy and adhering to environmental and governmental legislation. This work aims at presenting for the first time, the kinetic triplet (activation energy, pre-exponential constant and reaction rate) for the PET pyrolysis using the differential iso-conversional method. This is coupled with the in-situ online tracking of the gaseous emissions using mass spectrometry.

Results:
The differential iso-conversional method showed activation energy (E_a) values of 165-195 kJ.mol^{-1}, R^2 = 0.99659. While the ASTM-E698 showed 165.6 kJ.mol^{-1} and integral methods such as Flynn-Wall and Ozawa (FWO) (166-180 kJ.mol^{-1}). The in-situ Mass Spectrometry results showed the pyrolysis gaseous emissions which are C_1-hydrocarbon and H-O-C=O along with C_2 hydrocarbons, C_5- C_6 hydrocarbons, acetaldehyde, the fragment of O-CH=CH_2, hydrogen and water.

Conclusions:
The kinetic triplet along with the in-situ monitoring of the gaseous emissions of PET pyrolysis can benefit in the process modelling of this system to help better understand the process at scale. This ultimately aids in reactor optimization and design at scale, as it gives a better insight into the reaction mechanism. This can be used by plastic recyclers worldwide and the predictions made in this study can be used to determine how the rate of reaction changes based on temperature and heating rate beyond experimental results both isothermally, non-isothermally and in stepwise heating regimes.

Keywords:
Kinetic modelling, Plastic waste, Pyrolysis, Polyethylene terephthalate, Gaseous emissions, Plastic recycling
**Background**

Over nine billion tonnes of plastic have been produced globally since the 1940s, with an annual growth rate of 8.7% [1]. Plastic materials are subdivided into seven different types and fulfil different purposes in our daily life such as in electronics, construction materials, agriculture, household items and packaging films. The widespread use is due to their intrinsic properties i.e. chemical inertness, mechanical, pressure resistance, durability, versatility, flexibility, cheap production cost, along with the thermal stability from the additives and stabilisers used in the production phase [2]. Over the last 60 years, consumer plastic use has increased by approximately 20 times, where the annual production has dramatically increased from 15 million tonnes (Mt) in 1964, to 335 Mt in 2016, and is expected to reach 1124 Mt by the year 2050 [3, 4]. The annual consumption of water bottles alone has reached 500 billion units globally [5]. However, the disposal rate of these plastic debris has risen, making a huge negative impact on the environment as well as public human health. The plastic waste generated in 2015 was 6300 Mt, where only 9% has been recycled, 12% incinerated and the rest have been sent to landfills (79%) [6]. In the next five years, the plastic waste production rate will reach 220 Mt per annum, with its end-of-life destination deemed to be mainly in the sediment, biota and aquatic ecosystem such as oceans and rivers (micro-plastic (<5mm), nanoplastic (<1.2 μm)), [7] where the complete degradation of its polymers could take centuries. Furthermore, direct burning of those plastic wastes generates hazardous emissions along with chemicals such as phosgene, dioxins, and carbon monoxide that are linked to human cancers and endocrine disruption [8, 9]. However, it is possible to add additional value to this waste through processes such as pyrolysis, solvent dissolution, gasification and other valorisation approaches whilst promoting the circular economy [10]. Recently, the concept of waste-to-energy has gained great attention for this particular problematic feedstock to use the waste as energy carrier materials [11-14]. Closed-loop recycling refers to a product that is
recycled into another, near-identical product with similar value, whereas open-loop recycling means a product is converted into a new type of product and usually of lesser quality [15, 16]. There are mainly four different technologies in dealing with plastic waste management which are: re-extrusion that requires semi-clean plastic scrap, along with mechanical (physical), chemical (solvolysis and pyrolysis) and energy recovery (incineration) [2, 17, 18].

Various valorisation routes have been studied for hydrogen production via pyrolysis/reforming of plastic polymers, where different factors were reported such as temperature, residence time and steam/plastic ratio [19]. The most common polymers studied are polyethylene terephthalate (PET), High-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS), where the pyrolysis and reforming conditions were around 500 and 700°C, respectively. Nearly half of the total plastic market globally comes from PE (polyethylene) and PET with a contribution of 40% [20] in various sectors such as agriculture, drinking water bottles, food packaging and constructional materials. Thermoplastics account for 80% of the total plastic consumption [2]. PET (\(C_{10}H_{8}O_4\)) is the most abundant thermoplastic due to its characteristics to exist in different forms such as a one-dimensional fibre, 2D-films and 3D-bottles and containers [21, 22]. It is the third-most consumed polymer in Europe after PP and LDPE, and the most widely used plastic in the packaging industry [23-25]. The global consumption and demand for PET reached 60 Mt by 2011 and is increasing by 4.5% each year [26]. It has been reported in the literature that PET plastic material has a similar energy content than that of soft coal, with a higher heating value of 46.2 MJ.kg\(^{-1}\) and ultimate elemental analysis of >45 wt.% carbon, 36 wt.% hydrogen and 18 wt.% oxygen [16, 23, 27]. Most of those PET and plastic waste materials, in general, are non-biodegradable and their end-of-life destination is landfill or incineration. There is also another challenge that faces the recycling of these problematic materials, which is the difficulty of the selective and effective separation of the plastic mixture.
For instance, a standard PET bottle contains about 10-15 wt.% PE in the form of printed labels and cups, where their separation is usually difficult [20].

One of the most convenient methods for plastic recycling is pyrolysis owing to its environmentally friendly nature. The pyrolysis of addition polymers gains more attention recently, due to its competence for the recovery of monomers along with the production of fuel with low pollutant emissions [19]. Furthermore, unlike other recycling processes such as mechanical and chemicals methods, pyrolysis is a flexible process where plastic waste could be treated alongside municipal solid waste such as e-waste, biomass and others [28]. Interestingly, only 5% of the energy content of the plastic waste is being used in the endothermic cracking process, which in the case of PET is 214 kJ.kg$^{-1}$, which is 5% of its energy content (1440 kJ.kg$^{-1}$.°C$^{-1}$) [29]. The pyrolytic products of plastic are oil (22-49%), gases (18-30%), and solid char (30-50%); where different operating parameters could affect the process and product composition (plastic-type, residence time, pyrolytic temperature, ramping rate and reactor type) [29]. As the operating parameters can shift the product composition and alter the reaction pathway, it is important to use kinetic modelling to help describe the reaction mechanism during the thermal cracking of plastic polymers. During the pyrolysis process, two main reactions occur: cracking which breaks down the carbon chain and the charring reaction which aids to re-build up higher molecular weight products [30]. For instance, polyolefins (PP and HDPE) are composed of a saturated hydrocarbon chain, where the thermal decomposition takes place randomly by radical scission mechanism [19, 31]. However, due to the aromatic nature of PS, it decomposes into styrene monomers (70.6 wt.%), oligomers and other secondary aromatic products. On the other hand, PET is composed of terephthalic acid and ethylene glycol monomers, thus upon pyrolysis, various oxygenates and aromatics products are produced. The pyrolysis residue in the case of polyolefins was negligible, unlike PET that showed a value of 7 wt.% residue [19]. Barbarias et al. reported
that the main PET pyrolysis fraction was a gaseous stream (CO and CO\textsubscript{2}), with a product yield of 42.8 wt\%, along with 37.4 wt.% for the solid residue (benzoic and benzoyl formic acid) and 12.8 wt.% for oil fraction.

Ganeshan et al. [32] in their attempt to understand the PET pyrolysis process via kinetic modelling, used Coats–Redfern method that assumes the reaction is first order. They reported activation energies (E\textsubscript{a}) value in the range of 133-251 kJ.mol\textsuperscript{-1}, however, the value of R\textsuperscript{2} was low (<0.8). Thus, they concluded that the Coats–Redfern method is not always suitable for calculating the kinetic parameters. Mishra et al.[33] studied kinetic modelling approaches (Coats-Redfern method, Kissinger-Akahira-Sunose, Flynn-Wall and Ozawa method, Friedman method and Starink) for the co-pyrolysis of PET with biomass seeds. The KAS method of PET pyrolysis showed variation in the E\textsubscript{a} value from 210-241 kJ.mol\textsuperscript{-1} within reaction progress \(\alpha = 0.1-0.8\), where the average E\textsubscript{a} was 230.7 kJ.mol\textsuperscript{-1}. Under the same conditions, the FWO and Starink methods showed similar variation in the E\textsubscript{a} value from 211-241 kJ.mol\textsuperscript{-1} and 211-242 kJ.mol\textsuperscript{-1}, respectively with an E\textsubscript{a} average of 230.5 and 231.0 kJ.mol\textsuperscript{-1}. The Friedman method showed slightly lower variation in values under the same conditions with 208.6-236 kJ.mol\textsuperscript{-1} and an average E\textsubscript{a} of 225.6 kJ.mol\textsuperscript{-1}. They performed the kinetic modelling based on three heating rates of 10, 30 and 50 °C.min\textsuperscript{-1}, while for reliable evaluation of the kinetic parameters, it should be at low heating rates of less than 8 °C.min\textsuperscript{-1} (with a ratio between the lowest and the highest heating rate of >10) with four or five heating rates [34]. Das and Tiwari [21] measured the kinetic parameters for PET pyrolysis at high heating rates of 5, 10, 20, 40 and 50 °C.min\textsuperscript{-1} using the iso-conversional method. They reported E\textsubscript{a} values in the range of 196-217 kJ.mol\textsuperscript{-1}. Al-asadi and Miskolczi measured the emissions related to the uncatalyzed along with Ni/zeolite catalytic pyrolysis of PET but only at a high-temperature range of 600-900 °C [20]. To the best of the authors’ knowledge, this is the first detailed study in measuring and evaluating the kinetic triplet of PET plastic pyrolysis with the use of Advanced Kinetics and Technology Solutions
(AKTS) software. This work aims at presenting for the first time, the kinetic triplet (activation energy, pre-exponential constant and the rate of reaction) for the PET pyrolysis using the differential iso-conversional method. This is coupled with the *in-situ* online tracking of the gaseous emissions using mass spectrometry, as there are few and limited studies on oxygenated macromolecules such as PET in the literature [23, 25]. The kinetic triplet can benefit in process modelling systems to help better understand the process at scale, as these values are not influenced based on scale. This ultimately aids in reactor optimization and design at scale as it gives a better insight into the reaction mechanism. This can be used by plastic recyclers worldwide and the predictions made here can be used to determine how the rate of reaction changes based on temperature and heating rate beyond experimental results using isothermal, non-isothermal and stepwise heating regimes.

**Material and methods**

*Sample preparation and In-situ gaseous emission detection using Mass Spectrometry*

The PET sample was collected from used water bottles, then washed with deionized water, dried and finally crushed down into a form of small particles and sieved in the range of less than 100 µm to avoid the mass and heat transfer limitations during the kinetic modelling and pyrolysis tests as shown in Figure S1. The PET pyrolysis was performed in a fixed bed reactor, where the output of the reactor is coupled and attached to a mass spectrometer (MS) through a heated quartz capillary tube. To prevent any condensation, dissolution or adsorption on the tube wall, all the lines were heated to 150 °C, where the evolved gas mixtures were then directly fed to the mass spectrometer. The MS (Hiden Analytical instrument) was performed under vacuum and the rapid *in-situ* detection of the characteristic fragment ion intensity of the associated gaseous emissions such as hydrocarbons and other related emissions including characteristic ion species according to its mass to charge ratio (*m/z*) such as *m/z* = 15 (C₁ hydrocarbons), *m/z* = 27 (C₂ hydrocarbons), *m/z* = 42 (C₃ hydrocarbons), *m/z* = 78 (C₆ hydrocarbons), *m/z* = 84
(Krypton), \( m/z = 43 \) (acetic acid), \( m/z = 44 \) (acetaldehyde or carbon dioxide), \( m/z = 2 \) (hydrogen), \( m/z = 45 \) (CHO$_2$), \( m/z = 18 \) (water) and \( m/z = 29 \) (acetaldehyde).

**Kinetic modelling of PET Waste via AKTS:**

The evaluation of the kinetic parameters of the PET pyrolysis was determined using the TGA data (at different heating rates of 0.5, 1, 2, 4, and 8 °C.min$^{-1}$) under N$_2$ atmosphere with a ratio of 16 between the lowest and the highest heating rate. The heating rate of 4 °C.min$^{-1}$ was repeated for the reproducibility and accuracy of results. The TGA experiments were conducted in a simultaneous thermal analysis Mettler Toledo (TGA/DSC) Thermogravimetric analyser Pyris TGA/DSC1, changes in the mass of the sample were recorded during the ramping operation. To determine the kinetic parameters more accurately and to better understand the PET pyrolysis, Advanced Kinetics and Technology Solutions (AKTS) software utilised. AKTS software correlated and validated the practical experiments with theoretical calculations for the kinetic modelling of the pyrolysis process of the PET plastic waste along with calculating the activation energy \( E_a \) and the pre-exponential factor. Different kinetic modelling methods were employed such as ASTM-E698, Flynn-Wall and Ozawa (FWO), and differential iso-conversional (model-free) method such as the Friedman method. The latter method measures \( E_a \) and pre-exponential constant at different extents of reaction progress \( \alpha \) without requiring prior knowledge of the reaction mechanism [35]. Consequently, the iso-conversional method was used herein to measure the kinetic parameters using heating rates ranging from 0.5 to 8 °C.min$^{-1}$ as a function of reaction progress \( \alpha \). Where the rate of the thermal decomposition of the waste PET plastic can be expressed according to the iso-conversional method as a function of reaction temperature and \( \alpha \), where the latter is calculated from the initial, actual and final masses of PET waste. The Arrhenius equation defined the temperature-dependent function of the kinetic parameters as shown below in Equation 1.
\[
\frac{d\alpha}{dt} = k_0 e^{\left(-\frac{E_a}{RT}\right)} f(\alpha) \quad \text{Eq. 1}
\]

The non-isothermal iso-conversional method usually utilizes different heating rates, \(\beta = \frac{dT}{dt}\), thus the PET plastic pyrolysis can be expressed as in Equation 2 as shown below:

\[
\frac{d\alpha}{dT} = \frac{k_0}{\beta} e^{\left(-\frac{E_a}{RT}\right)} f(\alpha) \quad \text{Eq. 2}
\]

One of the examples of iso-conversional methods (the non-isothermal) such as ASTM-E698 as shown in Equation 3 below:

\[
\beta \frac{d\alpha}{dt} = k_0 e^{\left(-\frac{E_a}{RT}\right)} (1 - \alpha) \quad \text{Eq. 3}
\]

Whereas the Flynn-Wall and Ozawa (FWO) method is shown in Equation 4 as shown below:

\[
\ln \beta = \ln \left(\frac{k_0 E_a}{R g(\alpha)}\right) - 5.331 - 1.052 \frac{E_a}{R T} \quad \text{Eq. 4}
\]

The equation for the Kissinger-Akahira-Sunrose (KAS) methods is shown below in Equation 5:

\[
\frac{\ln \beta}{T^2} = \ln \left[\frac{k_0 R}{E_a g(\alpha)} \left(1 - \frac{2RT}{E_a}\right)\right] - \left(\frac{E_a}{R T}\right) \quad \text{Eq. 5}
\]

Finally, the isothermal iso-conversional method is represented in the Friedman method as shown below in Equation 6:

\[
\ln \beta \frac{d\alpha}{dT} = \ln[k_0 f(\alpha)] - \frac{E_a}{RT} \quad \text{Eq. 6}
\]

**Results and Discussion**

**The kinetic modelling results:**

The validation of the results along with the calculation of the kinetic parameters were completed using AKTS software. The data was obtained from the TGA curves, then AKTS calculated the derivatives to give the DTG curves. Baselines were then constructed to integrate the DTG results with respect to the PET plastic pyrolysis profile. The type of baseline used herein was horizontal. Figure 1 shows the practical results, their integration, and the subsequent
simulated results from the TGA kinetic modelling results at different heating rates from 0.5 to 8 °C.min⁻¹. Similar TGA results were reported in the literature [25, 29, 36, 37]. The high mass loss in PET pyrolysis is due to the high volatile matter content as reported by Lee et al., who reported a value of 86.1 wt.% [25], Oh et al. was 88.1%[27], while Park et al. stated 91.6% [37] in PET pyrolysis. While the DSC results of two heating rates (0.5 and 1°C.min⁻¹) showed two endothermic peaks, along with a small shoulder of an exothermic peak as shown in Figure S2. The first two endothermic peaks at 252 and 460 °C are due to the PET melting and pyrolysis, while the third peak at around 800°C is characteristic to the graphitization of the residual carbon material. This agrees with the work reported by Kamali et al. where the three peaks appeared at 254, 466 and 791 °C respectively [5].
Figure 1: The % integrated mass derived from TGA results of PET pyrolysis at heating rates of 0.5, 1, 2, 4 and 8 °C.min⁻¹. The integration of the DTG curve is shown in yellow and simulation results are shown by black lines.
It is obvious that there is a good match between the practical and theoretical simulation as shown in Figure 1 (a-e) from the lowest to the highest heating rate with R² = 0.99659.

Table 1. The thermogravimetric decomposition data of PET plastic pyrolysis at various heating rates from 0.5 to 8 °C.min⁻¹.

| Heating rates | 0.5 °C.min⁻¹ | 1 °C.min⁻¹ | 2 °C.min⁻¹ | 4 °C.min⁻¹ | 8 °C.min⁻¹ |
|---------------|--------------|------------|------------|------------|------------|
| Temperature (°C) | 261-442 | 284-455 | 284-485 | 321-509 | 328-535 |
| Time required (s)* | 49,447 | 25,502 | 13,650 | 7,190 | 3,789 |
| Peak maximum (°C, s⁻¹) | 374.4, 1 x 10⁴ | 389.2, 2 x 10⁴ | 402.1, 1 x 10⁴ | 417.5, 8 x 10⁴ | 433.3, 0 x 10⁴ |
| Peak height (%.min⁻¹) | 1.1 | 2.4 | 5.0 | 9.7 | 19.7 |
| Onset temperature (°C) | 351 | 366 | 394 | 399 | 413 |
| Offset temperature (°C) | 397 | 412 | 421 | 432 | 453 |

* Time required for complete reaction (s).

There is a clear shift towards a higher decomposition temperature by increasing the heating rate 16 times (from 0.5 to 8 °C.min⁻¹) as shown in Table 1 with R² = 0.99659. For instance, the temperature range for the pyrolysis reaction to occur at 0.5 °C.min⁻¹ was 261-442°C, while at 8 °C.min⁻¹, it increased to 328-535°C. Furthermore, the onset temperature increased from 351 to 413°C, respectively. By increasing the heating rates by 16 times, the offset temperature increased by 56 °C as shown in Table 1. Thus, it is not surprising that the peak maximum was shifting towards higher reaction temperature with increasing the heating rates, as 0.5, 1, 2, 4 and 8°C.min⁻¹ showed peak maximum at 374, 389, 402, 417 and 433°C, respectively. On the other hand, the time required for the pyrolysis reaction to finish has dramatically decreased by 13 times with increasing the heating rates by 16 times. Table 1 shows that the required time for completion at 0.5 °C.min⁻¹ was 49447 seconds, while at 8 °C.min⁻¹ was 3789 seconds. Based on the integrated DTG curves from the five heating rates shown in Figure 1, the average PET plastic weight loss up to 600°C was 82.898 ± 1.2 wt.% of its initial mass.
To obtain the kinetic parameters, first, the reaction progress ($\alpha$) was plotted versus the reaction temperature as shown in Figure 2, where the practical and theoretical results are shown in coloured and dashed-grey lines, respectively. Again, it is obvious that there is a good matching between practical and theoretical results.

**Figure 2:** Reaction progress ($\alpha$) versus the temperature for the PET pyrolysis where the coloured and dashed grey curves show the practical and theoretical calculations, respectively.

Figure 3 shows the practical and theoretical reaction rate against reaction temperature, where the coloured and dashed grey curves show the practical and theoretical calculations, respectively, with good matching in all the five heating rates. The maximum reaction rate of the PET pyrolysis at heating rates of 0.5, 1, 2, 4 and 8°C.min$^{-1}$ were found to be 0.000089, 0.000449, 0.00092, 0.00188 and 0.00386 s$^{-1}$, respectively. Thus, the reaction rate increased by
approximately 43 times with increasing the heating rates by 16 times i.e. from 0.5 to 8 °C.min⁻¹.

**Figure 3:** Reaction rate versus the temperature for the PET pyrolysis where the coloured and dashed grey curves show the practical and theoretical calculations, respectively.

One of the kinetic modelling methods, ASTM-E698 (Equation 3) was used to calculate the $E_a$ and showed 165.6 kJ.mol⁻¹ with $R^2 = 0.9989$ as shown in Figure 4 (a). This in agreement with the $E_a$ value reported by Saha and Ghoshal which was 162.15 kJ.mol⁻¹ using the ASTM-E698 method [38].

While the Flynn-Wall and Ozawa (FWO) method (Equation 4) showed a variation of $E_a$ during the reaction progress in the range of 166-180 kJ.mol⁻¹ as shown in Figure 4 (b). The results herein are lower than that reported by Yao et al. [39], who reported 184-269 kJ.mol⁻¹. This is maybe due to the fact that they did not specify the plastic waste that they used along with the high heating rates used (15, 25 and 35 °C.min⁻¹).
Figure 4: Kinetic parameters calculated by different methods (a) \( E_a \) using the ASTM-E698 method and (b) \( E_a \) using the Flynn-Wall and Ozawa (FWO) method for the PET pyrolysis.

The differential iso-conversional method also was used to calculate the kinetic parameters (\( E_a \) along with the pre-exponential factor (\( k_0 \))) using the AKTS software by plotting of the natural logarithm of the reaction rate in \( (s^{-1}) \) against the inverse of the temperature \( (T^{-1}) \) as shown in Figure 5(a). In Figure 5(b) a variation in the \( E_a \) value was shown to be in the range of 165-195 kJ.mol\(^{-1}\). Interestingly, the results herein are in line with the work done by Jenekhe and Sun,

\[
y = -20.943x + 25.176 \\
R^2 = 0.9989
\]
where they reported $E_a$ values of 173.6 – 205.8 kJ.mol$^{-1}$ using the iso-conversional method [40]. At the start of the PET pyrolysis reaction where $\alpha=0$, the activation energy was 165 kJ.mol$^{-1}$. This is in agreement with work done by Cooney and Wiles [41], where the $E_a$ value of the initial pyrolysis stage using Kissinger’s Method was 163 kJ.mol$^{-1}$. This activation energy value stayed relatively constant while the reaction progress was increasing up to $\alpha=0.3$ i.e. 30% of the reaction progress, while the pre-exponential factor; $\ln(A(\alpha) f(\alpha))$ is $\sim 22$ s$^{-1}$. This high $E_a$ value at the start of the pyrolysis reaction could be attributed to the depolymerization of the polyethylene terephthalate polymer, which requires high energy to cleave the bonding within the polymer structure for the PET pyrolysis reaction, to initiate and progress. With the pyrolysis reaction progressing $>\alpha=0.3$, the activation energy value slightly increased to reach 195 kJ.mol$^{-1}$ at $\alpha=0.9$, while the pre-exponential factor; $\ln(A(\alpha) f(\alpha))$ is $\sim 26$ s$^{-1}$. This is again, in-line with the work reported by Cooney and Wiles [41], where the $E_a$ value increased to 202 kJ.mol$^{-1}$.
Figure 5: Kinetic parameters calculated with the differential iso-conversional, a) Natural logarithm of the reaction rate in (s\(^{-1}\)) versus the inverse temperature, b) \(E_a\) and \(ln k_0\).
The prediction of PET pyrolysis

The step-based prediction of PET pyrolysis

The predictions of PET pyrolysis using a step-based heating regime are shown in Figure 6 (a-d). For all four predictions, the final pyrolysis temperature was set to 500 °C, as this was in line with total decomposition from the TGA results. Additionally, all heating regimes began at 20 °C to indicate heating from ambient room temperature. In Figure 6a, the PET was heated from 20-420 °C at 50 °C.min⁻¹ and then from 420-500 °C at 25 °C.min⁻¹. It is evident that the reaction had appeared to complete after 11 minutes from the reaction rate curve. Interestingly, the maximum reaction rate observed was 0.014 s⁻¹ at approximately 9.77 minutes. In Figure 6b, the heating regime of 20-400 °C at 100 °C.min⁻¹ and 400-500 °C at 50 °C.min⁻¹ was utilized. For this sample condition, the peak reaction rate was shown to be 0.029 s⁻¹ after approximately 5.42 minutes. From the reaction rate curve, it can be seen that the curve does not reach its baseline of 0 and is incomplete, therefore, implying an incomplete reaction. This is likely due to the heating rates used of 100 and 50 °C.min⁻¹, respectively. If the reaction had occurred for longer at 50 °C.min⁻¹ or dwelled at the final reaction temperature of 500 °C, it would have reached completion. Figure 6c, on the other hand, is subjected to a heating regime of 100 °C.min⁻¹ from 20-320°C and then 20 °C.min⁻¹ from 320-500 °C, respectively. However, in this case, the lower latter heating rate supplied allowed the observed reaction to reach completion. In this instance, the peak reaction rate observed was 0.010 s⁻¹ after 9.86 minutes. Finally, Figure 6d was heated from 20-450 °C at a heating rate of 100 °C.min⁻¹ and then from 450-500 at a heating rate of 5 °C.min⁻¹. The maximum observed reaction rate was 0.011 s⁻¹ after 5.42 minutes. Interestingly, the curve in this sample appeared to have a shoulder and this is likely due to the rapid change in heating rate from 100 to 5 °C.min⁻¹, respectively.
The isothermal prediction of PET pyrolysis showing 14 different isotherms at every 10 °C temperature change over the temperature range of 420-550 °C is shown in Figure 7 (a, b). Figure 7a shows the reaction progress over the first minute, whereas Figure 7b shows the reaction profile over the first five minutes. Evidently, from Figure 7a, at reaction temperatures of 490 °C and above, the reaction reached completion, (α=1) in the short timeframe of one minute. This rapid decomposition indicates that these temperatures would be ideal for rapid conversion. However, at lower than 490 °C, for example, 480, 470 and 460 °C, the reaction progress only reached α values of 0.93, 0.81 and 0.55, respectively after the first minute. As

Figure 6: Prediction of PET pyrolysis at different temperature and heating rates (a-d) using a step-based heating regime.

Isothermal prediction of PET pyrolysis
Figure 7b shows the decomposition over a broader time range, it is worth noting that temperatures such as 450-480 °C that did not reach ($\alpha$=1) in Figure 7a, have reached reaction completion when the timeframe is expanded to five minutes of operation. Below 450 °C shows a much slower reaction and indicates that the reaction has not reached completion in this case. This further indicates that in order for successful pyrolysis to occur of PET temperatures exceeding 450 °C should be used.

![Figure 7](image_url)

**Figure 7:** The isothermal prediction of PET pyrolysis showing 14 isotherms and the change in reaction progress against time in the temperature range of 420-550 °C and time range of 1 and 5 minutes, respectively.
Non-isothermal prediction of PET pyrolysis

Figure 8 shows the non-isothermal prediction of PET pyrolysis over the temperature range of 350-500 °C. It is not surprising that the decomposition temperature shifted slightly toward higher reaction temperature. For example, by increasing the heating rates from 10 up to 30 °C.min^{-1}, the peak reaction rates observed were 0.0051, 0.0077, 0.0104, and 0.0159 s^{-1}, respectively. In all four heating rates used (10, 15, 20 and 30 °C.min^{-1}) for the prediction, the reaction profile and reaction rate curves appeared to be consistent.

![Graph showing the non-isothermal prediction of PET pyrolysis](image)

Figure 8: The non-isothermal prediction of PET pyrolysis under a non-isothermal heating regime at higher heating rates of 10, 15, 20 and 30 °C.min^{-1} using AKTS thermokinetics software.

The in-situ gaseous monitoring of PET pyrolysis

The PET plastic consists of chain-like backbones of synthetic polymers that are made of bis-hydroxyethyl-terephthalate monomer and with thermal cracking or pyrolysis, it evolved various gaseous emissions. The PET pyrolysis is a complex process that releases different types
of products such as aromatic compounds, such as benzene and toluene and aliphatic hydrocarbons C₁-C₄ such as methane and ethane along with the typical pyrolytic emissions (CO₂, CO, H₂ and H₂O) [23, 42-44]. Furthermore, other species could be released such as aldehydes, carboxylic acids (benzoic acid, acetyl benzoic acid, methyl benzoic acid and ethyl benzoic acid), esters (vinyl benzoate and its derivatives), ketones (benzophenone and acetophenone) and terephthalic acid and vinyl terephthalate [23, 45-47]. The complexity of such reaction is due to the possibility of several side interactions between free radicals during the scission of the polymeric hydrocarbon chain such as intramolecular or intermolecular exchange and six-membered transition state reactions [29]. Figure 9 shows the in-situ monitoring of the evolved gaseous emissions using the mass spectrometer which offers rapid analysis and is not limited to the shape, colour, impurities or dimensional limit as in other techniques such as Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy [1]. Herein, the temperature was recorded using a thermocouple that was set in the middle of the fixed bed reactor as shown from the blue-dashed line in Figure 9. The PET pyrolysis herein occurred in one stage, which is in line with the TGA results with a similar heating rate, while the DSC results in Figure S2 showed that the pyrolysis occurred in two stages. Figure 9 shows the pyrolysis reaction was in the temperature range of 390-500°C, while the TGA result was in the range of 382-490°C (heating rate of 4 °C.min⁻¹). The in-situ MS data showed that the main emissions are C₁-hydrocarbons at m/z =15 and H-O-C=O (CHO₂) at m/z =45. The in-situ MS profile also showed some relatively low emissions as shown from the inset (Figure 9), that showed the evolution of various forms of hydrocarbons such as C₂ hydrocarbons at m/z = 27, C₅ hydrocarbons at m/z = 42 and C₆ hydrocarbons at m/z = 78. Furthermore, other related emissions were shown as acetaldehyde or carbon dioxide at m/z = 44, the fragment of O-CH=CH₂ at m/z = 43, hydrogen gas at m/z = 2, water at m/z = 18 and finally, m/z = 29 that confirms the existence of acetaldehyde as following the same trend as with m/z = 44. This is in
agreement with the work done by Garozzo et al. as they reported the presence of the O-CH=CH₂ fragment and m/z of 17 for -OH species that confirmed the metastable transitions of the fragments, implying the existence of the open-chain structure with C(=O)O and −CH=CH₂ groups [48]. Acetaldehyde was the first gaseous product that evolved and finished as shown in Figure 9, this was confirmed by the m/z = 44 and 29 with the same evolution trend. This is in line with the work reported by Dhahak et al. [23], as they reported that acetaldehyde was the first detected gas followed by the following gases; benzoic acid, terephthalic acid, and benzene. Traces of benzene was detected herein in two peaks as shown in Figure S3, with a large peak and small shoulder. This is also in agreement with the literature, as it was explained that those two peaks are due to the decarboxylation of benzoic acid (1st peak) and terephthalic acid (2nd peak) [36]. Dhahak et al. reported that the major three gaseous compounds detected during the pyrolysis of PET were acetaldehyde, benzoic acid and vinyl terephthalate [23]. During the PET pyrolysis, the depolymerisation reaction starts to occur at the weak bonding points within the ester polymeric structure, such as the C-O bonding and the polymer chain near the C=O bonding [29]. It is worth noting that the evolved short-chain hydrocarbon (C₁-C₄ hydrocarbons) emissions can be combusted to provide some of the required reaction heat during the pyrolysis process [29].
Figure 9: Mass spectrum profile of the evolved gaseous emissions during the PET pyrolysis under N₂ atmosphere for temperature up to 530 °C with a heating rate of 5 °C.min⁻¹. The blue-dashed line represents the temperature recorded via the thermocouple.
Conclusion:

Herein, with the aid of thermo-analytical data (TGA and DSC) along with kinetic modelling software, we evaluated and measured the kinetic triplet of polyethylene terephthalate pyrolysis to better understand the process at scale. Furthermore, three types of predictions (step prediction, non-isothermal and isothermal) were made at higher heating rates to represent a realistic scenario that would occur in industry. The differential iso-conversational method showed activation energy ($E_a$) values of 165-195 kJ.mol$^{-1}$, $R^2 = 0.99659$. Additionally, the activation energy for PET pyrolysis was also evaluated using the ASTM-E698 (165.6 kJ.mol$^{-1}$, $R^2 = 0.9989$) and integral methods such as Ozawa-Flynn-Wall (166-180 kJ.mol$^{-1}$). Finally, the in-situ online tracking of the gaseous emissions using mass spectrometry of PET pyrolysis showed that with the pyrolysis gaseous emissions, C$_1$-hydrocarbon ($m/z =15$) and H-O-C=O ($m/z =45$) are present along with C$_2$ hydrocarbons ($m/z = 27$), C$_5$ hydrocarbons ($m/z = 42$), C$_6$ hydrocarbons ($m/z = 78$), acetaldehyde at ($m/z = 44, 29$), the fragment of O-CH=CH$_2$ ($m/z = 43$), hydrogen ($m/z = 2$) and water ($m/z = 18$). Future work could involve the use of kinetic modelling approaches such as the methods used herein to help determine how certain impurities or mixed wastes alongside PET can affect kinetic parameters and the predictions made in this study to help visualise problems that may occur in real-world scenarios such as industrial pyrolysis processes.

This work can be used as a baseline kinetic modelling benchmark for pure PET bottle samples. The kinetic parameters evaluated herein can be used as a prerequisite in process modelling applications and the scale-up of PET pyrolysis worldwide. This will effectively allow this abundant waste stream to be converted into useful products such as energy and help promote concepts such as the circular economy and the waste management hierarchy. Additionally, it will alleviate the amount of waste plastic that is conventionally sent to landfill or end in the aquatic ecosystem, by providing another end-of-life pathway for this non-biodegradable waste.
Additional file (Supplementary Information): Figure S1: The PET sample used herein. Figure S2: The DSC-TGA thermogram of the PET pyrolysis at heating rate of 0.5 °C.min⁻¹ (a) and 1 °C.min⁻¹ (b) under nitrogen atmosphere. Figure S3: Benzene evolution during the PET pyrolysis.

Abbreviations: polyethylene terephthalate (PET), Flynn-Wall and Ozawa (FWO) method, activation energy ($E_a$) and million tonnes (Mt).

Acknowledgements: The authors would like to acknowledge the support UKRI project “Advancing Creative Circular Economies for Plastics via Technological-Social Transitions” (ACCEPT Transitions, EP/S025545/1).

Author Contribution: A.I.O. conceived the idea, prepared, and tested the PET pyrolysis. A.I.O, C.F, A.H.M, A.S.A, J.H and D.W.R extracted and discussed the kinetic modelling and emission tests. All authors discussed and contributed to the writing of the paper.

Competing interests: The authors declare no competing interests.

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Availability of data and material: The data and results obtained herein are available from the corresponding author on reasonable request.

Funding: The research is funded through UKRI project “Advancing Creative Circular Economies for Plastics via Technological-Social Transitions” (ACCEPT Transitions, EP/S025545/1).
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