Diaz-Silvarrey LS, Phan AN. [Kinetic studies of municipal plastic waste.](#)
International Journal of Hydrogen Energy 2016

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DOI link to article:

<http://dx.doi.org/10.1016/j.ijhydene.2016.05.202>

Date deposited:

01/07/2016

Embargo release date:

15 June 2017

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KINETIC STUDIES OF MUNICIPAL PLASTIC WASTE

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Abstract

Municipal Plastic Waste (MPW) comprises a mixture of thermoplastics (high and low density polyethylene, HDPE and LDPE; polypropylene, PP; polystyrene, PS; and polyethylene terephthalate, PET). The rate of MPW generation has increased steadily at 5% per year whilst that of MPW recycling is only at 3% per year. The remains are either incinerated or disposed in landfills. Pyrolysis, a thermochemical decomposition, provides an excellent alternative to valorise MPW into valuable products, such as hydrogen and hydrocarbons which could be further processed for fuels and chemicals like syngas (steam reforming). However, most MPW pyrolysis studies oversimplify the mechanism of reaction by assuming a first order decomposition, leading to inaccurate predictions of the process. This could cause big challenges in designing pyrolysers for MPW or scaling up pyrolysis process. This study was to develop a kinetic model to discover the true reaction mechanism of MPW pyrolysis experimentally and numerically by applying thermogravimetric analysis (TGA) and Matlab software. Several methods such as Kissinger–Akahira–Sunose, KAS; Málek and linear model fitting were applied to predict the mechanism of MPW pyrolysis and valuated by experimental data obtained from TGA. All components in MPW were decomposed in N₂ atmosphere over a set of heating rates (5, 10, 20 and 40°C/min), temperatures of 30-700°C and sample size range of 1–4mm. The results confirmed that a complex mechanism rather than simple 1st order occurs during the decomposition because the variation in the apparent activation energy with conversion and kinetic model with heating rate. The assumption that MPW decomposition mechanism is a mixture of series and parallel reactions agreed well with experimental data and was confirmed by the results obtained from Málek method and linear model fitting.

Keywords: kinetic model, plastic waste, pyrolysis, random scission, waste management

1 Introduction

Plastics products are highly convenient due to their resistance to degradation, versatility, light weight and low price. As a result, their use has increased by twenty fold in the past 60 years and so has the amount of plastic waste generated. EPA (U.S. Environmental Protection Agency) estimates that global carbon footprint of plastic waste is somewhere between 100 - 300 million tonnes of CO₂ equivalent. To put those figures into context, plastics waste carbon footprint is equivalent to the carbon emissions of 21- 63 million cars driven for one year [1], which represents 0.7 – 2 times the total number of vehicles registered in the UK at the end of 2015 [2].

Waste management is one of the European Union key priorities. Environmental waste policies try to maximise the efficient use of resources moving towards zero waste as stated by the waste hierarchy. Despite these efforts, over 50% of Europe's plastic waste were disposed in landfills during the past year. Every year the amount of plastic waste from packaging increases at a higher rate than the recycled fraction, meaning more plastic waste are diverted to landfill and incineration. Recycling of plastics is constrained by the addition of substances during their manufacture to improve the product quality and properties. At the end of the product life, those substances cannot be separated or removed and they decrease the quality of recycled products or even eliminates the possibility of recycling completely [3]. During 2013, only 26% of plastic waste were recycled/re-used in the UK whilst 29% was incinerated (142,353 tonnes of CO₂ equivalent) and 43% disposed in landfills (27,197 tonnes of CO₂ equivalent) [1, 4, 5]. Disposing plastic waste in landfills presents two problems: firstly, as they are not biodegradable, they break into small particles harmful for human and wild life; and secondly, 4% of the global oil production is used to manufacture plastics products [6], 50% of which have a short life so useful raw materials are disposed as waste in less than a year. Thermal treatments such as pyrolysis or gasification are excellent alternatives for sustainable energy recovery from MPW into fuels and chemicals [7].

Municipal Plastic Waste (MPW) consists mainly of high and low density polyethylene (HDPE and LDPE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) [5, 8, 9]. They present an average calorific value of 39.87MJ/kg, representing an energy content of 80-90% of that of diesel fuel (45.30 MJ/kg) [10] so they must be considered as an energy source rather than waste required treatment. Pyrolysis presents a number of advantages over gasification for plastic feedstock: pyrolysis operation temperature (450-550°C) is lower than gasification (700-900°C) reducing energy requirements; and unlike pyrolysis, gasification of MPW generates CO or CO₂.

Pyrolysis is a complex process under an inert environment. Plastics decomposes as the temperature of the system increases, transforming into gas, liquid and solid residue. A catalyst (acid zeolites or transition metal oxides) can be added during the pyrolysis or to the liquid product for upgrading into synthetic fuels. The characteristics of the pyrolysis products strongly depend on the type and size of the feedstock, pyrolysis temperature, residence time and heating rate.

66 Plastic waste pyrolysis gas comprised mainly of light hydrocarbons (C_1 - C_4) and hydrogen [11-14]. The
67 liquid product is similar to crude oil and comprise of a mixture of aromatic, aliphatic and olefins from
68 C_9 to C_{35} [11-15]. Its proportion highly depends on the type of plastic. PS yields dark liquids with higher
69 aromatic content. PET also presents higher aromatic content but the product has a yellow waxy
70 appearance. HDPE, LDPE and PP yield light colour waxy products with low aromatic and higher
71 aliphatic and olefin content.

72 Unlike incineration with energy recovery or mechanical recycling, pyrolysis products present a wide
73 range of applications. Gases present a high calorific value (49.5MJ/kg [13]) so they could be reused to
74 decrease pyrolysis heat requirements; however they contain hydrogen and, in the case of HDPE and
75 LDPE, the monomer that could be recovered. Light hydrocarbons (C_1 - C_4) could be directed into steam
76 reforming to maximise hydrogen yield [16, 17]. Liquid products are similar to crude oil and could be
77 distilled to recover gasoline, diesel, and other fractions [13]. They can also be used for steam reforming
78 [18].

79 The proportion of HDPE, LDPE, PP, PS and PET in the MPW mixture is unpredictable. It is important
80 to understand decomposition behaviour of individual and mixtures to enable the development of a kinetic
81 model that fully captures interplay between components. Several studies reported kinetic studies for
82 either individual fractions comprising the MPW mixture [19-25] or focused on simple binary and tertiary
83 mixtures [23, 26-28].

84 Results obtained from kinetic studies are scattered and inconsistent. Sorum et al. [20] reported the
85 activation energy (E_a) for commercial grade HDPE, LDPE, PP and PS as 445.1kJ/mol, 340.8kJ/mol,
86 336.7kJ/mol, and 311.5kJ/mol. However, Wu et al. [19] reported values of 233-326kJ/mol for HDPE,
87 194-206kJ/mol for LDPE, 184-265kJ/mol for PP, and 172kJ/mol for PS. Saha and Ghoshal [24] found
88 that E_a and pre-exponential values for different PET drinking bottles were in a range of 162.15 –
89 338.98kJ/mol and $2.83 \cdot 10^{11}$ – $1.18 \cdot 10^{25}$ depending on the bottle type and the method applied. Even
90 though plastic products are made of the same type of plastic, they could behave differently during
91 pyrolysis due to different manufacturing processes and incorporation of additives to improve their
92 properties.

93 HDPE, LDPE, PP and PS kinetic studies are more common than PET [21] as they represent over half of
94 the total plastic waste stream [15]. Most of them assumed a simple decomposition mechanism (first order
95 reaction) and some performed single heating rate experiments [20, 22, 28, 29] to obtain the kinetic model
96 leading to inaccurate results. According to Westerhout et al. [21] this is only true for high degrees of
97 conversion (over 70%) and low pyrolysis temperatures (<450°C).

98 More complex models were developed. However, although they are more accurate they are also
99 extremely complex and not really usable [21]. The most common ones are the infinite number of parallel
100 reactions [30], the weak bond model [31], the consecutive reaction model [32, 33], and the Simha and
101 Wall model [34]. Sánchez-Jiménez et al. [35] suggested that MPW pyrolysis followed the Simha and

Wall decomposition model [34] where random scissions occurred along hydrocarbon chains. This model was confirmed by Pérez-Maqueda et al. [29] whom also proved that the first order models could not accurately predict the actual plastic waste decomposition as they oversimplify MPW pyrolysis. There are strong interactions between pyrolysis products yielding to increasing E_a as the reaction proceeds [24] and therefore these must take into account. Vyazovkin [36] explained that the variation was due to the residue becoming more refractory at higher temperatures. The inconsistency in results found in literature suggests that thermal decomposition of MPW occurs through a complex mechanism and is required a thorough study to capture all possible steps in the process.

2 Experimental

2.1 Materials

Five types of MPW (HDPE, LDPE, PP, PET and PS) were used during this study. They were collected from O'Brien Recycling Centre in Wallsend (Newcastle upon Tyne, UK). HDPE, LDPE, PP and PET were cut into circular samples of 1mm size while PS was cut into circular sample of 4mm size.

Individual components in MPW were then characterised for its properties. As shown in Table 1, HDPE, LDPE and PP consisted mainly of carbon and hydrogen with very low ash content, except to HDPE. Their high heating value was found around 44-46MJ/kg, which is comparable with that of diesel oil. PET had the lowest high heating value, which was 22.96MJ/kg. This is because it contains around 30% oxygen content and high ash content (around 8 wt%). High ash content in HDPE could be caused by alterations in the structure of plastic due to additives. The volatile matters for all MPW samples were high, in a range of 80-90% while moisture content was negligible for all of them.

Table 1 MPW characterisation: High Heating Value (HHV), Moisture, Volatile Matter (VM), Ash (A), Fixed Carbon (FC), Carbon (C), Hydrogen (H), Nitrogen (N), Oxygen (O).

	HDPE	LDPE	PP	PET	PS	Average
Calorimetry analysis						
HHV / [MJ/kg]	44.81±0.36	46.52±0.01	46.50±0.11	22.96±0.03	38.54±0.36	39.87±0.52
Proximate Analysis						
Moisture / [%w/w]	0.1±0.1	0.1±0.1	0.1±0.1	0.4±0.3	1.0±0.4	0.3±0.5
VM / [%w/w]	77.7±1.6	99.8±0.6	97.7±0.1	85.7±1.9	98.8±0.3	91.9±2.6
A / [%w/w]	10.4±0.2	0.0±0.0	0.0±0.0	8.3±0.1	0.0±0.0	3.7±0.2
FC / [%w/w] (by difference)	11.9±1.6	0.2±0.6	2.3±0.1	6.0±1.9	1.2±0.3	4.4±2.6
Ultimate Analysis						
C±0.30 / [%w/w]	73.33	83.67	83.25	62.95	89.81	-
H±0.30 / [%w/w]	13.28	16.33	16.75	4.12	7.48	-

N±0.30 / [%w/w]	0.00	0.00	0.00	0.00	2.71	-
O±0.51 / [%w/w] (by difference)	0.00	0.00	0.00	32.93	0.00	-

2.2 Thermogravimetric analysis (TGA)

The input data for any kinetic model needs to be gathered by thermogravimetric or calorimetry analysis. This work was developed using thermogravimetric analysis in a Perkin Elmer STA6000. The sample (HDPE, LDPE, PP, PET and PS) was placed in a 4mm diameter alumina crucible for thermogravimetric analysis (TGA). Once the sample was loaded on the crucible the initial weight was recorded and thermal decomposition experiments were carried out between 30-700°C at a set heating rate (5, 10, 20 or 40°C/min). The system was constantly purged with 30ml/min of N₂ to ensure pyrolysis conditions inside the TGA furnace. For each experiment, data of weight loss (w_i / [wt%]), derivative weight loss (dw/dt / [wt%/min]), temperature (T / [°C]), and heat flow (ΔH / [mW]) were recorded every 0.1s. PP was used as reference material for repeatability. Two identical runs were performed and compared by single factor ANOVA showing no significant difference between them ($F = 1.04 < F_{crit} = 3.84$).

2.3 Kinetic modelling

The rate of MPW pyrolysis, is expressed as shown in Equation 1.

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-E_a/RT\right) \cdot f(\alpha) \quad (1)$$

where α is the conversion, i.e. the fraction already decomposed; da/dt the rate of reaction (s^{-1}); A the pre-exponential factor (s^{-1}); E_a the activation energy (J/mol); R the universal gas constant (8.314 J/mol K); T the temperature (K); and $f(\alpha)$ a mathematical function describing the conversion and named kinetic model.

Kinetic models predict the rate of reaction by determination of the so-called kinetic triplet. This term refers to the activation energy (E_a), the pre-exponential factor (A) and the kinetic model ($f(\alpha)$). Those three terms define how MPW decomposes and allows the prediction of the rate of reaction outside the experimental range.

Westerhout et al. [21] proved that non-oxidative thermal decomposition of MPW mixtures was similar to that of individual polymers decomposition behaviour. Hence, they can be simulated by applying an additive rule as presented in Equation 2.

$$\left(\frac{d\alpha}{dt}\right)_{MPW} = \sum_{i=1}^N w_i \cdot \left(\frac{d\alpha}{dt}\right)_i \quad (2)$$

where $(da/dt)_{MPW}$ is the rate of reaction of any MPW mixture, i the n^{th} polymers in the mixture (HDPE, LDPE, PP, PP, PET and PS); w_i the weight fraction of each polymer (%w/w); and $(da/dt)_i$ the rate of reaction predicted with the model for each polymer (s^{-1}).

Hence, determination of the kinetic triplet for each polymer would allow predictions of the rate of reaction of different simulated mixtures. This information is vital to design pyrolysis reactors and choose pyrolysis conditions in order to maximise yields of valuable products, i.e. hydrogen, monomers, hydrocarbons, etc.

Raw data from TGA was input into the Matlab code which was built based on the process (Figure 1) described by Vyazovkin et al. [36] to obtain the kinetic triplet of each MPW. Firstly, raw data from TGA analysis was used to obtain the activation energy (E_a) and pre-exponential factor (A) variation with conversion for each individual MPW through isoconversional methods (Kissinger-Akahira-Sunose, KAS, and Friedman). The average E_a and A were then used to determine the kinetic model, $f(\alpha)$, by applying model fitting methods. Finally, Equation 2 was used to simulate the rate of reaction of different MPW mixtures.

Figure 1. Steps followed to develop MPW thermal decomposition kinetic model (adapted from [36]).

Isoconversional methods

Isoconversional methods are a common methodology that is used for kinetic studies using differential scanning calorimetry (DSC) or TGA data. They are based on the principle that at a constant conversion (α_i), the rate of reaction ($(da/dt)_i$), only changes with the heating rate (β_j) [36]. This paper explains the main concepts behind this methodology however detailed information can be found elsewhere [37].

171 Isoconversional methods are mathematically described in Equation 3, which describes the rate of
 172 reaction for solid-state reactions under non isothermal conditions. It is obtained when a linear relation
 173 between the temperature, T, and the time, t, ($\beta = dT/dt$) is introduced in Equation 1.

$$174 \left(\frac{d\alpha}{dT}\right)_i = \frac{A_i}{\beta_j} \exp\left(-E_{a,i}/RT_i\right) f(\alpha_i) \quad (3)$$

175 where $(d\alpha/dT)_i$ is the rate of reaction under non-isothermal conditions (K^{-1}) at a constant conversion (α_i);
 176 β_j the different heating rates ($^{\circ}C/s$ or K/s); and the rest of terms are as explained for Equation 1.
 177 Reorganising Equation 3 for integration Equation 4 is obtained as follows.

$$178 \int_0^{\alpha} \frac{d\alpha}{f(\alpha_i)} = \frac{A_i}{\beta} \int_{T_0}^T \exp\left(-E_{a,i}/RT_i\right) dT \quad (4)$$

179 where all the terms are as explained above for Equation 3.

180 The difference between each isoconversional method lies on the mathematical approximation used to
 181 solve the integral on the right side of Equation 4 as it has not direct analytical solution. KAS and
 182 Friedman methodologies are the simplest while most accurate ones hence, their popularity. Although
 183 being the most flexible, Friedman yields to systematic errors when the reaction heat varies with heating
 184 rate and experimental data presents noise [38]; leaving KAS as the initial method applied in this study.
 185 The extent of conversion (α_i) for each value of the weight loss during TGA analysis was calculated by
 186 Equation 5.

$$187 \alpha_i = \frac{m_0 - m_i}{m_0 - m_f} \quad (5)$$

188 where m_0 is the initial mass of sample in the crucible (mg); m_f the final mass in the crucible at the end
 189 of the experiment (mg); and m_i the mass in the crucible at each instant of time (mg) calculated from the
 190 weight loss (w_i) by Equation 6.

$$191 m_i = w_i \cdot m_0 \quad (6)$$

192 where m_0 and m_0 represent the initial mass of sample in the crucible and the one at each instant of time
 193 (mg) and w_i the weight loss provided by the TGA analyser (%w/w).

194 Once the conversion has been calculated, the kinetic model select the data between $\alpha_{i0}=0.2$ and $\alpha_{if}=0.8$
 195 with a 0.01 step. The rest of the data is discarded as it lays outside the decomposition range of HDPE,
 196 LDPE, PP, PET and PS. Each of those selected values corresponds to a certain temperature ($T_{\alpha,i}$) also
 197 measured during TGA analysis. Equation 7 represents KAS equation and has the same form as a linear
 198 regression.

$$199 \ln\left(\frac{\beta_j}{T_{\alpha,i}^2}\right) = \ln\left(\frac{A_i R}{E_{a,i}}\right) - \ln\left(\frac{1}{f(\alpha_i)}\right) - \left(\frac{E_{a,i}}{R}\right)\left(\frac{1}{T_{\alpha,i}}\right) \quad (7)$$

200 where $\ln\left(\frac{\beta}{T_{\alpha,i}^2}\right)$ represents the dependent variable; $\ln\left(\frac{A_i R}{E_{a,i}}\right) - \ln\left(\frac{1}{f(\alpha_i)}\right)$ the intercept; $\left(\frac{E_{a,i}}{R}\right)$ the slope and
 201 $\left(\frac{1}{T_{\alpha,i}}\right)$ the independent variable.

KAS was applied to all MPW. KAS results for HDPE presented a total variation between each value of E_a and the average E_a higher than 30% limiting its application. Friedman (Equation 8) was thereby used for E_a and A determination on HDPE.

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln(A \cdot f(\alpha)) - \frac{E_{\alpha,i}}{R \cdot T_{\alpha,i}} \quad (8)$$

where all the variables are as explained above in this section.

Kinetic model, $f(\alpha)$

The kinetic model, $f(\alpha)$, is determined by two fitting methods called master plots or Málek method [27] and truncated Šesták-Berggren (SB) equation which is collected in Equation 9.

$$f(\alpha_i) = \alpha_i^m \cdot (1 - \alpha_i)^n \quad (9)$$

where $f(\alpha_i)$ is the kinetic model; α_i the conversion; m the nucleation factor and n the order of reaction. Málek method comprises of two different plots, one based on Equation 10 and the other on Equation 11, called $y(\alpha)$ and $z(\alpha)$ master plots respectively.

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)_{exp,i} \exp\left(\frac{E_{a,average}}{RT_i}\right) = Af(\alpha) \quad (10)$$

$$z(\alpha) = \left(\frac{d\alpha}{dt}\right)_{exp,i} T_i^2 \left[\frac{\pi(x)}{\beta T_i}\right] \approx \left(\frac{d\alpha}{dt}\right)_i T_i^2 = f(\alpha)g(\alpha) \quad (11)$$

$$\left(\frac{d\alpha}{dt}\right)_{exp,i} = \frac{-m_0}{m_0 - m_f} \frac{dw_i}{dt} \quad (12)$$

where $(d\alpha/dt)_i$ represents the experimental values of the rate of reaction at each constant conversion α_i obtained by Equation 12; m_0 and m_f the initial and final mass of sample in the crucible; dw_i/dt the derivative of the weight loss over time given by TGA analysis; $E_{a,average}$ the average activation energy for the whole reaction (J/mol); R the universal gas constant (8.314J/mol/K); T_i the reaction temperature at each constant conversion α_i ; A the average pre-exponential factor for the whole reaction (s^{-1}); $f(\alpha)$ the kinetic model; β the heating rate ($^{\circ}C/s$ or K/s); $\pi(x)$ a mathematical expression used to approximate the value of $(E_{a,average}/R) \cdot \int_{x_0}^x \exp(-x)/x^2 dx$ where x is the reduced activated energy and is defined by $x = E_a/RT$ and $g(\alpha)$ the integral form of $1/f(\alpha)$.

The experimental values were obtained through TGA analysis and corresponded to the middle part of Equations 10 and 11 while the right side of those two equations (Equations 10 and 11) corresponded to the theoretical values of the master plots. The appropriate kinetic model is obtained when theoretical $y(\alpha)$ and $z(\alpha)$ values and experimental ones matched. Table 2 [35, 37] collects $f(\alpha)$ equations for the most common solid-state reactions. Both experimental and theoretical values were normalize between 0 and 1 by feature scaling to ease comparison as what determined the correct kinetic model would be only the shape.

Table 2. Theoretical kinetic models [35, 37].

Name	$f(\alpha)$
------	-------------

Power law (n = 2,3,4)	$n(\alpha)^{(n-1)/n}$
Random Scission	$2(\alpha^{1/2}-\alpha)$
Mampel (first order)	$1-\alpha$
n^{th} order (n = 0.5,2,3)	$(1-\alpha)^n$
Avrami-Erofeev (nuclei growth) (n = 2,3,4)	$n(1-\alpha)(-\ln(1-\alpha))^{(n-1)/n}$
One-dimensional diffusion	$1/2\alpha^{1/2}$
Two-dimensional diffusion	$(-\ln(1-\alpha))^{-1}$
Three-dimensional diffusion	$3/2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$
Contracting cylinder (contracting area)	$2(1-\alpha)^{1/2}$
Contracting sphere (contracting volume)	$3(1-\alpha)^{2/3}$

233 ~~Experimental values of $(d\alpha/dt)_{\text{exp},i}$ were calculated with Equation 12 from experimental TGA analysis~~
234 ~~weight loss data $(dw/dt)_i$.~~

235 ~~$$\left(\frac{d\alpha}{dt}\right)_i = \frac{-m_g}{m_g - m_f} \cdot \left(\frac{dw}{dt}\right)_i \quad (11)$$~~

236 If Málek method results differ between all the tested heating rates, the kinetic model needs to be
237 determined by linear model fitting such as the truncated SB equation. This would indicate that the
238 mechanism of reaction was more complex than a single step decomposition. Combining Equations 1 and
239 8, Equation 13 is yielded.

240
$$\left(\frac{d\alpha}{dt}\right)_i = A_{\text{average}} \cdot \exp(-E_{a,\text{average}}/RT_i) \cdot \alpha_i^m \cdot (1 - \alpha_i)^n \quad (13)$$

241 where $(d\alpha/dt)_i$ represents the experimental rate of reaction calculated by Equation 12 (s^{-1}); A_{average} the
242 average pre-exponential factor calculated through KAS (LDPE, PP, PET and PS) or Friedman (HDPE)
243 (s^{-1}); $E_{a,\text{average}}$ the average pre-exponential factor from KAS (LDPE, PP, PET and PS) or Friedman
244 (HDPE) (J/mol); R the universal gas constant (8.314J/mol/K); T_i the temperature (K); α_i the
245 conversion; m the nucleation factor; and n the order of reaction.

246 Rearranging and linearizing Equation 13, the truncated SB equation for model fitting is obtained and
247 showed in Equation 14.

248
$$\ln\left(\left(\frac{d\alpha}{dt}\right)_i \frac{1}{\alpha_i^{m \cdot (1-\alpha)^n}}\right) = \ln(A_{\text{average}}) - \frac{E_{a,\text{average}}}{R} \frac{1}{T_i} \quad (14)$$

249 where $\ln\left(\left(\frac{d\alpha}{dt}\right)_i \frac{1}{\alpha_i^{m \cdot (1-\alpha)^n}}\right)$ represents the independent variable in a linear regression; $\ln(A_{\text{average}})$ the
250 intercept; $\frac{E_{a,\text{average}}}{R}$ the slope; and $\frac{1}{T_i}$ the dependent variable. When different values of “m” between -1
251 and 1 and of “n” between 0 and 3 were substitute in the independent variable in Equation 14, different
252 straight lines were yielded; each one associated to a Pearson linear coefficient. The “m” and “n” pair
253 that maximized the Pearson coefficient was the optimum combination and therefore the values chosen
254 to describe the appropriate kinetic model, f(α).

255 *Model predictions and validation*

256 Once the kinetic triplet of each MPW (HDPE, LDPE, PP, PET and PS) was obtained as described in
257 previous steps, the theoretical rate of reaction was calculated by Equation 1. Equation 1 was then solved
258 for each heating rate applying Runge Kutta through the existing Matlab command “ode15s” between
259 640-840K with $\alpha(0) = 0$ as initial condition. This calculation provided values for the theoretical
260 conversion of each MPW. The model was validated by comparison of the theoretical rate of reaction
261 calculated by Equation 1 and the experimental data obtained from TGA tests and Equation 12.

262 The validity of the predicted values was evaluated applying mean squared error (MSE) and difference
263 in the maximum rate of conversion, $(d\alpha/dt)_c$ as represented in Equations 15 and 16 respectively. If MSE
264 > 5 predictions were rejected. If $(d\alpha/dt)_c > 0.2$ the error between predictions and experimental data was
265 higher than 20% and predictions were rejected.

$$266 \quad MSE = \frac{1}{n} \sum_{i=1}^n (y_{theoretical} - y_{experimental})^2 \quad (15)$$

267 where MSE is the mean squared error, n the sample size, $y_{theoretical}$ the predicted rate of reaction
268 applying the kinetic triplet obtained with the model and Equation 1 and $y_{experimental}$ the rate of reaction
269 obtained from experimental TGA analysis and Equation 12.

$$270 \quad \left(\frac{d\alpha}{dt}\right)_c = \frac{(d\alpha/dt)_{max,exp} - (d\alpha/dt)_{max,theo}}{(d\alpha/dt)_{max,theo}} \quad (16)$$

271 where $\left(\frac{d\alpha}{dt}\right)_c$ represents the difference in the maximum rate of conversion, $(d\alpha/dt)_{max,exp}$ the
272 maximum experimental rate of reaction and $(d\alpha/dt)_{max,theo}$ the maximum predicted rate of reaction
273 applying the kinetic triplet and Equation 1.

274 **3 Results and Discussion**

275 **3.1 Thermogravimetric analysis (TGA)**

276 Figure 2 represents the weight loss (w_i) against temperature (T_i) for all MPW. All polymers followed
277 the same pattern: single step decomposition shifted to higher temperatures in the following order: PS <
278 PET < PP < LDPE < HDPE agreeing with findings in literature [20, 22-27, 29, 39]. The maximum
279 weight loss for each polymer was found as follows: around 25-30% for HDPE and PET and 0% for
280 LDPE, PP and PS. The difference is due to PET and HDPE higher ash and fixed carbon content.

281 Figure 3 plots the derivative weight loss (dw/dt) against temperature. They showed MPW thermal
282 decomposition is favoured by higher heating rates and varied between each type of MPW as follows:
283 HDPE > LDPE > PP > PET > PS. Hujuri et al. [23] already suggested that substituted/branched polymers
284 like PET or PP degrade at lower temperatures than linear polymers (HDPE and LDPE). MPW thermal
285 decomposition range was as follows: HDPE = 425-565°C; LDPE = 443-535°C; PP = 415-540°C; PET =
286 395-520°C; and PS = 372-452°C. When heating rate doubled, decomposition range increased around

287 20°C. The temperature where maximum decomposition rate occurred, i.e. the peak of each derivative
 288 plot, set pyrolysis temperature and was, in all cases, between 400-500°C.

a) HDPE

b) LDPE

c) PP

d) PET

e) PS

289
 290 Figure 2 Thermogravimetric plots (TGA plots) for a) HDPE, b) LDPE, c) PP, d) PET and e) PS at 5,
 291 10, 20 and 40°C.

Figure 3. Derivative thermogravimetric plots (DTG plots) for HDPE, LDPE, PP, PET and PS at 5, 10, 20 and 40°C.

As heating rates increased, the shape of the peak in DTG plots (Figure 3) changed. The area of each peak in Figure 3 is proportional to the change of mass (α_i) and the rate of reaction ($d\alpha_i/dt$). According to Equation 1, the rate of reaction depends on the kinetic triplet ($f(\alpha)$, E_a and A). E_a and A are a function of the temperature while $f(\alpha)$ is a mathematical function describing how the mass change (i.e. the mechanism of reaction). A different peak shape means a different way the mass changes, i.e. different mechanism of reaction. According to Kayacan and Dogan [39] the mechanism of HDPE thermal decomposition differed at lower heating rates ($<20^\circ\text{C}/\text{min}$) and at higher heating rates ($>20^\circ\text{C}/\text{min}$). Around $20^\circ\text{C}/\text{min}$, pyrolysis transforms from slow pyrolysis into fast pyrolysis altering the mechanism of reaction.

The results from Figures 2 and 3, indicated that the heating rate affected the temperature range where decomposition occurred. At higher heating rates, MPW decomposed easier over a wider range and needed higher pyrolysis temperatures to achieve the same conversion confirming previous findings found by Wu et al. [19].

3.2 Isoconversional methods

Figure 4 shows an example to illustrate KAS method for all tested MPW. When this method is applied to the range previously described ($\alpha_i = 0.2 - 0.8$), the values of E_a and A for each conversion (α_i) were obtain from the slope and the intercept of each straight line. Average results for the whole reaction are collected in Table 3.

Figure 4 Kissinger-Akahira-Sunose linear plots for (a) HDPE, (b) LDPE, (c) PP, (d) PET and (e) PS.

KAS assumed the error between any E_a value at constant conversions and the average E_a for the whole reaction must be below 30%. As shown in Figure 4(a) the straight lines for each constant conversion were not parallel yielding to a HDPE error around 60%. When this phenomena is present, KAS assumptions are not meet and results are not reliable so another isoconversional method is required as previously showed in Figure 1. Therefore, E_a and A for HDPE were determined by Friedman. Table 3 illustrates the results obtained for for HDPE (using Friedman methodology), LDPE, PP, PET and PS (using KAS methodology).

Table 3 Activation energy (E_a) and pre-exponential factor (A) for individual MPW.

KAS				
MPW	E_a / [kJ/mol]	RSD / [%]	A / [s ⁻¹]	RSD / [%]
HDPE	202.40 ± 9.47	4.7	$3.23 \cdot 10^{16} \pm 2.62 \cdot 10^{16}$	81.1
LDPE	267.61 ± 3.23	1.2	$7.86 \cdot 10^{19} \pm 5.26 \cdot 10^{19}$	66.9
PP	261.22 ± 5.13	2.0	$3.03 \cdot 10^{21} \pm 3.27 \cdot 10^{21}$	107.9
PET	197.61 ± 2.27	1.1	$4.84 \cdot 10^{14} \pm 2.30 \cdot 10^{14}$	47.5
PS	192.61 ± 0.76	0.4	$5.52 \cdot 10^{14} \pm 0.14 \cdot 10^{14}$	2.5
Friedman				
HDPE	375.59 ± 39.69	10.6	$9.47 \cdot 10^{29} \pm 7.33 \cdot 10^{63}$	N/A

323 Figure 5 compares HDPE (using Friedman methodology), LDPE, PP, PET and PS (using KAS
324 methodology). The variation in E_a of HDPE was high at conversion between 0.2-0.4, e.g. decreased from
325 around 880 KJ/mol at conversion of 0.2 to approximately 490KJ/mol at conversion of 0.3. At
326 conversions above 0.4, the apparent activation energy remained almost constant at around 313.39kJ/mol.
327 Wu et al. [19] reported values of the activation energy for HDPE between 233-326kJ/mol which
328 represents a difference around 4% between the highest value reported and results for conversion between
329 0.4-0.8. This indicates a clear change in the rate of HDPE thermal decomposition. This could be due to
330 the effect of additives/substances embedded in the plastic products which alter both the ash and fixed
331 carbon content (Table 1) and the mechanism of reaction.

332

333 Figure 5. Variation of the apparent activation energy with conversion for all MPW.

334 Regarding the pre-exponential factor, the values obtained in this model were higher than the ones
335 reported by Wu et al. [19]. However, comparison with literature is difficult as usually only the activation
336 energy is reported and not the pre-exponential factor.

337

338 According to the structure of each MPW, linear polymers (HDPE and LDPE) presented higher E_a while
 339 substitutions (PP > PET > PS) reduced E_a . Referring to literature values [19, 20] it can be concluded that
 340 one of the main issues of MPW pyrolysis is their thermal decomposition reaction largely varies
 341 depending on the nature of the MPW feedstock. Even the same type of individual MPW could lead to
 342 two very different sets of E_a and A values pointing the complexity of MPW pyrolysis simulations.

343 3.3 Málek method

344 Figure 6 shows an example of Málek method results. They presented large variation on the best fitting
 345 kinetic model depending on the heating rates. This trend was repeated for all tested MPW studied.
 346 Equation 9 in section 2.3 showed that $A \cdot f(\alpha)$ would equal $(d\alpha/dt)_i \cdot \exp(E_{a,average}/RT_i)$. Both A and
 347 E_a/R are constants and the shape was only a function of the kinetic model ($f(\alpha)$), the rate of reaction
 348 $(d\alpha/dt)$ and the temperature (T). At different heating rates, a certain value of conversion is achieved at
 349 higher temperatures, reducing the value of experimental $y(\alpha)$. However, when data is normalized those
 350 differences in scale are eliminated and the shape of the master plot remains invariable even though the
 351 heating rates changes [36]. This phenomena implied Málek method assumption of single step
 352 decomposition was incorrect for MPW thermal decomposition.

353

354

355

Figure 6 Master plots for a) LDPE and b) PS.

MPW thermally decomposed by an initial cracking into wax ($C_{13+} - C_{28}$ hydrocarbons) followed by further cracking of the waxes as temperature increases. Hence, MPW decomposition consist of, at least, three steps:

The findings of this study agreed with the proposed mechanism for HDPE as shown in Figure 7 by Aguado et al. [40].

364

Figure 7 Proposed mechanism of reaction for MPW thermal decomposition where solid lines are primary reactions and dashed lines secondary reactions [40].

366

Despite differences in the structure between each MPW, HDPE, LDPE and PP have a similar linear structure and hence, a very similar behaviour and mechanism of reaction would be expected. On the other hand, PET and PS present contain oxygen and aromatic rings on their structures which cause alterations on their thermal behaviour.

3.4 Linear model fitting: truncated Šesták-Berggren (SB) equation

Table 4 collects results from linear model fitting of the truncated SB equation as well comparison of the order of reaction found in literature [19, 24]. The decomposition of LDPE, PP and PS was first order while HDPE was second order and PET third order. The parameter “m” was zero in all cases as expected. “m” represents the nucleation factor and would only differ from zero in certain types of reactions, such as autocatalytic reactions, which is not the case with MPW pyrolysis. Results in Table 4 differed from literature findings [19, 24] between 20-60% depending on the MPW tested. This deviations point once again the dependence between the nature and source of the MPW tested and the kinetic model obtained, struggling the development of accurate MPW pyrolysis predictions.

Table 4. SB equation results for HDPE, LDPE, PP, PET and PS.

Experimental Results				Wu et al. [19]	Saha et al. [24]
MPW	m	n	Pearson	n	n
HDPE	0	1.70	-0.9928	0.74	-
LDPE	0	0.95	-0.9968	0.63	-
PP	0	0.75	-0.9584	0.9	-

380

PET	0	2.80	-0.9650	-	1-1.82
PS	0	0.90	-0.9541	0.5	-

381 The results obtained in Table 4 were used to predict MPW decomposition conversion against
382 temperature as presented in Figure 8. Predictions present the same shape as experimental data from
383 TGA analysis. The best fit between predicted conversion and experimental conversion against
384 temperature according to Figure 8 are PET and PS. Ahmed et al. [7] also predicted PS thermal
385 decomposition at low heating rates (8,10 and 12K/min). Both models agree on the shape of the curves
386 although Ahmed et al. [7] decomposition range was at higher temperatures as it includes gasification as
387 well as pyrolysis.

388 Table 5 shows the results of model validation parameters. Although predicted values using this model
389 and experimental data from TGA analysis agreed well at heating rates below 20°C/min; the method
390 could not predict mechanism at higher heating. This suggests that the proposed mechanism, initial
391 cracking into wax (C_{13+} - C_{28} hydrocarbons) followed by further cracking of the waxes as temperature
392 increases, is more complex and strongly dependent upon the heating rate. Further analysis for higher
393 heating rates (>40°C/min) as well as analysis of products along the reaction would clarify this difference.

394 Table 5 Mean of Squared Error (MSE) and difference between conversion for maximum experimental
395 $((d\alpha/dt)_{p,exp})$ and predicted $((d\alpha/dt)_{p,theo})$ rate of reaction. Rejected values are marked in bold.

	$\beta = 5^\circ\text{C/min}$				$\beta = 10^\circ\text{C/min}$			
	MSE	$(d\alpha/dt)_{p,exp}$	$(d\alpha/dt)_{p,theo}$	$(d\alpha/dt)_c$	MSE	$(d\alpha/dt)_{p,exp}$	$(d\alpha/dt)_{p,theo}$	$(d\alpha/dt)_c$
HDPE	0.57	0.57	0.52	0.10	0.22	0.56	0.56	0.00
LDPE	6.72	0.65	0.48	0.35	0.10	0.62	0.60	0.03
PP	1.55	0.57	0.65	0.12	0.003	0.62	0.63	0.02
PET	10.77	0.50	0.22	1.27	9.37	0.47	0.21	1.24
PS	1.52	0.63	0.54	0.17	0.30	0.57	0.55	0.04
	$\beta = 20^\circ\text{C/min}$				$\beta = 40^\circ\text{C/min}$			
	MSE	$(d\alpha/dt)_{p,exp}$	$(d\alpha/dt)_{p,theo}$	$(d\alpha/dt)_c$	MSE	$(d\alpha/dt)_{p,exp}$	$(d\alpha/dt)_{p,theo}$	$(d\alpha/dt)_c$
HDPE	0.09	0.62	0.61	0.02	-	-	-	-
LDPE	0.20	0.64	0.63	0.02	0.46	0.51	0.57	0.11
PP	-	-	-	-	18.98	0.31	0.72	0.57
PET	8.86	0.43	0.20	1.15	8.95	0.43	0.20	1.15
PS	1.41	0.46	0.52	0.12	6.77	0.33	0.47	0.30

396

Figure 8 Comparison between predicted and experimental conversion for a) HDPE, b) LDPE, c) PP, d) PET and e) PS.

Figure 9 shows the predicted rate of reaction of various simulated MPW mixtures. Four different mixtures were simulated. The first one represented all fractions of MPW equally (a); the second one (b), the average MPW composition in the European Union; the third one (c), a mixtures comprised mainly by linear plastics; and the last one (d), a mixture formed by plastics with aromatic rings.

Figure 9 Simulated rate of reaction for different mixtures of MPW.

Higher amounts of PET and PS in the mixture would produce lower rates of reaction while HDPE, LDPE and PP would yield higher ones; meaning that to achieve a given extent of conversion, PET and PS require lower temperature than HDPE, LDPE and PP. To reduce MPW pyrolysis temperature so the energy requirements of the process are lower, Figure 9 seems to point at MPW mixtures with higher fractions of PET and PS than HDPE, LDPE and PP. However, further studies on the composition of MPW pyrolysis products are being conducted to confirm results from Figure 9.

Actually, according to Scheirs and Kaminsky [41], PET is a non-desirable feedstock for plastic pyrolysis due to the formation of terephthalic acid and benzoic acid in the liquid fraction and high solid yield [41, 42]. PS seems to produce oils similar to gasoline while feedstock rich in HDPE, LDPE, and PP yields waxy products with higher alkane content that could be further process trough steam processing for hydrogen, monomer recovery or other applications.

4 Conclusions and Further Work

MPW pyrolysis mechanism of reaction cannot be modelled as single step decomposition. Instead, pyrolysis liquid and gas are formed after at least three different parallel stages. Although providing a quick overview of the mechanism of reaction, the Málek method is very limited. For instance, when experimental results fall between two theoretical models, the mechanism remains unknown. Linear

model fitting provided MPW decomposition kinetic model by optimising “n” (order of reaction) and “m” (nucleation factor). MPW presented $m = 0$. The order of reaction was as follows: HDPE = 1.70, LDPE = 0.95, PP = 0.75, PET = 2.80, PS = 0.90. KAS and Friedman methods provided values of E_a and A of HDPE = 375.59kJ/mol and $9.47 \cdot 10^{29} \text{ s}^{-1}$; LDPE = 267.61kJ/mol and $7.86 \cdot 10^{19} \text{ s}^{-1}$; PP = 261.22kJ/mol and $3.03 \cdot 10^{21} \text{ s}^{-1}$; PET = 197.61kJ/mol and $4.84 \cdot 10^{14} \text{ s}^{-1}$; and PS = 192.61kJ/mol and $5.52 \cdot 10^{14} \text{ s}^{-1}$. These results allowed prediction of the rate of reaction for each MPW. They fitted experimental data accurately for low and intermediate heating rates however higher heating rates were not well represented. Those predictions implied a more complex mechanism dependant on the heating rate as well as the type of MPW analysed.

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