Kinetics of Polyethylene Terephthalate (PET) and Polystyrene (PS) Dynamic Pyrolysis

S.M. Al-Salem and P. Lettieri

Abstract—Thermo-chemical treatment (TCT) such as pyrolysis is getting recognized as a valid route for (i) materials and valuable products and petrochemicals recovery; (ii) waste recycling; and (iii) elemental characterization. Pyrolysis is also receiving renewed attention for its operational, economical and environmental advantages. In this study, samples of polyethylene terephthalate (PET) and polystyrene (PS) were pyrolysed in a micro-thermobalance reactor (using a thermogravimetric-TGA setup). Both polymers were prepared and conditioned prior to experimentation. The main objective was to determine the kinetic parameters of the depolymerization reactions that occur within the thermal degradation process. Overall kinetic rate constants (k_o) and activation energies (E_o) were determined using the general kinetics theory (GKT) method previously used by a number of authors. Fitted correlations were found and validated using the GKT, errors were within ± 5%. This study represents a fundamental step to pave the way towards the development of scaling relationship for the investigation of larger scale reactors relevant to industry.

Keywords—Kinetics, PET, PS, Pyrolysis, Recycling, Petrochemicals.

I. INTRODUCTION

OVER the past seventy odd years, the plastic industry has witnessed a drastic growth, namely in the production of synthetic polymers represented by polystyrene (PS) polyethylene terephthalate (PET). Plastic materials production have reached global maximum capacities levelling at 150 million tonnes per year, where in 1990 production capacity was estimated at 80 million tonnes [1]. In the year 2004, the consumption of plastic materials in Western Europe was 43.5 million tonnes, increasing by 4% per year. It is estimated that the production of plastics worldwide is growing at a rate of about 5% per year [2]. This results in high estimates of almost 60% of plastic solid waste (PSW) being discarded in open space or landfilled in many developing and developed countries [3]. The total world production of plastics grew to 260 million tonnes in 2007 from a mere 1.5 tonnes in 1950 (see **Fig.1**). An analysis of plastic materials consumption on a *per capita* basis shows that this has now grown to approximately 100 kg in the North America Free Trade Agreement (NAFTA) countries and Western Europe, with the

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potential to grow towards 140 kg per capita by 2015.

In the UK, almost 4.5 million tonnes of plastics products were used in 2001 [4]. It was also reported that 3.5 million tonnes of plastic solid waste (PSW) required disposal back in 2000. A breakdown of the UK plastic consumption by sector will show that packaging (like many developed countries) is more dominant than the rest. Packaging accounts for 37.2% (by wt%) of all plastics consumed in Europe and 35% worldwide [5]. In Fig.2, a breakdown of the UK market is given showing consumption of selected polymers in the main sectors in the year 2000. An estimate of 4.13 million tonnes of primary plastic materials was consumed by the UK manufacturing sector. In addition, the import of plastic goods and components exceeded exports by an estimated 320,000 tonnes. A total of approximately 4.45 million tonnes of plastic were consumed in the UK during 2000.

The high consumption of plastics (especially PET bottles) represent the key drive for authorities in the UK to consider plastic recycling, recovery and treatment as a prime target, together with the need for extending existing local authorities collection systems. The packaging sector is not the only plastic consuming sector in the UK, recent surveys have shown that plastic waste arising from packaging in the kerbside collections system is also creating a major problem for recyclers. Such packaging waste (accounting for 11% of kerbside collection) is accumulating daily and few local authorities in the UK currently collect packaging plastic at the kerbside [8].

Based on these estimates, both PS (including EPS and ABS) and PET account for 28% of the UK's plastic consumption by weight. This leads to drastic quantities in the UK municipal solid waste (MSW) final stream, where plastic is estimated to be around 7% [9]. These estimates drive research towards investigating innovative techniques to manage waste and enhance product and energy recovery.

Advanced thermo-chemical treatments (TCT) of PSW in the presence of heat under controlled temperatures (*i.e.* thermolysis) provide a viable and an optimum engineering solution. It has been shown [10-11] that TCT can be used to recover monomer fractions up to 60% and aid the production of valuable petrochemicals including gases (rich with low cut refinery products and hydrocarbons), tars (waxes and liquids very high in aromatic content) and char (carbon black and/or activated carbon). Thermolysis processes can be divided into advanced thermo-chemical or pyrolysis (thermal cracking in an inert atmosphere), gasification (in the sub-stoichiometric

presence of air usually leading to CO and CO_2 production) and hydrogenation (hydrocracking) [12]. Thermal degradation processes allow obtaining a number of constituting molecules, combustible gases and/or energy, with the reduction of landfilling as an added advantage [13]. The pyrolysis process is an advanced conversion technology that has the ability to produce a clean, high calorific value gas from a wide variety of waste and biomass streams. A number of studies have demonstrated that pyrolysis is a viable route to treat PSW [14-17], or other waste including biomass [18] and rubbers [19-21]. Pyrolysis also provides a number of other advantages, such as (i) operational advantages, (ii) environmental advantages and (iii) financial benefits. Operational advantages involve the possibility to use the char produced as a fuel or as a feedstock for other petrochemical processes. Environmentally, pyrolysis provides an alternative solution to landfilling and reduces greenhouse gas (GHGs) and CO_2 emissions. Financially, pyrolysis produces a high calorific value fuel that could be easily marketed and used in gas engines to produce electricity and heat. In this work, PS and PET were thermo-chemically treated (as a recycling route) via pyrolysis in dynamic thermogravimetry. The behaviour of the materials was investigated and kinetics of the depolymerization reaction was determined via the general kinetics theory (GKT), which was also used to validate the fitted correlations found in this study.

Fig..2. Plastic consumption (selected polymer type and sectors) through the main manufacturing cycle of the UK in the year 2000 [7].

Abbreviations: ABS, acrylonitrile butadiene styrene; EPS, expanded polystyrene; HDPE, high density polyethylene; LDPE, low density polyethylene; PET, polyethylene terephthalate, PP, polypropylene; PS, polystyrene; PVC, polyvinyl chloride; Agri, agriculture sector; mt, million tonnes.

All samples were milled to below 0.1 mm before experimentation, to avoid mass and heat transfer resistance. Fifteen mgs were weighted and used in all experiments. PET and PS samples were subjected to dynamic pyrolysis in a thermobalance reactor (Universal V3.7A) with a 1.5 bar inlet gauge pressure and 50 ml min^{-1} of pure nitrogen gas flow. Five constant heating rates (β) were used, 3, 15, 50, 100 and 120 ^{o}C min^{-1}. **Fig.3** shows a schematic representation of the thermobalance reactor used.
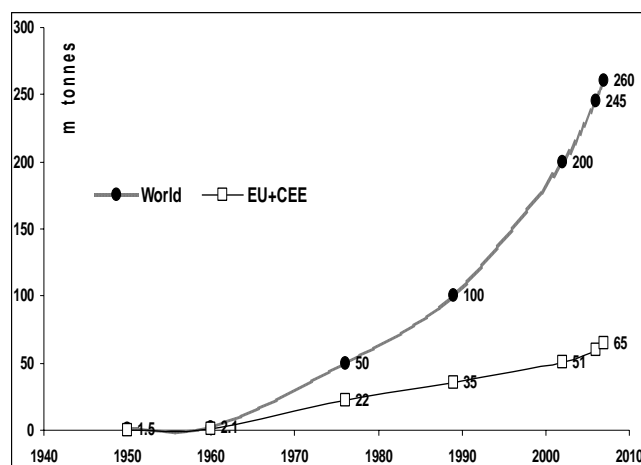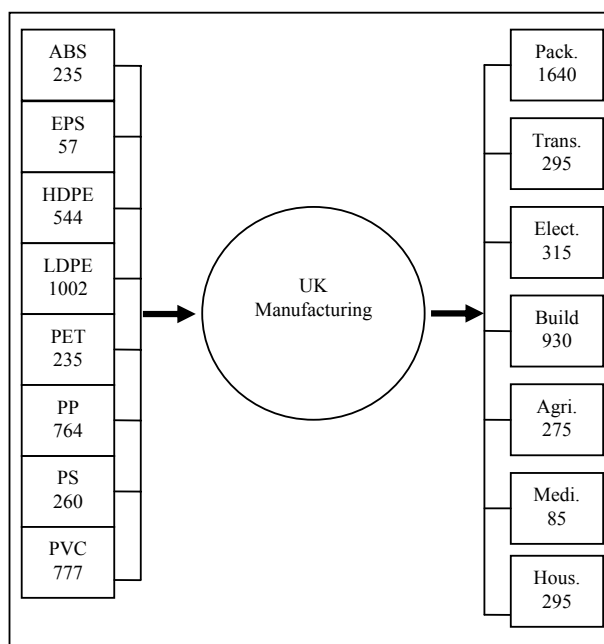

Fig. 1 World and Europe plastic production (1950-2007), including thermoplastics, PU, thermosets, elastomers, adhesives, coatings, sealants and PP fibres. PET, PA and polyacryl-fibres were excluded [6]. Abbreviations: CEE, central Europe and Russian trust.

II. MATERIALS AND METHODS

A. Polymers, Protocols and Procedure

Commercial grades of PET (ρ = 1.35 gm cc^{-1}; T_m = 260 ^{o}C) and PS (ρ = 1.03 gm cc^{-1}; T_m = 240 ^{o}C) were supplied from Ravago Plastics Co. (Arendonk, Belgium). Experimental runs where conducted in the R&D division at Ravago.

B. Kinetic Parameters Evaluation

In this study, we have determined the apparent activation energy (E_a) and the overall activation energy (E_o) using the general kinetics theory (GKT) previously used by Oh et al. [22]. Polymers subjected to thermal cracking, mainly under the influence of a fixed heating rate, undergo complicated processes, such as random chain scission, end chain scission, chain stripping, cross linking and coke formation. Apparent dynamic kinetics, useful for engineering design, is the focus of
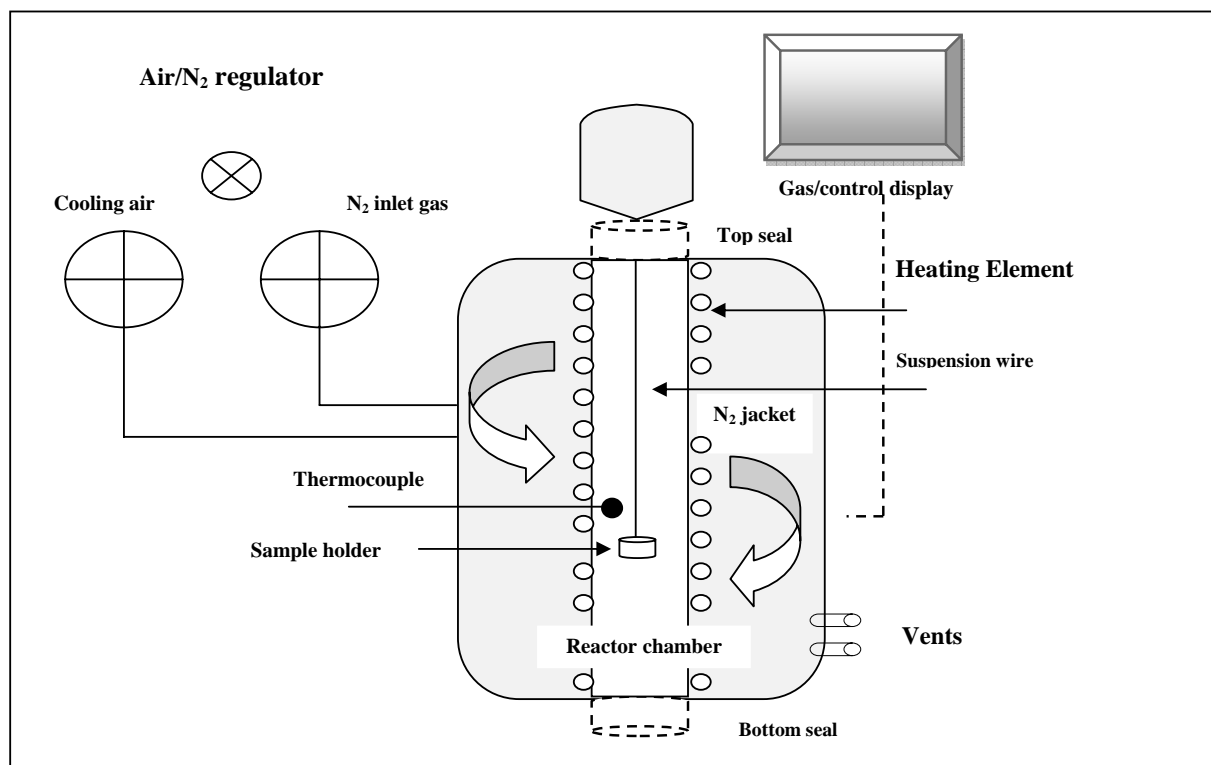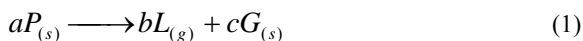
Fig. 3. Thermobalance reactor (TGA set-up) schematic showing main parts.

this section. For a given polymer, the degradation reaction is:

$$aP_{(s)} \longrightarrow bL_{(g)} + cG_{(s)} \quad (1)$$

The polymer degradation rate can be expressed as follows:

$$dx/dt = k(1-x)^n \quad (2)$$

where x is the polymer weight fraction decomposed at time t and k is rate constant given by the Arrhenius 1st order expression as follows:

$$k = A \exp(\frac{-E}{RT}) \quad (3)$$

where A is the frequency (pre-exponential) factor; E is the activation energy of the reaction (j/mol). Knowing that, A is not strictly a constant but depends on the collision theory parameter (A_o) and temperature (T), it is expressed as follows:

$$A = A_0 T^{1/2} \quad (4)$$

Substituting eqs.(3-4) in eq.(2), it gives:

$$dx_p/dt = A_0 T^{1/2} (1-x_p)^n \exp(\frac{-E}{RT}) \quad (5)$$

where x_p is the polymer weight fraction pyrolysed (weight loss) of a polymer, A is the Arrhenius fitting pre-exponential factor (min^{-1}), n is the reaction order and E_a is the activation energy (apparent) of a single path reaction (J mol^{-1}).

Dynamic kinetic rate constants depend not only on factors such as atmosphere, sample weight, shape and type, heating rate and flow rate, etc., but also upon the mathematical treatment used to evaluate certain parameters [22]. In this study, since the weight loss is determined prior to any analysis, the reaction order (n) was assumed to be equal to 1 for simplicity. The average activation energy was determined using the Coats and Redfern [23] approximation; after determining the apparent activation energies from each single heating rate:

$$E_{avg} = \frac{\sum_{i=1}^{n} E_i (x_i - x_{i-1})}{x_f} \quad (6)$$

where E_i is the activation energy corresponding to point i and time (t), x_i is the weight loss fraction at point i and x_f is the weight loss fraction at the final status of maximum degradation. An objective function was set to be minimized (maximizing the correlation coefficient between experimental and calculated values) to solve eq.(5). The objective function corresponds to the sum of %absolute errors calculated between the $-E/RT$ and the rest of the expression as follows:

$$OF = Minimize \sum_{i=1}^{n} \frac{|(E/R.T) - \ln(C)|}{E/RT} \quad (7)$$

i = 1, 2, 3, …. n (Maximum degradation temperature)

where OF is the objective function, E is the activation energy (J mol^{-1}) obtained at a given temperature (K), R is the universal gas constant (8.314 J mol^{-1}K^{-1}) and C is the expression given below:

$$C = \ln\left(\left[\frac{dx_s}{dT}\right].\frac{1}{A_o T^{1/2}.(1-x_s)^n}\right) \qquad (8)$$

III. RESULTS AND DUSCUSSION

A. Materials Behaviour under Dynamic Conditions

Fig.4 shows the solid conversion (x_s) as a function of temperature (^{o}C), in the case of PET, using five heating rates (3, 15, 50, 100 and 120 ^{o}C min^{-1}). Results show that PET starts to decompose at around 190 ^{o}C, whereas previous reports report that PET starts to decompose at temperatures up to 252 ^{o}C [24], depending on the polymer grade and experimental set-up. Subsequently, the polymer rapidly decomposes between 320-350 ^{o}C and at around 450 ^{o}C all samples have lost half of their initial weight. Saha and Ghoshal [25] studied the pyrolysis kinetics of two PET samples under dynamic conditions and reported on their behaviour. Both samples exhibited 70-80% weight loss between 380-515 ^{o}C; this was possibly attributed to the slower heating rates used in their study (10, 15 and 25 ^{o}C min^{-1}). At higher temperatures, between 490-650 ^{o}C, the samples continued decomposing smoothly with no appreciable decomposition reaction. The TG derivative curve (calculated from the data by diving the solid conversion difference and the difference in temperature) indicates a single step reaction. However, the reaction peak showed an inverse compared with the classical behaviour of other polymer, such as polyolefins. This is in agreement with the results obtained by Andel et al. [11], who also showed that PET under pyrolysis conditions exhibits high conversion with a single step reaction (namely PET to terephthalic acid). Fig.5 shows also that smaller peaks are obtained for higher heating rates.

In the case of PS, the solid conversion was achieved to maximum value ($\approx$ 1) at all heating rates (Fig.6). For $\beta = 3$ ^{o}C min^{-1}, PS totally decomposed at a temperature below 450 ^{o}C. Whilst at higher heating rates, the polymer reached its total conversion state at temperatures in excess of 550 ^{o}C. The reaction peak was observed at $\beta = 15$ ^{o}C min^{-1} (Fig.7). A shift of the reaction range was also observed at higher ramps, in agreement with previous findings in the literature [26-27].

B. Activation Energy and kinetic Rate Constants Estimation

Determination of the kinetic coefficients from dynamic experiments has been a matter of controversy [29]. This arises from deficiencies in the Arrhenius equation, the so called 'kinetic compensation effect'. It is known that the influence of the heating rate ($\beta = dT/dt$) must be considered in those processes that do not operate at constant temperatures, such as the non-isothermal experiments reported in this paper.
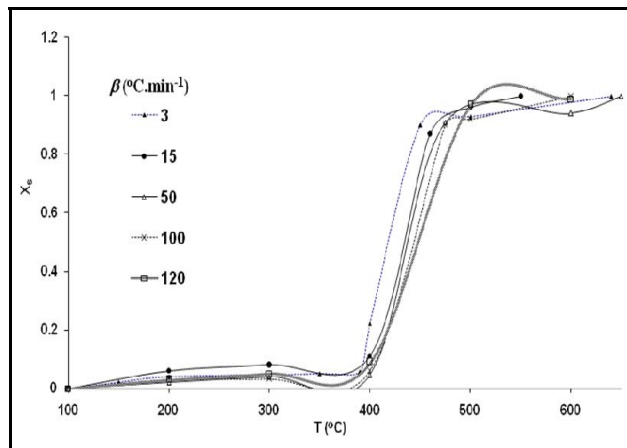

Fig. 4 Solid conversion as a function of temperature (^{o}C) for different heating rates on polyethylene terephthalate (PET).

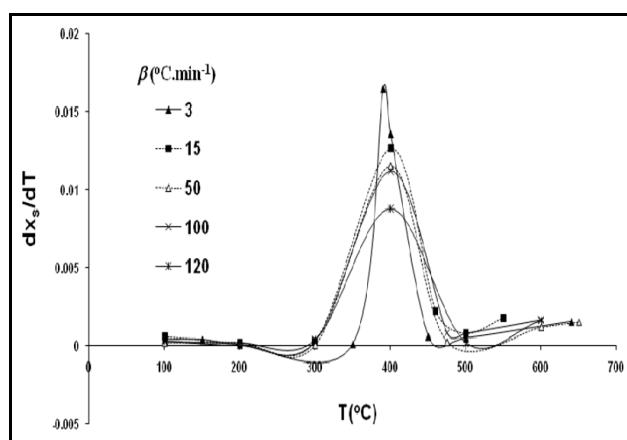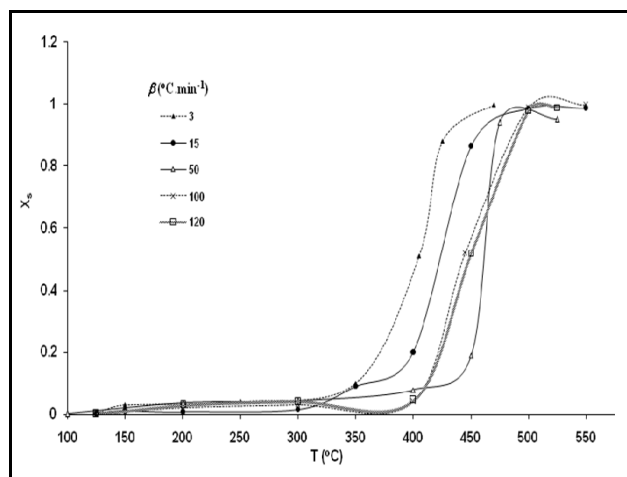Fig. 5. Values of dx_s/dT as a function of temperature (^{o}C) for different heating rates on polyethylene terephthalate (PET).

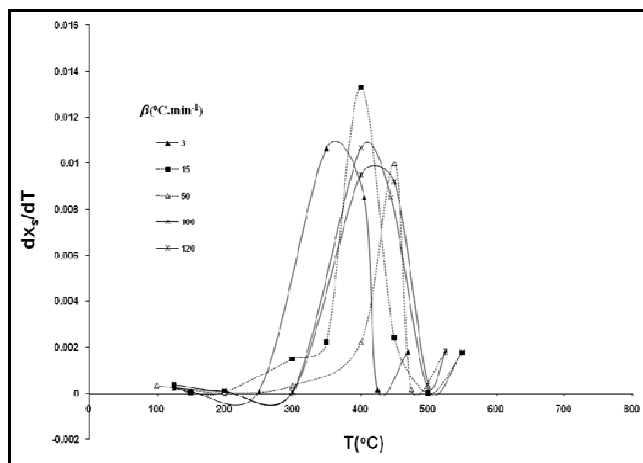Fig. 6. Solid conversion as a function of temperature (^{o}C) for different heating rates on polystyrene (PS).

Fig. 7. Values of dx_s/dT as a function of temperature (°C) for different heating rates on polystyrene (PS).

In this work, the GKT method was used to calculate the kinetic parameters of the polymer thermal cracking reactions investigated. Table 1 shows the estimated parameters (*i.e.* E_a, A_o and corresponding errors) obtained from the GKT for PET. The overall activation energy was estimated to be 180.02 kJ mol^{-1} (using the Coats and Redfren approximation). Overall activation energy estimation has always been dependant on the numerical methods used. Previous estimates of E_o reported by Martin-Gullon et al. [28] were between 186-203 kJ mol^{-1}, with a reaction order $n = 1$-1.02. Our work shows agreement with these estimations giving a reaction order equal to 1. Saha and Ghoshal [25] developed a low conversion n^{th} order model and determined the overall activation energy of PET (in conditions as low as 70% conversion) to be in the range of 322-338 kJ mol^{-1}. The work presented in this study is in agreement with their model estimates of the 1st order reaction. In the GKT approach, the E_a was decreasing with higher heating rates (β), similar to the semi-GKT (first part) model they have presented (derived from Coats and Redfern method).

Table 2 shows the estimated parameters (*i.e.* E_a, A_o and corresponding errors) obtained from the GKT for PS. The overall activation energy was estimated to be 157.78 kJ mol^{-1} from the GKT. Kim and Kim [26] reported values for E_o in the range of 164-249 kJ mol^{-1}, in agreement with the work carried out by Bouster et al. [27] and also this study.

In this following section, a model based on the weight loss of the polymers as a function of temperature was utilized to fit the experimental results. The GKT was used to validate the fit and re-calculate the apparent activation energy and collision theory parameter, based on results obtained.

The approach used in this research is based on modelling of the weight loss (in terms of solid conversion) against temperature. No reported literature carries out similar methodology, in fact, most dynamic modelling is concerned with the estimation of kinetic parameters rather than with the investigation of the behaviour of the polymer in a reactor chamber (hence the temperature element). Obtained models

could be coupled with the basic kinetic rate equations to predict product yields and evolution of the polymer under a number of conditions. The main equation used in solid conversion (x_s) prediction in the reactor chamber is expressed as follows (S-curve fit):

TABLE I

GENERAL KINETICS THEORY PARAMETERS, COLLISION THEORY PARAMETER (A_O), %ERROR BETWEEN THE EQ.(2) EQUALITY AND ACTIVATION ENERGIES ESTIMATED AT EACH HEATING RATE (β) FOR POLYETHYLENE TEREPHTHALATE (PET)

β °C/min	Temp (K)	- E/R.T	Error	Mean error (%), A_o and E_o (kJ mol^{-1})
3	373	57.97	0.416	
	423	51.12	0.33	
	473	45.71	0.21	
	623	34.71	0.013	ME = 0.14%
	663	32.61	0.07	$A_o = 9.99 \times 10^{+9}$ 1/(K$^{1/2}$.s)
	673	32.13	0.05	$E_a = 179.78$ kJ mol^{-1}
	723	29.90	0.05	
	773	27.97	0.11	
	913	23.68	2×10^{-8}	
15	373	52.58	0.36	
	473	41.46	0.16	
	573	34.22	8×10^{-9}	ME = 0.13%
	673	29.14	0.04	$A_o = 1 \times 10^{+10}$ 1/(K$^{1/2}$.s)
	733	26.75	0.13	$E_a = 163.03$ kJ mol^{-1}
	773	25.37	0.19	
	823	23.83	0.01	
50	373	51.59	0.33	
	473	40.68	0.14	
	573	33.58	0.07	ME = 0.19%
	673	28.59	0.07	$A_o = 9.99 \times 10^{+9}$ 1/(K$^{1/2}$.s)
	748	25.72	0.25	$E_a = 160$ kJ mol^{-1}
	873	22.04	0.37	
	923	20.85	0.13	
100	373	51.27	0.33	
	473	40.43	0.08	
	573	33.37	0.02	ME = 0.15%
	673	28.41	0.08	$A_o = 9.99 \times 10^{+9}$ 1/(K$^{1/2}$.s)
	748	25.56	0.21	$E_a = 159$ kJ mol^{-1}
	773	24.74	0.25	
	873	21.90	0.07	
120	373	50.30	0.32	
	473	39.66	0.12	
	573	32.74	0.03	ME = 0.20%
	673	27.88	0.10	$A_o = 9.99 \times 10^{+9}$ 1/(K$^{1/2}$.s)
	773	24.27	0.29	$E_a = 156$ kJ mol^{-1}
	873	21.49	0.31	

TABLE II
GENERAL KINETICS THEORY PARAMETERS, COLLISION THEORY PARAMETER (A_o), %ERROR BETWEEN THE EQ.(2) EQUALITY AND ACTIVATION ENERGIES ESTIMATED AT EACH HEATING RATE (β) FOR POLYSTYRENE (PS)

β °C/min	Temp (K)	- E/R.T	Error	Mean error (%), A_o and E_o (kJ mol^{-1})
3	398	47.74	0.31	ME = 0.11% A_o= 9.99x10^{+9} K$^{-1/2}$ s^{-1} E_a = 157.99 kJ mol^{-1}
	423	44.92	0.21	
	523	36.33	0.07	
	623	30.50	0.01	
	678	28.02	0.05	
	698	27.22	0.10	
	743	25.57	2.2 x 10^{-9}	
15	398	47.14	0.33	ME = 0.14% A_o= 9.00x10^{+8} K$^{-1/2}$ s^{-1} E_a = 156 kJ mol^{-1}
	423	44.35	0.24	
	473	39.66	0.16	
	573	32.74	0.07	
	623	30.11	0	
	673	27.88	0	
	723	25.95	0.07	
	773	24.27	0.26	
	823	22.79	0.13	
50	373	49.98	0.32	ME = 0.19% A_o= 9.98x10^{+9} K$^{-1/2}$ s^{-1} E_a = 155 kJ mol^{-1}
	473	39.41	0.09	
	573	32.53	0.04	
	673	27.70	0.16	
	723	25.78	0.14	
	748	24.92	0.28	
	798	23.36	0.27	
100	398	45.02	0.23	ME = 0.18% A_o= 9.99x10^{+9} K$^{-1/2}$ s^{-1} E_a = 149 kJ mol^{-1}
	473	37.88	0.06	
	573	31.27	0.13	
	673	26.62	0.15	
	718	24.96	0.21	
	773	23.18	0.30	
	823	21.77	0.18	
120	398	44.72	0.24	ME = 0.20% A_o= 9.99x10^{+9} K$^{-1/2}$ s^{-1} E_a = 148 kJ mol^{-1}
	473	37.63	0.06	
	573	31.06	0.16	
	673	26.45	0.16	
	723	24.62	0.22	
	773	23.02	0.31	
	798	22.30	0.25	

$$x_s = a + \left[\frac{(b-a)}{1+\exp(-(T_d - c)/d)} \right] \quad (9)$$

where at a given time (t, s) in the reactor chamber, x_s and T_d are the polymer's solid conversion and instantaneous dynamic temperature (K), and a, b, c, and d are optimized numerical constants which depend on the reaction range and heating rate (β). In the case of PET, high regressions were obtained for $\beta <$ 100 °C min^{-1} resulting in regression coefficients > 0.90. Eqs.(10-11) show the expressions obtained from fitting the experimental data for PET weight loss (expressed as solid conversion, x_s):

$$x_s = 9x10^{-5} + \left[\frac{0.99}{1+\exp(-(T_d - 699)/12.64)} \right];$$
$$\beta < 100 \text{ °C min}^{-1} \quad (10)$$

$$x_s = 0.001 + \left[\frac{0.99}{1+\exp(-(T_d - 715)/14)} \right];$$
$$\beta \geq 100 \text{ °C min}^{-1} \quad (11)$$

Figs. 8 and 9 show experimental and modelled results as a function of temperature range and Table 3 shows the GKT parameters estimated using the predicted values obtained from the model; %error between experimental and modelled results are also reported in the table. The overall activation energy (E_o) estimated from the modelled results was 180.08 kJ mol^{-1}, with a 0.03% error from the value estimated from experimental results (180.02 kJ mol^{-1}). The same methodology was used to develop the expressions of PS shown below. High regressions were estimated for $\beta < 50$ °C min^{-1} resulting in regression coefficients > 0.90. Eqs.(12-13) show the expressions obtained from fitting the experimental data for PS weight loss (expressed as solid conversion, x_s):

$$x_s = 0.0009 + \left[\frac{0.99}{1+\exp(-(T_d - 678)/10)} \right];$$
$$\beta < 50 \text{ °C min}^{-1} \quad (12)$$

$$x_s = 0.001 + \left[\frac{0.94}{1+\exp(-(T_d - 729)/4)} \right];$$
$$\beta \geq 50 \text{ °C min}^{-1} \quad (13)$$

Figs. 10 and 11 show experimental and modelled results as a function of temperature; Table 4 shows the GKT parameters estimated from the model including the %error between experimental and predicted results. The resulting activation energy was estimated at 158.15 kJ mol^{-1} with a 0.64% error.
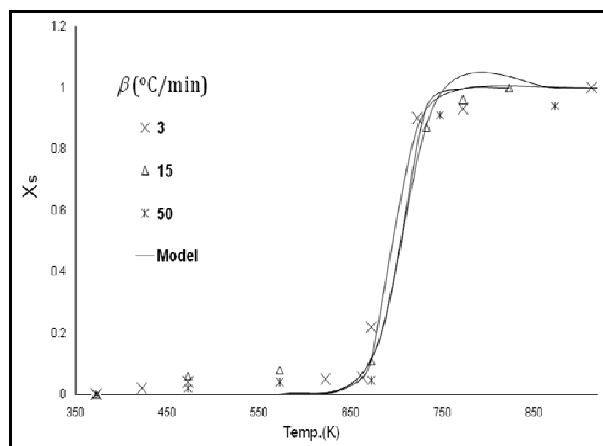

Fig. 8. Model and experimental solid conversion as a function of temperature (K) for = 3, 15 and 50 °C min^{-1} obtained for PET.

Fig. 9. Model and experimental solid conversion as a function of temperature (K) for β = 100 and 120 ^{o}C min^{-1} obtained for PET.

Fig. 10. Model and experimental solid conversion as a function of temperature (K) for β = 3, 15 and 50 ^{o}C min^{-1} obtained for PS.
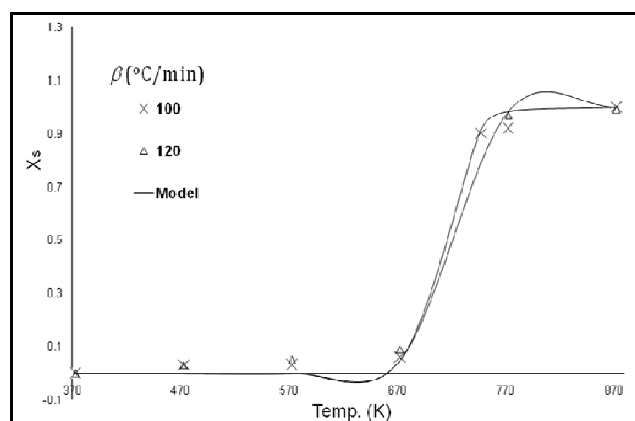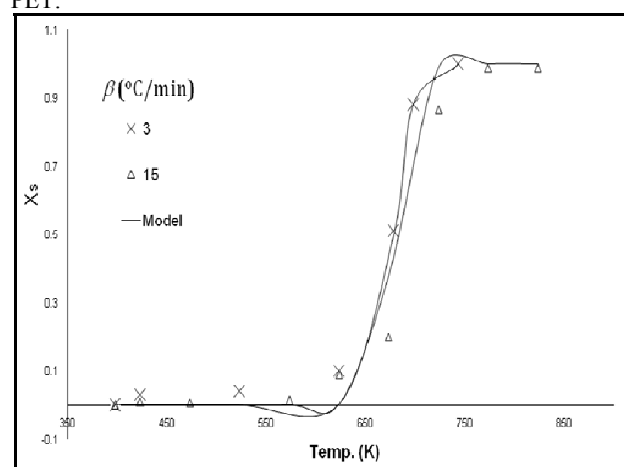

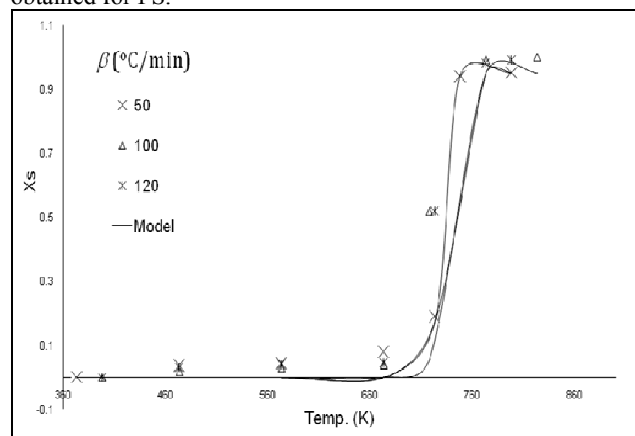Fig. 11. Model and experimental solid conversion as a function of temperature (K) for β = 50, 100 and 120 ^{o}C min^{-1} obtained for PS

TABLE III
GKT PARAMETERS USING MODELLED RESULTS FOR DYNAMIC TGA ON PET

β ^{o}C/min	Temp (K)	- E/R.T	Error	Mean error (%), A_o and E_o (kJ mol^{-1})
3	373	57.97	0.10	
	423	51.12	0.06	
	473	45.71	0.18	
	623	34.71	0.05	ME = 0.14%
	663	32.61	0.06	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	723	29.90	0.009	E_a = 180.06 kJ mol^{-1}
	773	27.97	0.01	
	913	23.68	0.24	
15	373	52.58	0.38	
	473	41.46	0.19	
	573	34.22	0.02	ME = 0.13%
	673	29.14	0.01	A_o= 1x10^{+10} 1/(K$^{1/2}$.s)
	733	26.75	0.10	E_a = 168 kJ mol^{-1}
	773	25.37	0.15	
	823	23.83	0.04	
50	373	51.59	0.33	
	473	40.68	0.15	
	573	33.58	0.06	ME = 0.19%
	673	28.59	0.06	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	748	25.72	0.24	E_a = 161 kJ mol^{-1}
	873	22.04	0.36	
	923	20.85	0.12	
100	373	51.27	0.33	
	473	40.43	0.09	
	573	33.37	0.02	ME = 0.15%
	673	28.41	0.07	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	748	25.56	0.21	E_a = 160 kJ mol^{-1}
	773	24.74	0.24	
	873	21.90	0.07	
120	373	50.30	0.33	
	473	39.66	0.13	
	573	32.74	0.02	ME = 0.20%
	673	27.88	0.09	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	773	24.27	0.27	E_a = 158 kJ mol^{-1}
	873	21.49	0.29	

IV. CONCLUSION

Current quantities of plastic waste produced all over the world have negative implications on the environment. Pyrolysis could have an important role in converting plastic waste into economically valuable hydrocarbons, which can be used either as fuels or as feed stock in the petrochemical industry. Dynamic pyrolysis most importance for industrial scale operations in which plastic waste composition represents a key issue for the end product yield and its properties. PET and PS are commonly present in high percentage in co-mingled waste plastics. In this work, dynamic pyrolysis of PET and PS was conducted using thermogravimetry in a thermobalance fixed reactor. It was concluded that:

- In the case of PET, a single step reaction was detected from the first derivate graph. Smaller peaks are associated with higher heating rates. It was also observed that the polymer rapidly decomposes between 320-350 ^{o}C, and at around 450 ^{o}C all samples have lost half of their initial weight.

TABLE IV
GKT PARAMETERS USING MODELLED RESULTS FOR DYNAMIC TGA ON PS

β $^oC/min$	Temp (K)	- E/R.T	Error	Mean error (%), A_o and E_o (kJ mol^{-1})
3	398	47.74	0.14	
	423	44.92	0.02	
	523	36.33	0.001	ME = 0.05%
	623	30.50	0.01	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	678	28.02	0.05	E_a = 157.99 kJ mol^{-1}
	698	27.22	0.10	
	743	25.57	0.015	
15	398	47.14	0.11	
	423	44.35	0.08	
	473	39.66	0.02	ME = 0.09%
	573	32.74	0.01	A_o= 9.00 x10^{+9} 1/(K$^{1/2}$.s)
	623	30.11	0.04	E_a = 1156.00 kJ mol^{-1}
	673	27.88	0.002	
	723	25.95	0.07	
	773	24.27	0.14	
	823	22.79	0.31	
50	373	49.98	0.20	
	473	39.41	0.76	ME = 0.31%
	573	32.53	0.37	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	673	27.70	0.15	E_a = 155 kJ mol^{-1}
	723	25.78	0.14	
	748	24.92	0.29	
	798	23.36	0.27	
100	398	45.02	0.11	
	473	37.88	0.84	ME = 0.40%
	573	31.27	0.43	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	673	26.62	0.23	E_a = 149 kJ mol^{-1}
	718	24.96	0.21	
	773	23.18	0.65	
	823	21.77	0.36	
120	398	44.72	0.11	
	473	37.63	0.85	ME = 0.45%
	573	31.06	0.44	A_o= 9.99x10^{+9} 1/(K$^{1/2}$.s)
	673	26.45	0.20	E_a = 148 kJ mol^{-1}
	723	24.62	0.23	
	773	23.02	0.63	
	798	22.30	0.33	

- For PS, the solid conversion was achieved to maximum value ($\approx$ 1) for all heating rates. At $\beta = 3$ ^oC min^{-1}, PS totally decomposed at a temperature below 450 ^oC, whilst at higher heating rates, the polymer reached its total conversion state at temperatures in excess of 550 ^oC.

- Fitting correlations were used to model the experimental data obtained for the polymers' solid conversion (x_s) as a function of temperature. This enabled to obtain the overall activation energy (E_o). For PET, values of (E_o) estimated from the modelled were 180.08 kJ mol^{-1}, with a 0.03% error compared with the experimental results (180.02 kJ mol^{-1}). For PS, the resulting activation energy was estimated at 158.15 kJ mol^{-1}, with a 0.64% error compared with the experimental results.

This investigation provides a fundamental understanding on the behaviour of these plastics during pyrolysis. This is an essential step towards the development of scaling relationship to larger scale processes.

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