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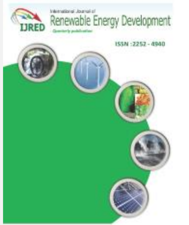

Research Article

Kinetics and Thermodynamic Analysis of Thermal Decomposition of Waste Virgin PE and Waste Recycled PE

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Abstract. Polyethylene is one of the key components of plastic wastes that can be utilized for resource recovery through pyrolysis method. Understanding of thermal decomposition properties and reaction mechanism of pyrolysis are necessary in designing an efficient reactor system. This study investigated the kinetics and thermodynamics parameters for individual waste virgin polyethylene (WVPE) and waste recycled polyethylene (WRPE) by using distributed activation energy model (DAEM). The calculated kinetic parameters (activation energy (Ea) and pre-exponential factor (A) were used to determine thermodynamic parameters (enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS). The activation energy (Ea) values for the WVPE estimated at conversion interval of 5%-95% were in the range of 180.62 to 268.04 kJ/mol while for the WRPE, the values were between 125.58 to 243.08 kJ/mol. This indicates the influence of exposure to weathering and mechanical stress during recycling on the course of the WRPE degradation. It was also found that the pyrolysis reaction for both WVPE and WRPE were best fitted using the two-dimensional diffusion (D2) model. The WVPE exhibited higher enthalpy and lower ΔG compared to WRPE, suggesting that less energy is required to thermally degrade recycled waste PE into products of char, gases and pyro-oils. Both kinetics and thermodynamics analyses were useful for the development of the plastic waste management through pyrolysis process.

Keywords: pyrolysis, degradation kinetics, iso-conversional, DAEM, polyethylene waste

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1. Introduction

Plastic materials which are made up from synthetic organic polymers have invaded every sector of the market because of their durability, lightweight, relatively low maintenance cost, corrosion resistance, good insulation, versatility and wide range of applications (Li *et al.*, 2018; Min *et al.*, 2020; Belmokaddem *et al.*, 2020). According to Ncube *et al.* (2021), it was estimated that 370 million tonnes of plastic was produced worldwide in 2019 and it is projected to increase exponentially in the future. Packaging sector, together with building and construction sector represent the largest end-use markets, accounting for almost 39.6% and 20.4% respectively. Automotive industry is the third biggest end-use market that constitute around 6.2% of the total plastic demand (Tiseo, 2021; Ncube *et al.*, 2021).

Polyethylene (PE) has been identified as the key component of the plastic waste generated with contribution of around 50% of the total plastic wastes produced (Singh & Devi, 2019). The PE waste can be classified as waste virgin polyethylene (WVPE) generated by domestic consumers and waste recycled polyethylene (WRPE) derived from plastic recycling industry. The main difference between both wastes is their physical stress history. Compared to WVPE, the WRPE have experienced mechanical recycling processes such as grinding, separation, washing and also thermal stress (Darus *et al.*, 2020; Schyns & Shaver, 2020).

Regardless of their post usage degradation history, plastic wastes are commonly disposed of by landfill or incineration (Singh & Sharma, 2016). The landfill approach is not suitable due to usage of large valuable space (Zamboulis *et al.*, 2019; Awoyera & Adesina, 2020) and loss of resource from the trapping of the plastic waste without further use (Mortezaeikia *et al.*, 2021). Besides, the piling of lumped plastic waste at landfill without a proper waste management system in place may release toxic chemicals and contaminate the surrounding water sources. On the other hand, incineration method requires a special treatment scheme to deal with hazardous combustion gases (Gourmelon, 2015; Tait *et al.*, 2020). Incomplete burning of plastic fragments may still exist and can be transported to the environment (He *et al.*, 2019). Considering the complexity of incineration process, pyrolysis has been considered as a more reliable and sustainable way to deal with plastic waste. It is an established technology, able to fully convert the plastic waste into valuable char, high calorific value gas and hydrocarbon-rich pyrolytic oil.

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Pyrolysis is a thermochemical process that is typically conducted in a custom-built reactor. For effective reactor design, knowledge of reaction kinetics and mechanism pathways for the degradation of polymeric waste by pyrolysis must be obtained. Thermogravimetric analysis (TGA) was commonly utilized to study the kinetics of thermal degradation of polymer during pyrolysis (Navarro *et al.*, 2018; Ng *et al.*, 2018; Saadatkhah *et al.*, 2020). The pyrolysis kinetics parameters of low- and high-density polyethylene (LDPE and HDPE) and polypropylene (PP) were studied by Aboulkas *et al.*, (2010) using iso-conversional method utilizing Friedman (FR), Kissinger-Akahara-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) models. Meanwhile, Coats Redfern and Criado methods were used to determine the reaction model. Pan *et al.*, (2021) investigated the migration of polyvinyl chloride (PVC) during pyrolysis. They conducted kinetic analysis by using FWO model and found higher activation energy (Ea) was associated with the second stage of pyrolysis at temperatures ranging from 360 to 550 ^{o}C. A recent study by Singh *et al.*, (2021) observed the synergistic effect during co-pyrolysis of corn cob and LDPE at various heating rates. They observed that the average activation energy (Ea) for LDPE varies for different types of iso-conversional kinetic models employed.

Although the iso-conversional method is widely used to model pyrolysis process of plastic, the derived reaction rate expression can only be used to describe processes with the same underlying reaction mechanism. This limits the applicability of this method since pyrolysis product ratios are strongly dependent on the reaction conditions. Such relationships between process conditions and product yields can be included in the reaction schemes in model-fitting methods but not for iso-conversional method (Burnham & Dinh, 2007, Samuelson, 2016). In addition, Junmeng *et al.*, (2017) suggested that iso-conversional kinetic method can lead to significant error in activation energy estimation as the method is derived by assuming constant activation energy from the beginning of the reaction until the desired conversion is achieved. In view of these limitations, Soriaverdugo *et al.*, (2015) suggested that a more accurate results can be achieved by using distributed activation energy model (DAEM). In this model, the activation energy is not assumed to remain constant throughout the pyrolysis process, rather it changes with the progress of the reaction and the value distribution obeyed the Gaussian or Gamma function (Ng *et al.*, 2018). Latifa *et al.*, (2020) conducted a study by applying the modified DAEM to obtain kinetic parameters for pyrolysis of raw and recycled PET. The authors reported that the activation energy (Ea) for raw and recycled polyethylene terephthalate (PET) were in the range of 120– 150 kJ/mol and 159–185 kJ/mol respectively.

An accurate kinetics analysis can lead to good prediction of thermodynamics properties of plastic pyrolysis. For example, Mumbach *et al.*, (2019) pyrolyzed various plastics waste to determine the energy changes throughout the pyrolysis process by estimating the value of enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS). It was found that the ΔS values can be used to predict the reactivity order of different plastic wastes.

Despite the relatively adequate availability of publications that dealt with calculating kinetics parameters for polymers, most of these studies focused on virgin polymers with less attention given to recycled polymers. To the best of our knowledge, kinetics analysis for PE wastes using simplified DAEM approach has not been attempted. Therefore, this study aims to examine the kinetics and thermodynamics parameters of waste PE (WVPE and WRPE) pyrolysis by using simplified DAEM. A comparison between WVPE and WRPE pyrolysis by analyzing the thermodynamics parameters together with identifying the reaction mechanisms involved was investigated to assess the influence of physical stress history of the wastes.

2. Materials and Method

2.1 Thermal decomposition data extraction and kinetics expressions

In this study, WRPE and WVPE were considered for simulation samples. The thermal decomposition data for both PE wastes were obtained from experimental data using TGA and its derivatives (DTG) curve published by Duque *et al.*, (2020). In their study, the samples were heated at 5, 10, 15, and 20 °C/min in the temperature range of 20 °C to 670 °C at an initial mass of 15 mg. This study considered the conversions interval between 5% to 95% for both plastic wastes. Firstly, the thermal decomposition data (mass loss as a function of temperature) for both WRPE and WVPE were extracted and simulated by KAS model to determine the reliability and reproducibility of the extracted kinetics data. Next, the extracted data were used in kinetics simulation using DAEM. Microsoft Excel was used to perform the calculations leading to preparation of the simulated TGA curve and determination of kinetics parameters by KAS and DAEM models.

Eqs. (1)-(3) represent the kinetics expressions used to evaluate the pyrolysis process. Eq. (1) shows the reaction equation in which f(x) represent the rate of solid decomposition and k is the reaction rate constant. Eq. (2) depicted Arrhenius equation which express the temperature dependence of reaction rate. Where A is pre-exponential factor (min^{-1}) and Ea is activation energy (kJ ·mol^{-1}). R is universal gas constant (8.314 J/mol.K) and T is the temperature (K). The reaction model represented by Eq. (3) shows the fraction conversion (x) which indicates the fraction of the total mass loss during pyrolysis process. m_0, m_i, and m_f represent the initial, instantaneous and final masses of the sample (mg) respectively.

$$\frac{dx}{dt} = k(T)f(x) \tag{1}$$

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

$$x = \frac{m_0 - m_i}{m_0 - m_f} \tag{3}$$

Combining Eq. (1) and (2) leads to Eq. (4), that describes the rate of decomposition of a single-step process (Duque *et al.*, 2020). For constant heating rate non-isothermal conditions ($\beta = dT/dt$), Eq. (4) can be written in the form of Eq. (5).

$$\frac{dx}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(x) \tag{4}$$

$$\beta\frac{\mathrm{dx}}{\mathrm{dT}} = \mathrm{Aexp}\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)\mathrm{f(x)} \tag{5}$$

where, β represents heating rate (°C/min), R is universal gas constant (8.314 J/mole·K), T is the temperature (K), and f(x) represents reaction model.

The TGA curve and its derivatives DTG curves provide the onset temperature, $\mathrm{T_{on}}$ and offset temperatures, $\mathrm{T_{off}}$ indicating the start and end of the sample thermal conversion. Peak temperature, $\mathrm{T_{peak}}$ shows the maximum rate of sample degradation at the corresponding temperature of their peaks. This value was used to determine the thermodynamic properties for both plastic waste samples.

2.2 KAS Model

By plotting Ln(β/T²) against 1/T, the kinetics parameters can be calculated from the slope at each given x (Jiang *et al.*, 2020).

$$\mathrm{Ln}\left(\frac{\beta}{\mathrm{T^2}}\right) = \mathrm{Ln}\left(-\frac{\mathrm{AR}}{\mathrm{E_a\,Ln(1-x)}}\right) - \frac{\mathrm{E_a}}{\mathrm{R}}\frac{1}{\mathrm{T}} \tag{6}$$

where, x is conversion rate of the waste sample (%), β is heating rate (°C/min), T is reaction temperature (K), R is universal gas constant (8.314 J/mol·K), A is pre-exponential factor (min^{-1}), and $\mathrm{E_a}$ is activation energy (kJ·mol^{-1}). A straight line was obtained by plotting $\mathrm{Ln}\left(\frac{\beta}{\mathrm{T^2}}\right)$ versus $\frac{1}{\mathrm{T}}$ at various conversions, from which apparent activation energy ($\mathrm{E_a}$) can be determined from the slope (Lawner & Mattu, 2012).

2.3 DAEM

Activation energy, $\mathrm{E_a}$ was estimated using Eq. (7) (Soriaverdugo *et al.*, 2015). Arrhenius equation of DAEM relates the main parameters of pyrolysis kinetics, the $\mathrm{E_a}$ and the pre-exponential factor, A at different heating rate for a determined temperature, T.

$$\ln\left(\frac{\beta}{\mathrm{T^2}}\right) = \ln\left(\frac{\mathrm{AR}}{\mathrm{E_a}}\right) + 0.6075 - \frac{\mathrm{E_a}}{\mathrm{R}}\frac{1}{\mathrm{T}} \tag{7}$$

The activation energy at various conversions can be obtained from the slope of a family of straight lines (Yan *et al.*, 2020). Extent of conversion, x for four heating rates were determined from the extracted data. Then, the Arrhenius plot was prepared followed by calculation and plotting of $\mathrm{Ln}\left(\frac{\beta}{\mathrm{T^2}}\right)$ versus $\frac{1}{\mathrm{T}}$ at selected values of conversion. Finally, the activation energy, $\mathrm{E_a}$, and the pre-exponential factor, A, were determined from the slope (m), and intercept of the Arrhenius plot as given in Eq. (8) and (9):

$$\mathrm{E_a} = -\mathrm{m.R} \tag{8}$$

$$\mathrm{A} = -\mathrm{m.exp(n - 0.6075)} \tag{9}$$

2.4 Thermodynamics Parameters Estimation

The thermodynamics parameters such as ΔH, ΔG and ΔS for pyrolysis reaction were determined using Eqs. (10)-(12) (Pradhan *et al.*, 2020 and Xu & Chen, 2013).

$$\Delta H = E_a - RT \tag{10}$$

$$\Delta G = E_a + RT_m In\left(\frac{K_b T_m}{hA}\right) \tag{11}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{12}$$

Where, E_a, K_b, R, T_m, h and A represent the activation energy (kJ·mol^{-1}), Boltzmann constant ($1.38 \times 10^{-23}\,\mathrm{kg.m^2s^{-2}K^{-1}}$), universal gas constant (8.314 J/mol·K), peak degradation temperature, Planck's constant ($6.626 \times 10^{-34}\,\mathrm{kg.m^2s^{-1}}$) and pre-exponential factor (min^{-1}) respectively.

3. Results & Discussion

3.1 Raw data reliability analysis

The data of mass loss against temperature for WVPE and WRPE pyrolysis were extracted from the published TGA and DTG curves and processed using Microsoft Excel. Table 1 shows the percentage deviation between the simulated kinetic parameters ($\mathrm{E_a}$ and A) values for WVPE and WRPE by using KAS method and the actual published parameters. As can be seen, the extracted data can be considered reliable as the percentage deviation was less than 3%. The data were subsequently used in the kinetics modelling using DAEM.

3.2 Determination of kinetic parameters

The extracted thermal decomposition data were processed by applying simplified DAEM to determine kinetics parameters for both WVPE and WRPE samples. The linear fit plot of Ln(β/T²) versus 1/T corresponds to different conversion rates of WVPE and WRPE pyrolysis are illustrated in Fig. 1 (a) and (b). Both Arrhenius plots were identical to each other showing a negative value for the slope. It can be observed that the individual plot tends to shift to the right as the conversion rate decreases. The $\mathrm{E_a}$and pre-exponential factors, A were determined from the slope and the intercept of solid lines.

Table 2 summarized the results of kinetic parameters of WVPE and WRPE calculated by using simplified DAEM at different conversions. In all the cases, the value of R^2 exceeded 0.98 indicating that the DAEM method could well predict the kinetics behaviour of the polymer pyrolysis. The results indicated that Eₐ and A values obtained for WVPE ranging from 180.622 to 268.043 kJ/mol and 6.604×10^{12} to 8.931×10^{17} min^{-1} respectively. Meanwhile, for WRPE it was found that the Ea and A values were lower than WVPE with values of 125.583 to 243.085 kJ/mol and 5.839×10^{8} to 1.425×10^{16} min^{-1} respectively. The range of values of activation energy obtained for the pyrolysis of virgin PE and recycled PE were comparable to those reported by Alsewailem & Almutabaqani, (2013) which confirmed that the recycled polymers require less activation energy than the virgin polymers.

Table 1
Percentage deviation between simulated and actual (Duque *et al.*, 2020) E_a and A of WVPE and WRPE by using KAS method

Waste Virgin Polyethylene (WVPE)

Conv. (%)	Sim. Ea (kJ/mol)	Ref. Ea (kJ/mol)	% dev.	Sim. A (1/min)	Ref. A (1/min)	% dev
5	180.62	182.30	0.92	6.219E+11	5.03E+11	-0.24
10	188.22	190.89	1.40	3.053E+12	8.77E+11	-2.48
15	194.40	198.30	1.97	9.794E+12	1.07E+13	0.08
20	217.97	221.94	1.79	6.038E+14	4.54E+14	-0.33
25	227.34	234.17	2.92	3.260E+15	1.59E+15	-1.06
30	230.33	235.70	2.28	5.987E+15	5.59E+15	-0.07
35	239.39	237.95	0.60	2.623E+16	6.10E+16	0.57
40	241.63	241.00	0.26	3.873E+16	5.00E+16	0.22
45	250.72	252.51	0.71	1.870E+17	6.74E+16	-1.77
50	250.69	254.04	1.32	1.961E+17	5.00E+16	-2.93
55	250.65	252.51	0.74	1.984E+17	1.93E+17	-0.03
60	250.61	255.57	1.94	1.920E+17	2.35E+17	0.18
65	260.12	255.57	1.78	9.446E+17	6.40E+17	-0.48
70	260.10	262.40	0.88	1.010E+18	5.24E+17	-0.93
75	261.13	258.63	0.97	1.316E+18	2.59E+18	0.49
80	263.29	264.74	0.55	2.059E+18	2.73E+18	0.25
85	263.97	267.80	1.43	2.137E+18	2.87E+18	0.25
90	264.76	260.87	1.49	2.628E+18	3.01E+18	0.13
95	268.04	268.10	0.02	4.912E+18	2.06E+18	-1.38

Waste Recycled Polyethylene (WRPE)

Conv. (%)	Sim. Ea (kJ/mol)	Ref. Ea (kJ/mol)	% dev.	Sim. A (1/min)	Ref. A (1/min)	% dev.
5	125.58	123.65	-1.57	5.50E+07	2.08E+07	1.64
10	144.18	147.58	2.31	1.63E+09	9.67E+08	0.69
15	156.31	164.83	5.17	1.46E+10	2.38E+10	-0.39
20	163.44	179.00	8.70	5.70E+10	3.97E+11	-0.86
25	179.61	193.26	7.06	1.03E+12	3.52E+12	-0.71
30	201.27	206.72	2.64	4.31E+13	5.13E+13	-0.16
35	219.17	214.91	-1.98	9.22E+14	3.07E+14	2.00
40	239.74	226.88	-5.67	3.31E+16	2.11E+15	14.68
45	236.01	229.16	-2.99	1.87E+16	3.07E+15	5.10
50	231.97	229.16	-1.22	9.31E+15	3.97E+15	1.35
55	228.78	232.86	1.75	5.86E+15	1.10E+16	-0.47
60	224.22	236.65	5.25	2.79E+15	1.43E+16	-0.80
65	223.90	238.14	5.98	2.83E+15	2.11E+16	-0.87
70	226.87	241.84	6.19	4.86E+15	2.72E+16	-0.82
75	227.86	242.63	6.09	6.09E+15	3.52E+16	-0.83
80	225.32	243.33	7.40	4.20E+15	3.97E+16	-0.89
85	231.89	244.13	5.01	1.18E+16	6.62E+16	-0.82
90	235.23	244.13	3.64	2.02E+16	5.12E+16	-0.61
95	243.08	246.33	1.32	7.84E+16	6.62E+16	0.18

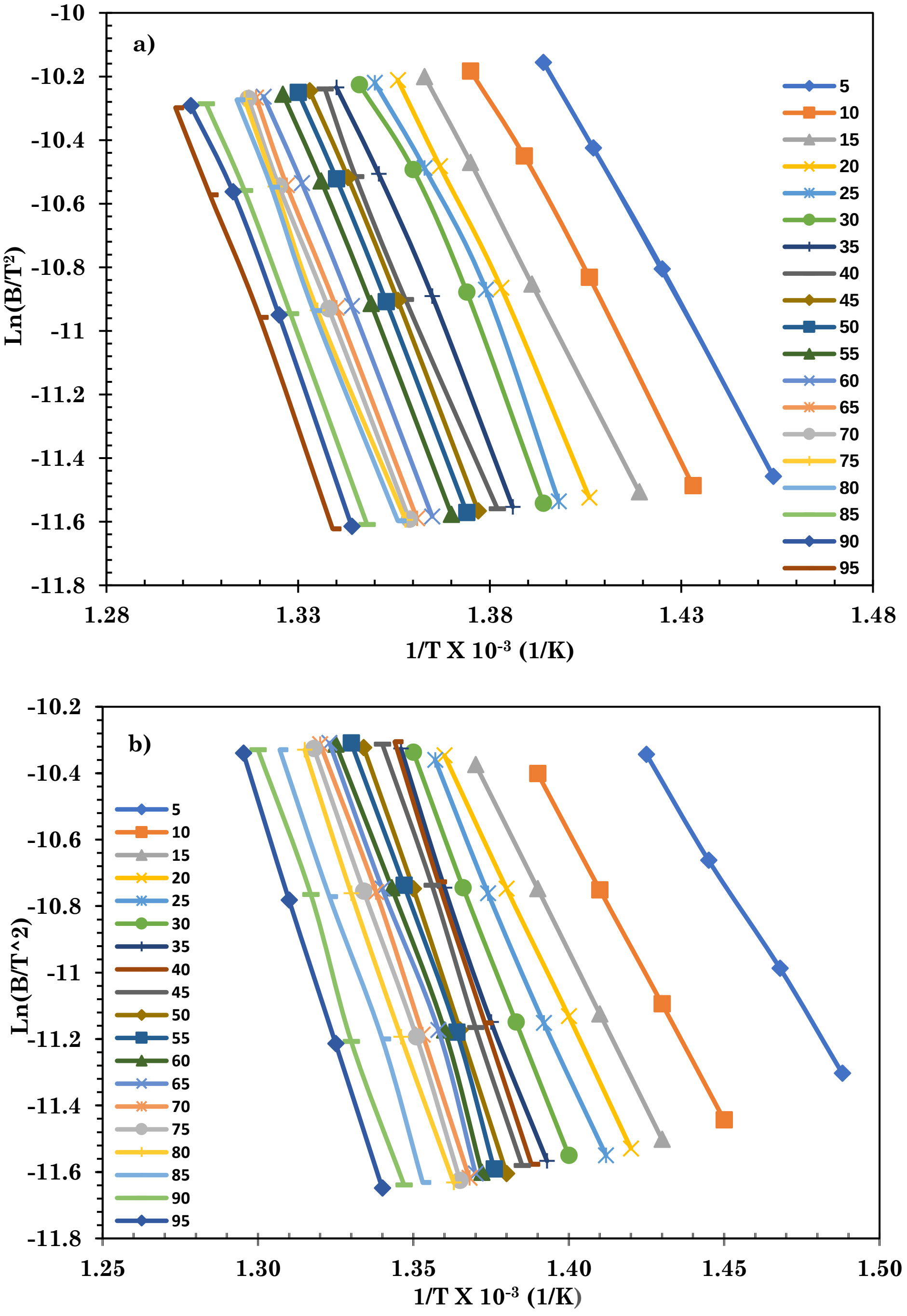

Fig 1. Arrhenius plot by using DAEM for a) WVPE and b) WRPE at different conversion

This is likely due to thermal degradation experienced by the recycled polymers when exposed to weathering including high temperature and humidity conditions. Thus, low activation energy was required to initiate the thermal degradation reaction at low temperature.

Furthermore, it was also noted from results tabulated in Table 2 that the activation energy showed an increasing trend with conversion. This is more pronounced for WVPE which is consistent with energy requirement to pyrolyzed the reactant into products like pyro-oil, gases, wax and coke-like residue. On contrary the material with degradation history as in the case of WRPE exhibited a fluctuated increment trend.

3.3 Analysis of reaction mechanisms

The $f(x)$ value was calculated at various conversions by using Eq. (5) and algebraic equations as listed in Table 3. The calculation was conducted to predict the reaction mechanisms for pyrolysis of both plastic wastes. The model which best suited the reaction mechanisms of both plastic wastes was obtained by comparing the Ea value from DAEM in Table 2 at 50% conversion with the Ea value determined from equations in Table 3. The results shown in Table 4 suggested that the thermal degradation mechanism of WVPE is most likely to be of two-dimensional diffusion (D2) model since the Ea value was 250.66 kJ/mol, similar to the value obtained by DAEM at

250.69 kJ/mol (Table 2). In the same way, the rate controlling mechanism for WRPE degradation was examined and proposed to be of D2 model. The value of the Ea, which was around 231.59 kJ/mol, was similar to the Ea obtained by DAEM 231.96 kJ/mol.

However, the mechanisms obtained by DAEM were different to reports on the rate controlling mechanisms for pyrolysis process of the PE obtained by the iso-conversional kinetics model. Aboulkas *et al.*, (2010) reported that the contracting spheres model was the likely rate controlling mechanism for pyrolysis of the PE. Other models, one dimensional diffusion, D1 (Saha *et al.*, 2021), nth order reaction model (Alam *et al.*, 2020) and 3D diffusion model, D3 (Singh *et al.*, 2021) were also reported as rate controlling mechanisms.

3.3 Estimation of thermodynamics parameters

The thermodynamics properties were determined using Eq. (10), (11), and (12). The variations of ΔH, ΔG and ΔS at various conversions for the virgin and recycled PE are given in Figs. 2 to 4. From Fig. 2, it can be seen that the enthalpy value (ΔH) was positive indicating the pyrolysis of WVPE and WRPE was endothermic process. It was observed that the difference between ΔH and Ea in Table 2 was relatively small for both plastic wastes (< 10 kJmol^{-1}) which indicates that the degradation of the plastic waste requires extra energy for it to be converted into product. Interestingly, the ΔH values recorded for the WVPE (182.17-258.37 kJ/mol) were consistently higher than the WRPE (138.26-228.82 kJ/mol) across the conversions studied. The results proved that when recycled polymers were pyrolyzed, the energy required was less than that of the virgin polymer. This may also imply that energy can be saved when processing recycled polymers by pyrolysis. It was thought that prolonged post-usage exposure of WRPE to heat and sunlight in the presence of oxygen may have altered chemical bonds within the polymer chain leading to formation of chemical functionalities such as carbonyl (Alsewailem & Almutabaqani, 2013). The changes to molecular structure of WRPE was compounded by the mechanical stress occurred during recycling process.

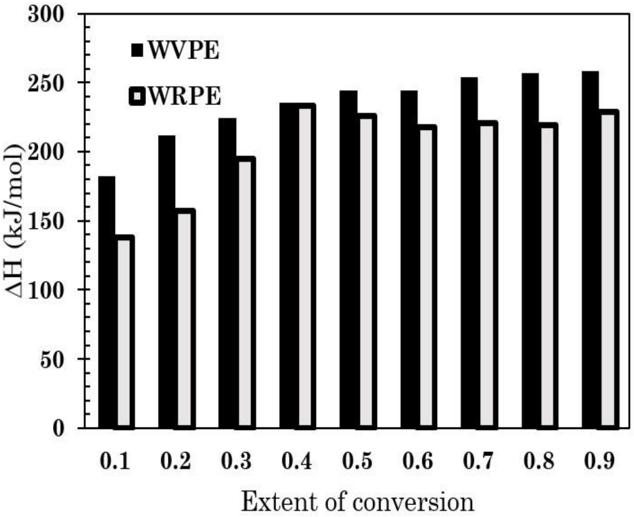

Fig. 2 The change of enthalpy(ΔH) versus extent of conversion for WVPE and WRPE.

Table 2
Activation energies, pre-exponential factor and correlation coefficient of WVPE and WRPE by DAEM

Conversion %	WVPE			WRPE		
	Ea (kJ/mol)	A (1/min)	R^2	Ea (kJ/mol)	A (1/min)	R^2
5	180.622	6.604E+12	0.9977	125.583	5.839E+08	1
10	188.221	1.578E+13	0.9979	144.181	8.450E+09	0.9999
15	194.398	3.283E+13	0.9863	156.312	4.920E+10	0.9997
20	217.968	1.474E+15	0.9981	163.437	1.391E+11	0.9998
25	227.338	6.172E+15	0.9991	179.607	1.958E+12	0.9996
30	230.331	9.144E+15	0.9991	201.274	6.576E+13	0.9925
35	239.385	3.317E+16	0.9996	219.165	1.166E+15	0.9986
40	241.630	4.130E+16	0.9990	239.743	3.527E+16	0.9994
45	250.717	1.704E+17	0.9950	236.010	1.707E+16	0.9959
50	250.692	1.541E+17	0.9952	231.969	7.317E+15	0.9950
55	250.650	1.353E+17	0.9921	228.776	4.000E+15	0.9952
60	250.609	1.141E+17	0.9916	224.220	1.659E+15	0.9931
65	260.120	4.901E+17	0.9989	223.896	1.469E+15	0.9916
70	260.095	4.570E+17	0.9960	226.872	2.199E+15	0.9989
75	261.134	5.173E+17	0.9997	227.862	2.392E+15	0.9960
80	263.288	6.970E+17	0.9998	225.318	1.421E+15	0.9997
85	263.970	6.136E+17	0.9996	231.894	3.387E+15	0.9998
90	264.759	6.216E+17	0.9925	235.228	4.778E+15	0.9996
95	268.043	8.931E+17	0.9984	243.085	1.425E+16	0.9925

Table 3
Algebraic expression functions of the most common

Mechanism	$\mathbf{f(x)}$
Power Law (P2)	$2x^{1/2}$
Power Law (P3)	$3x^{2/3}$
Power Law (P4)	$4x^{3/4}$
Avarami-Erofe've (A2)	$2(1-x)[-In(1-x)^{1/2}]$
Avarami-Erofe've (A3)	$3(1-x)[-In(1-x)^{2/3}]$
Avarami-Erofe've (A4)	$4(1-x)[-In(1-x)^{3/4}]$
Contracting Sphere (R2)	$2(1-x)^{1/2}$
Contracting Cylinder (R3)	$3(1-x)^{2/3}$
One-dimensional diffusion (D1)	$1/2x$
Two-dimensional diffusion (D2)	$[-In(1-x)]^{-1}$
Three-dimensional diffusion, Jander (D3)	$3(1-x)^{\frac{2}{3}}/[2(1-(1-x)^{1/3})]$
Ginstling-Brounshtein (D4)	$3/2((1-x)^{-1/3}-1)$
First-order (F1)	$(1-x)$
Second-order (F2)	$(1-x)^2$
Third-order (F3)	$(1-x)^3$

Table 4
Ea of WVPE and WRPE obtained by substituting of algebraic equation.

Model	**WVPE**	**WRPE**
	Activation energy (kJ/mol)	**Activation energy (kJ/mol)**
P2	219.3068	191.4649
P3	218.5274	190.4675
P4	218.8434	190.8718
A2	218.9868	191.0553
A3	218.2429	190.1032
A4	218.5765	190.5302
R2	231.5354	207.1151
R3	234.8323	211.3345
D1	245.1169	224.4967
D2	250.6622	231.5937
D3	262.9423	247.3099
D4	195.6335	161.1676
F1	225.5649	199.4741
F2	225.1389	198.9288

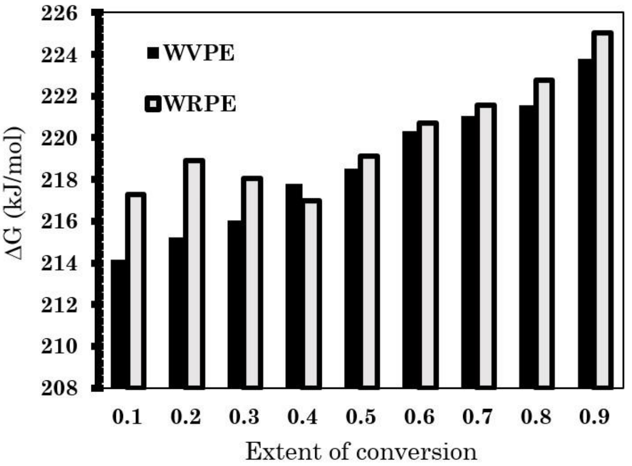

Fig. 3 The change of Gibbs free energy (ΔG) versus extent of conversion for WVPE and WRPE.

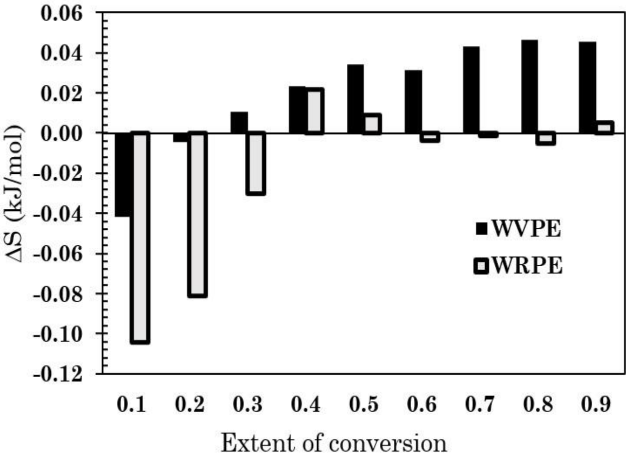

Fig. 4 The change of entropy (ΔS) versus extent of conversion for WVPE and WRPE.

Meanwhile the change in Gibbs free energy (ΔG) reflects the amount of available energy from plastic wastes pyrolysis reacting system. As can be seen in Fig. 3, the availability of energy within the system increases with conversions and that the WRPE pyrolysis exhibited slightly higher ΔG values compared to the WVPE. The values of ΔG for WVPE and WRPE were in the range of 214.15 to 223.77 kJ/mol and 217.27 to 225.05 kJ/mol respectively. Unlike WVPE which shows gradual increment of ΔG values as conversion increases from 10% to 90%, the trend for WRPE shows a decrease after 20% conversion before picking up again above 40% conversion. The ΔG for both samples were closely matched at conversion higher than 40% due to similarity in molecular species present in the reactions (Moldoveanu, 2019) considering both PE wastes comprises of long carbon chain with two hydrogen atoms attached to each carbon atom (Ghatge *et al.*, 2020).

The changes in entropy (ΔS) showed both negative and positive values for the WVPE and WRPE as shown in Fig. 4. Low reactivity and delayed response of system to form activated complex occur at lower values of ΔS while large values of ΔS correspond to the high reactivity and quicker response of system to form the activated complex (Alsewailem, 2009). As indicated by Fig. 4, reactivity of the pyrolysis system increases with conversion for the WVPE as signalled by the positive change in ΔS magnitudes. On contrary, the pyrolysis of WRPE exhibited lower reactivity as indicated by the low ΔS values throughout the conversion interval studied. The irregular trend in ΔS obtained from the WRPE pyrolysis shows that the decomposition is rather complex for the recycled PE.

4. Conclusions

In this study, kinetics parameters, pyrolysis mechanisms and thermodynamics parameters for WVPE and WRPE wastes pyrolysis were investigated using DAEM model fitting. The kinetics results suggested that pyrolysis of the WRPE required less activation energy compared to pyrolysis of the WVPE indicating the influence of weathering and mechanical stress history on the course of the WRPE carbon chain degradation. Thus, WRPE can be considered as a potential candidate for pyrolysis since it can be pyrolyzed at lower energy consumption. Further evaluation on the thermal degradation of the WVPE and WRPE found that pyrolysis of both materials was best fitted with two-dimensional diffusion (D2) model. The feasibility and spontaneity of the pyrolysis process was predicted through the determinations of thermodynamics parameters such as ΔH, ΔG, and ΔS. The WRPE exhibited lower enthalpy and higher ΔG, indicating that recycled waste PE required less energy than virgin waste polymer to degrade thermally into pyrolysis products of char, gases and pyro-oils. The knowledge obtained from this study may contribute to energy recovery from waste plastic for better solid waste management through pyrolysis as an alternative to landfill and incineration.

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