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Investigating kinetic behavior and reaction mechanism on autothermal pyrolysis of polyethylene plastic

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ABSTRACT

To reduce the energy supply for pyrolysis, autothermal pyrolysis is one of the most promising approaches to upcycle plastic waste. In this work, both single-step and multi-step methods were applied to perform kinetic studies of low-density polyethylene (LDPE) pyrolysis under oxidative atmospheres (0, 5, and 10% O₂ balanced by N₂) by changing the heating rate from 5 to 20 K min⁻¹. Miura integral method was then used to estimate the apparent activation energy. The major findings showed that the multi-step method using asymmetric double sigmoidal (Asym2Sig) deconvolution procedure was more appropriate to study kinetic behaviors of LDPE autothermal pyrolysis. The activation energy needed for LDPE pyrolysis under N₂ was 271 kJ·mol⁻¹, while the activation energies of the three pseudo-reactions under 5% O₂ were 71, 153 and 189 kJ·mol⁻¹, and under 10% O₂ were 74, 224 and 169 kJ·mol⁻¹, indicating that LDPE autothermal pyrolysis was more energy-saving than conventional LDPE pyrolysis. Additionally, the reaction mechanism was proposed to provide an accurate and critical guideline for commercializing this novel technical route, which is beneficial to achieving sustainable plastic waste management and mitigating plastic pollution, simultaneously.

1. Introduction

Plastic has been widely used due to its characteristics including low production cost, high plasticity, low density, etc. [1,2]. It was estimated that the amount of plastic produced worldwide was up to 367 million tons in 2020 [3]. Most plastic produced was either landfilled or dumped into the natural environment, taking 200-500 years to completely degrade [4], while only about 14% was recycled [5]. Inappropriate treatment of the plastic waste has led to several environmental pollution such as contamination of aquatic ecosystems [6]. So far, plastic pollution has been considered as one of the most severe environmental concerns besides climate change [7]. It's estimated that the plastic waste is expected to be accumulated up to 12 billion tons by 2050 [8]. Recycling plastic waste in a sustainable and practical manner has attracted arousing interest. Among various plastic recycling method, chemical recycling of plastic waste into value-added products has been studied extensively [9]. With the advantages of generating combustible gases and oil, pyrolysis has attracted considerable attention from both academic and industrial communities for upcycling of plastic waste [10, 11]. However, the pyrolysis is an endothermic process and can be affected greatly by heat and mass transfer [12]. With the expansion of reactor scale, the increase rate of heat demand exceeds that of heat supply, which makes the up scale and commercialization of pyrolysis a problem [13,14]. Recently, oxidative pyrolysis or autothermal pyrolysis has been explored for biomass pyrolysis, in which small amount of oxygen is introduced into the pyrolysis reactor leading the partial oxidation of pyrolysis products [15]. Compared to the conventional pyrolysis in an inert atmosphere (allothermal pyrolysis), autothermal pyrolysis can realize in-situ heating and energy self-sufficiency of pyrolysis process, greatly simplifying the pyrolysis reaction system, without significantly affecting the yields and distributions of final products [16,17]. Chen et al. [18] studied the pyrolysis of rice straw, corn straw and corncob under both inert and oxidative atmospheres. It shows that the component of liquid products changed moderately except benzene and phenol with the increasing of O₂ concentration. Peterson et al. [16] studied the effect of oxygen addition on the formation of phenolic oligomers from the pyrolysis of red oak. The results showed that the

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Nomenclature	Subscripts			
	0 mean			
Abbreviations	f final			
HDPE High-density polyethylene	p peak			
LDPE Low-density polyethylene	t at any time			
LLDPE Linear low-density polyethylene				
PP Polypropylene	Symbols			
DTG Derivative thermogravimetric	E Activation energy, kJ·mol ⁻¹			
PVC Polyvinyl chloride	A Pre-exponential factor, s^{-1}			
TC Thermogravimetric	<i>R</i> Gas constant, $J \cdot mol^{-1}K^{-1}$			
Acum 20 Acummetric double sigmeidel	R^2 Coefficient of determination			
DEAM Distributed active energy model	T Temperature, K			
DEAM Distributed active energy model	t Time, s			
Greek letters	w Weight percentage, %			
α Conversion rate	w_1 Full width of half maximum			
β Heating rate, K·min ⁻¹	<i>w</i> ₂ Variance of low-energy side			
θ Amplitude	<i>w</i> ₃ Variance of high-energy side			

Table	1

Literatures using multi-step method by dividing temperature ranges.

Raw material	Conversion rate/ Temperature ranges	E_0 for each stage	Ref.
Beech wood	528–593 K, 528–707 K, 603–708 K	76 \pm 21 kJ mol ⁻¹ , 143 \pm 10 kJ mol ⁻¹ , 44 \pm 6 kJ mol ⁻¹	[27]
Fire retardant	533–603 K, 603–673 K, 673–773 K	155, –, 329 kJ mol ⁻¹	[28]
Cladophora glomerata	493–573 K, 573–673 K, 973-750 K	160-170, 221–239, and 157–168 kJ mol ^{–1}	[29]
Plastics, tire	0.05–0.20,0.20–0.45, 0.45–0.95	65-87, 34–92, 138–208 kJ mol ^{–1}	[30]
PVC cable sheath	530–630 K, 670–800 K, 930–1000 K	142 and 235 kJ mol $^{-1}$ for the first two stage	[31]

Literatures using multi-step method employing deconvolution functions.

Raw material	Deconvolution method	E_0 for pseudo- component	Ref.
Pine wood and PE	Fraser-Suzuki	137, 167, 227, 246 kJ mol ^{–1}	[32]
Pine sawdust, edible fungi spent substrate	Bi-Gaussian	212-343, 139–172 and 128–147 kJ mol ^{–1}	[33]
Bamboo waste	Asym2Sig	176, 200 and 158 kJ mol^{-1}	[34]
Plastic solid waste	Asym2sig	171, 182, 267 kJ mol ⁻¹	[35]
Tobacco stem	Asym2Sig	192, 189, 176 kJ mol ⁻¹	[36]
Imperata Cylindrica	Asym2sig	195, 180 and 220 kJ mol^{-1}	[37]

atmosphere only led to a slight difference in the ultimate analysis, weight-average molecular weight and number-average molecular weight of products. Pham et al. [17] conducted oxidative pyrolysis of pine wood, wheat straw and miscanthus pellets, and the results showed that the peak temperature during pyrolysis for all feedstock was up to 993 K. Polin et al. [19] investigated the impact of oxygen-to-biomass equivalence ratio for autothermal process. It was found that the amount of oxygen required for autothermal pyrolysis was only about one tenth of that needed for complete combustion. Previous study also suggests that heat transfer is improved significantly during biomass oxidative pyrolysis. Heat transfer limitation was only observed when feedstock was chunked in the reactor [20].

Though the references have indicated the potential of autothermal pyrolysis in biomass conversion for the production of valuable chemicals and fuels, there were only scattered studies that focused on autothermal pyrolysis of plastic. The knowledge learned from biomass autothermal pyrolysis does not lend itself to plastic, due to the distinct difference between the thermochemical properties of the natural and synthetic polymer. In this study, the kinetic behaviors and reaction network of plastic autothermal pyrolysis will be explored.

Pyrolysis of solid fuels is a very complex process, in which a set of competitive, parallel, and sequential reactions occur simultaneously [21,22]. With incorporation of oxygen, autothermal pyrolysis of plastic is even more complex [23,24]. The kinetic studies of pyrolysis can be mainly classified into single-step and multi-step methods. Single-step method, considering the whole process as a global reaction, showed some deficiencies to perform precise kinetic analysis of complex pyrolysis process. Compared to single-step method, multi-step method that separated the whole process into several stages has been approved more appropriate to study the kinetically complex reactions [25,26]. In multi-step method, the pyrolysis process can be separated into multi-stage processes based on the degradation temperature range (or conversion rate range). Some previous studies were list in Table 1.

Deconvolution procedure is more commonly applied in multi-step method to separate the whole process into multiple reactions. Symmetric and asymmetric functions can be employed during the algorithm process of deconvolution. A comparative study of symmetric functions and asymmetric functions for fitting curves of solid fuels reactions has been conducted by Perejón et al. [38]. Under the condition of E_0 at 200 kJ·mol⁻¹, pre-exponential factor (A) at 6×10^{17} min⁻¹, contracting cylinder kinetic model, the coefficient of determination R^2 for using Gaussian, Lorentzian, Weibull, and Fraser-Suzuki functions were 0.905, 0.898, 0.976, and 0.998, respectively, revealing that the asymmetric functions showed a more accurate fit. The asymmetric functions, including Fraser-Suzuki [32], Bi-Gaussian [33], Weibull [39], asymmetric double sigmoidal (Asym2Sig) functions [34], are preferred for the pyrolysis of solid fuels (see Table 2). The Asym2Sig has been widely used in the kinetic study of biomass pyrolysis to deconvolute the whole pyrolysis process to several stages well, and the kinetic results proved to be reliable and accurate [34-37].

Polyolefins, mainly composed of high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and polypropylene (PP), are the most used plastic in the world, accounting for more than 60% of the global solid waste [40]. LDPE is commonly used for plastic bags and food wrapping [41], and the global production of which has reached 20.9 million tons in 2016, growing with a certain rate every year [42]. Thus, LDPE was chosen as raw material in this study. The kinetics of LDPE autothermal pyrolysis under different oxygen concentrations (0, 5, and 10% O₂ balanced by N₂) have



Fig. 1. TG and DTG curves of LDPE under pure N_2 (a), 5% O_2 (b), and 10% O_2 (c) atmospheres at different heating rates.

been analyzed using both single-step and multi-step methods. Temperature range-based procedure and Asym2Sig deconvolution procedure were also compared for the multi-step method. The Miura integral method was used to calculate the apparent activation energy.

2. Materials and methods

In this study, LDPE was firstly pyrolyzed in the thermal analyzer under both inert and oxidative atmospheres at different heating rates. The kinetic analysis of LDPE pyrolysis was then performed using Miura integral method by employing both single-step and multi-step method.

2.1. Materials

The LDPE (average Mw \sim 4000 by GPC, average Mñ1700 by GPC) powder purchased from Sigma-Aldrich, was used directly in this study without any treatment before experiment.

2.2. Thermogravimetric analysis

The experiments in this study were carried out using a TGA/DSC 3+ synchronous thermal analyzer from METTLER TORLED Co., Ltd. A given weight of 8.5 ± 0.2 mg of LDPE was put into a 70 µL alumina crucible. To explore the effects of different pyrolysis atmospheres and heating rates on the thermal characteristics of LDPE plastic, the non-isothermal experiments were conducted from room temperature to 1173 K under three different atmospheres (0, 5 and 10% O₂ balanced by N₂) with a total flow rate of 100 mL·min⁻¹ at heating rates of 5, 10, and 20 K min⁻¹.

2.3. Kinetic study

2.3.1. Miura integral method

Miura integral method is originated from distributed activation energy model (DAEM) but offers a numerical solution to DAEM, and is reported to be a feasible way to determine the kinetic parameters [43–45]. DAEM assumed that a series of reactions occurred simultaneously, and can be expressed as Eq. (1):

$$\frac{w_t}{w_f} = 1 - \int_0^\infty exp \left[-A \int_0^t exp \left(-\frac{E}{RT} \right) dt \right] f(E) dE$$
(1)

where A (s⁻¹), E (kJ·mol⁻¹), R (J·mol⁻¹ K⁻¹), T (K), and t (s) represent pre-exponential factor, activation energy, gas constant, temperature and time, respectively. w_t is the weight percentage at time t and w_f is the weight percentage at the final of the reaction. f(E) (kJ·mol⁻¹) denotes the activation energy distribution, and conforms to Eq. (2):

$$\int_{0}^{\infty} f(E)dE = 1 \tag{2}$$

Based on the DAEM function, the Miura integral method, assuming the reaction being first-order, is given as Eq. (3):

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT}$$
(3)

where β (K·min⁻¹) is the heating rate. By plotting $\ln \frac{\beta}{T^2}$ versus $\frac{1}{T}$, the activation energy can be obtained from the slope. The quality of the regression was evaluated using coefficient of determination (R^2), root mean square error (RMSE) and mean absolute error (MAE), as expressed



Fig. 2. $\ln(\beta \cdot T^{-2})$ against $1000 \cdot T^{-1}$ linear fitted curves and $E_{\alpha} \cdot \alpha$ estimated by Miura integral method under N₂ (a) and (b), 5% O₂ (c) and (d), 10% O₂ (e) and (f) for LDPE pyrolysis (the two borders of the blue area represented the activation energy above and below the 20% of E_0). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Pre-exponential factors of LDPE pyrolysis under N₂.

-		10 0							
А	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
A (s ⁻¹)	1.5	3.5	5.9	2.2	1.8	1.4	1.4	1.6	2.6
	$^{ imes}$ 10 ¹⁴	$^{ imes}$ 10 ¹⁶	$^{ imes}$ 10 ¹⁷	$^{ imes}$ 10 ¹⁹	$^{ imes}$ 10 ¹⁹	$^{ imes}$ 10 ²⁰	$^{ imes}$ 10 ²¹	$^{ imes}$ 10 ²¹	$^{ imes}$ 10 ²⁰

Table 4

Summary of temperature ranges of peak-1, peak-2 and peak-3 obtained by changing heating rates under 5% and 10% O2 atmospheres.

Heating rate (K·min ^{-1})	T _{range} under 5% C	T _{range} under 5% O ₂ (K)			T _{range} under 10% O ₂ (K)			
	peak-1	peak-2	peak-3	peak-1	peak-2	peak-3		
5	571-628	628–701	701–742	557-606	606–682	682–767		
10	588-647	647–707	707–725	573-623	623–676	676–755		
20	606–671	671–718	718–728	589–644	644–683	683–723		

in Eqs. (4)-(6):

$$R^{2} = 1 - \frac{\sum_{i=1}^{n} (h_{i} - m_{i})^{2}}{\sum_{i=1}^{n} (h_{i} - \overline{y})^{2}}$$
(4)

RMSE =
$$\sqrt{\frac{1}{n} \sum_{i=1}^{n} (h_i - m_i)^2}$$
 (5)

$$MAE = \frac{1}{n} \sum_{i=1}^{n} |h_i - m_i|$$
(6)

where *n* is the number of data, h_{i} , \overline{h} , m_{i} represents the calculated value, the average of calculated value and experimental value, respectively.

2.3.2. Judgement of single-step reaction

According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC), if the deviation of E_{α} to E_0 fluctuates within 20% of E_0 , the reaction can be considered as a single-step reaction. Otherwise, it should be a multi-step reaction [46]. It can be judged according to Eq. (7) and Eq. (8):

$$E_0 = \frac{\sum_{\alpha=0.1}^{0.9} E_{\alpha}}{9}$$
(7)

$$E_0 - 20\% E_0 < E_a < E_0 + 20\% E_0 \tag{8}$$

where E_{α} (kJ·mol⁻¹) is the activation energy at α .

2.3.3. Asymmetric double sigmoidal (Asym2Sig) function The Asym2Sig can be expressed as Eq. (9):

$$y = \frac{\theta}{1 + \exp\left(\frac{-(T - T_p + \frac{w_1}{2})}{w_2}\right)} \left[1 - \frac{1}{1 + \exp\left(\frac{-(T - T_p + \frac{w_1}{2})}{w_3}\right)}\right]$$
(9)

where θ is the amplitude, T_p is the peak temperature of each curve; w_1 presents full width of half maximum ($w_1 > 0$), and w_2 and w_3 are shape parameters, presenting variance of low-energy side and high-energy side ($w_2 > 0$ and $w_3 > 0$). The parameters of Eq. (9) were adjusted for the purpose of getting a satisfying value of nonlinear coefficient of determination R^2 from the experimental and calculated values.

3. Results and discussion

3.1. Thermal behavior of LDPE

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) curves of LDPE pyrolysis under N₂ at different heating rates are presented in Fig. 1 (a). It showed that there was only one decomposition peak, and the temperature range for active pyrolysis under this condition was narrow, with the start temperature being around 573 K and the end temperature about 823 K, which was in accordance with previous studies [47–49]. The weight losses of active pyrolysis stage with heating rates of 5, 10, and 20 K·min⁻¹ were 96.8%, 96.2%, and 94.8%, respectively.

As displayed in Fig. 1, compared with LDPE pyrolysis under N₂, the decomposition temperature ranges for active pyrolysis under oxidative atmospheres were relatively wider (425-909 K). Lv et al. [50] analyzed the pyrolysis of high-protein microalgae in argon and discovered the main degradation temperature range was 473-823 K. Guo et al. [51] studied the oxidative pyrolysis of microalgae and reported the end of decomposition temperature was up to 973 K, indicating the temperature range of thermal decomposition was wider in oxidative atmosphere compared to that of inert atmosphere. Senneca et al. [52] classified the oxidative pyrolysis of solid fuels according to the DTG curves into three cases: (a) there are two peaks, with one overlapping with the DTG curve in inert atmosphere, the other representing the combustion of char; (b) there is only one peak that might be in different shape with that in inert atmosphere; (c) there are two peaks, different from case (a), the first peak being corresponding to the DTG curve in inert atmosphere but having a different shape and the second peak being related to heterogeous oxidation. As displayed in Fig. 1 (b) and (c), there were two main stages under oxidative atmosphere. The first stage was related to the DTG curve in N2 and the second stage was caused by the oxidation of products, so the oxidative pyrolysis of LDPE was the case (c). For the first degradation stage under oxidative atmospheres (shown in Fig. 1 (b) and (c)), two peaks were mainly observed, excepting those obtained at the heating rate of 20 K·min⁻¹. Huang et al. [53] investigated that the first peak could be caused by the breakage of the branched chains and the second peak could be attributed to the cleavage of the main chains, with the oxidation of products contributed to the third peak, which offers a possible mechanism for LDPE oxidative pyrolysis.

For autothermal pyrolysis, the shape of DTG curves was greatly affected by the oxygen concentration. Compared to pyrolysis under 5% O_2 (423–909 K), the overall decomposition temperature range of LDPE pyrolysis under 10% O_2 shifted to 443–909 K. It can be seen from Fig. 1 (b) and (c) that the height of first and second decomposition peaks were almost the same under 5% O_2 , whereas the first degradation peak was the main peak under 10% O_2 . This can be attributed to the more violent reactions happened under higher O_2 concentration, in accordance with



Fig. 3. E_{a^{-a}} a estimated by Miura integral method for LDPE pyrolysis by separating peak temperature ranges under 5% O₂ (a-c) and 10% O₂ (d-f).

the oxidative pyrolysis of other plastics [54,55]. In addition, the weight losses of third decomposition peak under 10% O₂ (5.3–10.4 wt%) were higher than that of 5% O₂ (1.6–8.3 wt%), implying oxidation of products was enhanced at higher oxygen concentration.

As the heating rate increased, the overall decomposition temperature range shifted to a higher temperature side under both inert and oxidative atmospheres. This can be the reason of the thermal hysteresis, which was the result of the heat transfer limitation caused by the temperature difference between the sample and furnace. The higher the heating rate is, the more obvious the hysteresis is. Similar phenomena have also been observed by other researchers [48,56]. In addition, degradation peak intensity was increased with the increment of heating rates, because the pyrolysis was more intense under higher heating rates. When the heating rate increased from 10 K·min⁻¹ to 20 K·min⁻¹ under 5% O₂, the first



Fig. 4. Experimental and calculated curves of each pseudo-reaction of LDPE autothermal pyrolysis under 5% O_2 (a–c) and 10% O_2 (d–f) atmospheres at heating rate of 5, 10, and 20 K min⁻¹ using Asym2Sig deconvolution method.

two peaks merged into a single peak.

3.2. Kinetic study

3.2.1. Kinetic analysis using single-step method

The kinetics of LDPE conventional and autothermal pyrolysis were

firstly investigated using single-step method in this study, assuming the whole process as a single reaction. The data obtained under different atmospheres was used to calculate the apparent activation energy using the Miura integral method. By plotting $\ln(\beta \cdot T^{-2})$ against $1000 \cdot T^{-1}$, the activation energy under certain conversion rate (E_a) can be estimated from the slope of the lines in the plots. The fitted curves and $E_a \cdot \alpha$ plots

Asym2Sig function parameters of each pseudo-reaction under 5% and 10% O₂ atmospheres at different heating rates.

Pseudo-reaction	Heating rate (K·min ^{-1})	T_p		θ		<i>w</i> ₁		<i>w</i> ₂		<i>w</i> ₃	
		5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
reaction-1	5	629	602	1.46	1.50	30.9	32.9	32.7	22.0	17.6	15.4
	10	656	621	1.51	1.52	30.9	41.1	32.7	22.5	16.3	20.1
	20	692	657	0.90	0.93	68.9	92.6	40.7	27.2	5.9	12.1
reaction-2	5	682	715	1.82	0.56	14.9	42.6	11.2	25.4	16.0	10.1
	10	709	729	1.06	0.40	20.9	42.3	13.9	26.4	10.9	8.4
	20	736	744	0.82	0.11	21.9	42.6	18.7	28.3	6.2	8.7
reaction-3	5	835	810	0.14	0.15	69.5	68.8	18.0	12.0	12.0	10.2
	10	854	838	0.06	0.12	69.8	68.8	19.8	19.0	11.8	8.2
	20	873	861	0.04	0.07	70.2	68.5	16.2	23.2	15.2	10.1

Note: T_p is the peak temperature of each curve; θ is the amplitude; w_1 presents full width of half maximum; w_2 and w_3 are shape parameters.

under different atmospheres are shown in Fig. 2 and the value of E_{α} was displayed in Table S1, and R^2 , *RMSE*, *MAE* were displayed in Table S2.

For pyrolysis under N₂ atmosphere, the R^2 were all higher than 0.98, implying the high accuracy of the estimated activation energies. E_0 under this condition was 271 kJ·mol⁻¹, which is in agreement with the values reported by Hu et al. [30]. Aboulkas et al. [47] studied the pyrolysis of LDPE under N2, and the activation energy is 215-221 kJ·mol⁻¹. Xu et al. [48] calculated E_0 of conventional pyrolysis of LDPE using model-free method, which was only around 175 kJ mol⁻¹. This variation may be caused by the different raw materials used in the experiments as well as the different kinetic models adopted for activation energy calculation. The value above and below 20% of E_0 was 216 and $324 \text{ kJ} \cdot \text{mol}^{-1}$, and the range was colored in blue in Fig. 2 (b). It can be observed that only the E_{α} at α =0.1 was out of the range, and this could be attributed to the complexity of the initial reaction. Thus, the conventional pyrolysis process of LDPE can be considered as a single-step reaction. Furthermore, the pre-exponential factors (A) (Table 3) were calculated from the intercept of the lines in Fig. 2 (a). A, closely related to activation energy, represents the number of collisions in per unit time in order to obtain the suitable orientation for the further reaction [57]. For LDPE pyrolysis under N_2 , the value of A was all higher than 10^9 , indicating the complexion of the reaction [58].

The Miura integral method was applied to estimate the activation energy of oxidative pyrolysis of LDPE (shown in Fig. 2 (c) and (e)). The results showed that R^2 at all conversion rates were lower than 0.95 under 5% O₂ (Table S2). Under 10% O₂, R^2 at the conversion rates of 0.1–0.3 and 0.7 were also lower than 0.95 (Table S2). *RMS* and *MAE* were higher than that under N₂. The corresponding E_α-α profiles were shown in Fig. 2 (d) and (f). E_α greatly varied from -77 to 356 kJ·mol⁻¹ under 5% O₂. E_α fluctuated more dramatically from -503 to 433 kJ·mol⁻¹ under the atmosphere of 10% O₂. The deviations from average value for both conditions were much higher than 20%, implying the oxidative pyrolysis process cannot be considered as a single reaction. Hence, single-step method was not suitable to calculate the activation energy of LDPE oxidative pyrolysis.

3.2.2. Kinetic analysis using multi-step method

3.2.2.1. Process separation based on temperature ranges. To solve the kinetic triplets for the LDPE oxidative pyrolysis, multi-step method was used in this study by dividing the process based on temperature ranges (or the conversion rate ranges). As shown in Fig. 2 (d) and (f), there were three trends can be observed in the activation energy—small fluctuation, increase and decrease. Under 5% O_2 , the conversion rate ranges are 0.1–0.4, 0.4–0.8 and 0.8–0.9. The ranges for 10% O_2 are 0.1–0.4, 0.4–0.7, 0.7–0.9. DTG curves were separated into three temperature ranges according to the conversion rate ranges, namely peak-1, peak-2, and peak-3, respectively. The detailed temperature range of each peak is listed in Table 4.

Herewith, each separated decomposition range was assumed as a global reaction, and Miura integral method was used for estimating the

activation energy of each temperature range. E_{α} and R^2 for 5% and 10% O₂ are shown in Table S3, and the plots of E_{α} - α are displayed in Fig. 3. For both cases, activation energies for peak-1slightly varied as conversion rate increased, with deviations less than 20%. However, activation energies of peak-2 generally increased with increasing conversion rate with deviations more than 20% from average values. In terms of peak-3, the activation energy showed a strange trend, and the variation was up to 267%. In conclusion, the peak-2 and 3 cannot be simply considered as a single reaction, and thus multi-step method based on temperature ranges was also not appropriate to study the kinetic behaviors of LDPE autothermal pyrolysis.

3.2.2.2. Process separation using Asym2Sig deconvolution procedure. As reported in previous studies [37,59], multi-step method combined with the deconvolution procedure, which is more accurate and feasible to peak the overlapped curves, could be a better solution for the kinetic study of LDPE autothermal pyrolysis. For deconvolution, only temperature range between 423 and 973 K was considered, because almost no weight loss occurred before 423 K and after 973 K. In this study, the Asym2Sig deconvolution function was adopted to separate autothermal pyrolysis of LDPE. As discussed in Section 3.1, three reactions were involved in the autothermal pyrolysis of LDPE, thus the whole process was deconvoluted into three pseudo-reactions, marked as reaction-1, reaction-2, and reaction-3, respectively. The five parameters of the Asym2Sig function were determined by simulating the experimental curves with the purpose of getting a satisfying value of R^2 . The calculated curves for all cases were well matched with the experimental data, as shown in Fig. 4. The R^2 of each pyrolysis condition was higher than 0.99, implying results derived from Asym2Sig deconvolution were appropriate to be used for investigating kinetic behaviors of LDPE autothermal pyrolysis.

Table 5 presents the parameters of the Asym2sig deconvolution obtained at different heating rates under 5% and 10% O_2 atmospheres. As heating rates increased, peak temperature T_p shifted to a higher value for all the pseudo-reactions under both 5% and 10% O₂ atmospheres. This is caused by the thermal hysteresis as explained in Section 3.1. Hidayat et al. [37]. studied the pyrolysis of imperata cylindrica using Asym2Sig deconvolution method and reported similar results. The amplitude of each peak (θ) reveals the degradation rate of each pseudo-reaction. For all cases, degradation rates generally decreased with increasing heating rates. The full width of half maximum (w_1) is on behalf of the temperature range of each pseudo-reaction. No obvious trends by changing heating rate were observed for reaction-2 and reaction-3 under both 5% and 10% O₂ atmospheres. For reaction-1, as the heating rate increased from 10 K·min⁻¹ to 20 K·min⁻¹, w_1 increased dramatically from 30.9 to 68.9 under 5% O₂, and from 41.1 to 92.6 under 10% O₂. w₂ and w₃, respectively representing the variation of low and high energy side of the peak temperature, did not show obvious trends with heating rates.

The deconvolution parameters were significantly affected by the oxidative atmosphere. As O₂ concentration increased from 5% to 10%, T_p for reaction-1 and reaction-3 shifted to a lower temperature side, in



Fig. 5. E_a-a estimated by Miura integral method for LDPE autothermal pyrolysis by Asym2Sig deconvolution method under 5% O₂ (a-c) and 10% O₂ (d-f).

accord with the results in previous studies [52,60]. For reaction-1, this can be attributed to the fact that more heat was produced from decomposition of branched chain as O_2 concentration increased, resulting in a reduction in heat supply from the outside [54]. With more O_2 introduced, the oxidation of products was more severe and less energy was needed for reaction-3 [15]. However, T_p for reaction-2 shifted to a higher temperature side, and this can be explained by the net

stabilizing influence of O₂, namely as more O₂ induced, the release of heat-induced tension within the macromolecules or through promotion of cross-linking reactions was enhanced, causing the thermal stability of main chains increased, further contributing to the breakage of the main chain being more difficult [18]. In terms of θ and w_1 , only those of reaction-2 varied with O₂ concentration. As volumetric O₂ concentration increased to 10% from 5%, θ for reaction-2 decreased and w_1 for

Pre-exponential factors at different conversions of three pseudo-reactions under 5% and 10% O₂ (s⁻¹).

a	a reaction-1		reaction-2		reaction-3	_
	5% O ₂	10% O ₂	5% O ₂	10% O ₂	5% O ₂	10% O ₂
0.1	6.79 imes 10 ⁵	3.48×10^7	3.11×10^{12}	9.11×10^{16}	$rac{2.09 imes}{10^9} imes$	$rac{2.63}{10^{13}} imes$
0.2	$\begin{array}{c} 2.27 \times \\ 10^5 \end{array}$	3.57×10^{6}	6.66×10^{10}	1.23×10^{16}	${1.65 imes 10^{10}}$	$rac{6.00}{10^{10}} imes$
0.3	$1.14 imes 10^5$	8.23×10^5	$rac{2.02}{10^{10}} imes$	4.92×10^{15}	${5.53 imes 10^{10}}$	7.08×10^9
0.4	7.15×10^4	2.83×10^5	1.08×10^{10}	3.10×10^{15}	1.30×10^{11}	2.68×10^9
0.5	$5.42 imes$ 10 4	1.27×10^5	1.02×10^{10}	2.60×10^{15}	2.46×10^{11}	$1.76 imes 10^9$
0.6	$5.07 imes$ 10 4	$7.12 imes 10^4$	$\frac{1.44}{10^{10}}\times$	2.86×10^{15}	3.96×10^{11}	$1.64 imes 10^9$
0.7	$6.39 imes 10^4$	4.98×10^4	${}^{\rm 4.11\times}_{\rm 10^{10}}$	4.29×10^{15}	5.52×10^{11}	$1.99 imes$ 10 9
0.8	$1.39 imes 10^4$	4.52×10^4	2.02×10^{11}	1.01×10^{16}	6.57×10^{11}	$3.23 imes 10^9$
0.9	$\begin{array}{c} \textbf{5.24}\times\\ \textbf{10}^{4} \end{array}$	5.97×10^4	7.54×10^{12}	6.18×10^{17}	6.14×10^{11}	8.30×10^9

that increased, indicating that higher O_2 concentration lowered the decomposition rate and enlarged the temperature interval of LDPE main chain cleavage reaction. O_2 concentration also affected the asymmetry of the reaction peaks. For reaction-3, values of w_2 and w_3 generally decreased with increasing O_2 concentration. For reaction-1 and 2, as more O_2 was introduced, w_2 and w_3 showed opposite trends.

Miura integral method was then used to estimate the activation energy of each pseudo-reaction derived from the Asym2Sig deconvolution. The fitted curves of $\ln(\beta \cdot T^{-2})$ -1000 T⁻¹, E_{α} , R^2 , *RMSE*, *MAE* are provided in Fig. S1, Table S4 and Table S5. The plots of E_{α} - α are shown in Fig. 5. The results showed that almost all of the deviation of E_{α} to E_0 fluctuated within 20% of E_0 , except for α =0.1 for reaction-1and reaction-3 under

10% O₂, indicating each pseudo-reaction can be considered as a singlestep reaction. Besides, the R^2 were all higher than 0.95, implying a good fit. E₀ for pseudo-reaction-1, 2, and 3 under 5% O₂ was 71, 153 and 189 kJ·mol⁻¹, respectively. However, this order was changed with more O₂ introduced. Under 10% O₂, E_0 was 74, 224 and 169 kJ·mol⁻¹ for reaction-1, 2, and 3, respectively. Higher O₂ concentration significantly increased activation energy for reaction-1 and 2 (LDPE branched and main chains cleavage) while lowered activation energy for reaction-3 (oxidation of products). The pyrolysis of LDPE is considered as a free radical thermal degradation process, and the reactions are occurred through sequential bond-scissions [61,62]. Peterson et al. [63] concluded that during the thermal decomposition of PE, the reaction was initiated at weak links. According to Oluwoye et al. [64], during the thermal degradation process of LDPE, breakage of branched and main chains happened, further yielding the monomer. In addition, a consecutive of chain reactions were involved, namely free radical mechanism, proceeding the decomposition process, in which series of H-abstraction, C-C scission, and both intramolecular and intermolecular hydrogen transfer were included. With more O₂ introduced, the competition between hydrogen transfer and the combination of O-H was severe, causing more energy needed for reaction-1 and 2, while the oxidation was more violent for reaction-3 under 10% O2, causing less energy needed. Furthermore, the apparent activation energy under oxidative atmosphere was lower than that under N₂. E_0 under N₂ (271 kJ·mol⁻¹) was higher than that of every pseudo-reaction under oxidative atmospheres (71–224 kJ·mol⁻¹). Oluwoye et al. [64] also reported the activation energy under inert atmosphere was 150–260 kJ·mol⁻¹, compared to 80–143 kJ mol⁻¹ under oxidative atmosphere. The lower activation energy suggested that less external energy input may be required to drive the oxidative pyrolysis.

The pre-exponential factors calculated from the intercept under oxidative atmospheres are listed in Table 6. A for reaction-1 were much smaller than 10^9 , revealing the breakage of branched chains was easier. For reaction-2, *A* were higher than 10^9 , indicating the difficulty to break



Fig. 6. Proposed reaction network for LDPE pyrolysis under oxidative atmosphere.

the C–C bonds in the LDPE main chains. A for reaction-2 under $10\% O_2$ was larger than that under $5\% O_2$. This trend is in consistency with that of activation energy, indicating their inherent connections.

Based on the data and discussion above-mentioned, a possible reaction mechanism for LDPE oxidative pyrolysis is illustrated in Fig. 6. With increasing temperature, the breakage of branched chains happens at first, followed by the scission of main chains, in accord with the study of Huang et al. [53]. During these processes, the C–H bonds fractured, accompanied by the H-abstraction and inter- or intra-molecular transfer of hydrogen atoms [64]. Oxygen is not supposed to be directly involved in the reaction, but by means of binding to hydrogen atoms. As the oxygen concentration increases, the combination of O and H atoms becomes more intense, leading to the enhanced competition for transfer with hydrogen atoms. As speculated, the weakened transfer of H atoms makes C–C breaking difficult, which leads to an increase in the activation energy of the reaction. Subsequently, oxygen participates in the oxidization of the intermediate products to yield final gaseous, liquid and solid products.

4. Conclusions and prospects

A comprehensive kinetic analysis of LDPE using the thermogravimetric analyzer under oxidative atmospheres (0, 5 and 10% O₂ balanced by N₂) at different heating rates (5, 10, 20 K·min⁻¹) was performed in this study. The pyrolysis of LDPE under N₂ could be considered as a single-step reaction, and the estimated E_0 was 271 kJ·mol⁻¹. However, the oxidative pyrolysis of LDPE was a more complex process. The multistep method by peaking temperature ranges and employing Asym2Sig deconvolution function were both studied. The results showed that the deconvolution method provided a good solution to separate the overlapped peaks, namely dividing the whole process into three pseudoreactions. E_0 of the three pseudo-reactions under 5% O₂ were 71, 153 and 189 kJ·mol⁻¹, and were 74, 224 and 169 kJ·mol⁻¹ under 10% O₂. The activation energy under oxidative atmospheres was lower than that under inert atmosphere, proving that the energy needed for autothermal pyrolysis was less than that of allothermal pyrolysis.

The kinetic study of LDPE oxidative pyrolysis can provide a significant guideline in the designing, optimization, and scaling up of the oxidative pyrolysis reactor [65]. We are expected to explore the heat and mass transfer law of the oxidative pyrolysis reactor in the future. The deconvolution method in this study was conducted using mathematical modeling, which was accurate and reliable but has a limited applicability comparing to machine learning, using generic hybrid intelligent [66] or ANFIS model [67] as reported in previous studies.

Credit author statement

Wen Xie: methodology, experimental & analysis, writing (review and editing), and visualization; Jing Su: writing (review and editing); Xiangkun Zhang: data analysis, writing (review and editing); Tan Li: writing (review and editing), and visualization; Cong Wang: writing (review and editing); Xiangzhou Yuan: conceptualization, writing (review and editing), and visualization; Kaige Wang: conceptualization, writing (review and editing), Visualization, and supervision. The manuscript was finished through the efforts of all authors. And all of the authors approve the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2023.126817.

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