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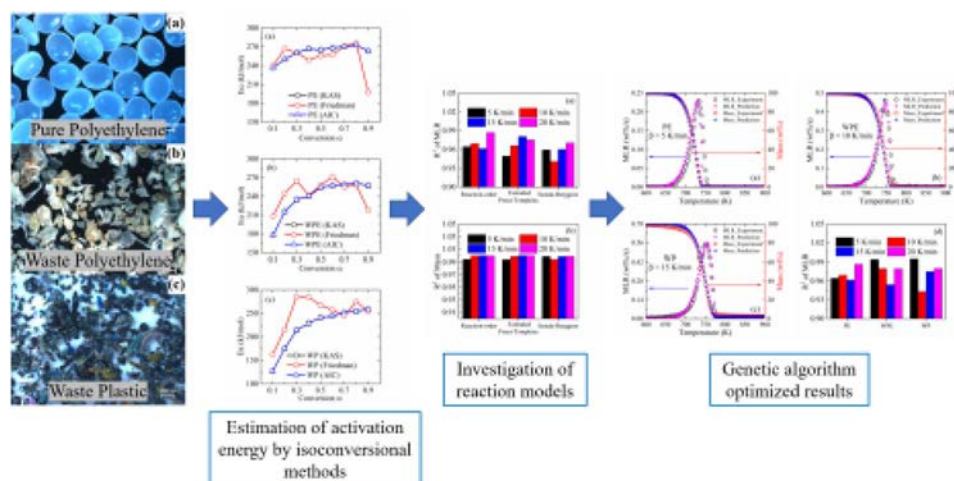
Investigating Waste Plastic Pyrolysis Kinetic Parameters by Genetic Algorithm Coupled with Thermogravimetric Analysis

Ruming Pan¹ · João Vitor Ferreira Duque^{1,2,3} · Gérald Debenest¹

Abstract

Pyrolysis of waste plastic (WP) is a promising method to solve the plastic pollution issue. WP is mainly composed of polyethylene (PE). Moreover, the products of waste polyethylene (WPE) pyrolysis could serve as high quality fuels and the feedstocks of petrochemicals. Therefore, it is essential to investigate the WPE and WP pyrolysis process. This study evaluates pure PE, WPE and WP pyrolysis kinetic parameters by the use of genetic algorithm (GA) and isoconversional methods coupled with thermogravimetric analysis (TGA), respectively. Additionally, three representative reaction models, i.e. reaction-order, extended Prout–Tompkins and Sestak–Berggren models, are investigated for obtaining the most suitable model, which could describe the PE, WPE and WP pyrolysis process more accurately. Consequently, the reaction-order model turns out to be the optimal method for appropriately describing PE, WPE and WP pyrolysis processes. Hence, the pyrolysis parameters optimized by GA are proven to be accurate and reliable, in comparison of calculated values of activation energy by isoconversional methods and experimental data. Moreover, it might be applicable of GA coupled with TGA with reaction-order model to the future industrial WPE and WP pyrolysis circumstances that have variable heating rates.

Graphic Abstract



Keywords Waste plastic · Reaction models · Genetic algorithm · Thermogravimetric analysis · Pyrolysis

Statement of Novelty

This study utilized the genetic algorithm (GA) coupled with thermogravimetric analysis (TGA) and different reaction models to conduct the kinetic study of the waste

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polyethylene (WPE), the waste plastic (WP), and the pure polyethylene (PE) as a reference. Three representative reactions models, i.e. reaction-order, extended Prout–Tompkins and Sestak–Berggren models, were investigated. The activation energy calculated by the isoconversional methods provided a reference to the GA optimized results. Consequently, the reaction-order model turned out to be the proper model. Subsequently, the kinetic parameters of the PE, the WPE and the PE were determined by the GA with the reaction-order model.

Introduction

Plastic is an essential industrial product in the modern society. It has multiple usages in both daily life and industrial applications due to its superior performance. Hence, a large amount of different types of plastic produced annually worldwide. According to the literature [1], 335 million tons of plastic produced globally in 2016. Moreover, this figure is continuing increasing as the results of the global population growth [2] and economic swift development [3]. Accordingly, vast irreplaceable petroleum consumed yearly since the plastic is the chemical product based on the petroleum. Furthermore, in the entire quantity of plastic produced since 1950, nearly 70% of plastic has been obsoleted and 84% has been landfilled or discarded directly in the environment [4]. This results in severe plastic pollution because of the durable of plastic [2]. For the purpose of minimizing the plastic waste, i.e. landfill of waste plastic (WP), recycling is one of promising methods. The WP recycling could be divided into two categories, namely mechanical recycling [5] and chemical recycling [6]. Herein, owing to the exacting demand for products with high added value, WP mechanical recycling is fairly challenging contemporarily [2]. However, the products of WP chemical recycling could serve as fuels [7,9] and the feedstocks of petrochemicals [10]. This makes WP chemical recycling very attractive and competitive. In additional, the WP could also be utilized for energy recovery, i.e. incineration. While it turns out to be unfavorable since its low heating value (42.6 MJ/kg) [11] and hazardous dioxins producing [12].

Pyrolysis is a promising method to decompose WP, which is treated with difficulties by mechanical recycling [13]. As its price is moderate, waste polyethylene (WPE) becomes the primary material serving as the feedstock of pyrolysis [13,14]. Besides, polyethylene (PE) represents more than 90% of WP [15]. Moreover, in the range of polyolefins, the PE plays a main role of the world plastic usage [1]. Therefore, it is essential to investigate the pyrolysis process of PE.

Currently, many researchers utilize the thermogravimetric analysis (TGA) to investigate the PE and other materials pyrolysis characteristics [16–23]. Kple et al. [16]

and Bercic et al. [17] used TGA for PE thermal pyrolysis kinetics investigation. Zheng et al. [18] and Xiang et al. [19] investigated PE co-pyrolysis behavior and thermal kinetics by TGA. Furthermore, the activation energy, calculated based on the TG experimental data, provided a reference for co-pyrolysis mechanism analysis. Das et al. [20] and Aboulkas et al. [21] conducted the thermal pyrolysis kinetics and behaviors investigations of different types of plastics by TGA. TGA was also adopted in the kinetic researches of municipal solid waste (MSW) [22] and plant seeds [23] thermal pyrolysis processes. Moreover, plenty studies have been conducted by exploiting different isoconversional methods coupled with TGA [24,25]. Wang et al. [26] investigated new and aged PE with TGA coupled with Friedman [27], Kissinger–Akahira–Sunose (KAS) [28] and Flynn–Wall–Ozawa (FWO) [29] methods. They concluded that pyrolysis of PE could be described by ‘Contracting Cylinder’ (R2) model [30]. Aboulkas et al. [21] adopted Friedman, KAS and FWO methods to calculate the PE activation energy. Furthermore, the Coats–Redfern [31,32] and Criado methods [33] were used to determine the proper reaction model for describing PE pyrolysis with accuracy. It was also reported that the ‘Contracting Cylinder’ (R2) model was suitable for the PE pyrolysis process. Vyazovkin [30] proposed an advance isoconversional method (AIC) to promote the accuracy of the isoconversional method. Moreover, Das et al. [20] utilized AIC to investigate the PE pyrolysis in nitrogen. They compared reliability of AIC, Friedman, FWO and Starink [34] methods. Accordingly, they drew the conclusion that AIC was the more accurate method for describing PE pyrolysis process than other isoconversional methods.

In the majority of researches, the plastic pyrolysis reaction kinetic parameters (e.g., activation energy E , pre-exponential factor A and the reaction order n , etc.) are not determined simultaneously. For instance, the calculation of pre-exponential factor is based on the calculated activation energy. Moreover, the reaction model needs to be determined by the Coats–Redfern [31,32] or Criado methods [33]. The reaction model candidates are the representative ones, such as Power-law, Contracting geometry, Prout–Tompkins, etc. [35]. Therefore, some researchers turned to explore the different methods to conduct the kinetic modelling. According to the literatures [36–39], the genetic algorithm (GA) could calculate multiple parameters contemporaneously. Moreover, GA could be used for searching the global optimal parameters despite of the scopes of the parameters. Thus, GA was adopted to evaluate the reaction kinetic parameters [40]. Furthermore, Jiang et al. [41] and Chen et al. [41] conducted the kinetic study on plastic pyrolysis with GA coupled TGA. The most widespread reaction-order model was adopted in their researches. The consistency between experimental data and the GA calculated results indicated

that GA is a promising method to evaluate the pyrolysis kinetic parameters of polymers.

For the purpose of instructing the further application of chemical recycling of WPE and WP, this study adopts GA coupled with TGA to study the pyrolysis processes of WPE and WP at heating rates varied from 5 to 20 K/min in argon. Moreover, in order to obtain a better understanding of the pyrolysis processes, the pure PE from commercial corporation is utilized as a comparison. Three isoconversional methods are adopted to calculate the activation energy values. The results provide a reference to the GA calculated kinetic parameters. Additionally, three representative reaction models are investigated to determine the most favorable one which could describe the WPE and WP pyrolysis processes.

Experimental and Kinetic Modeling

Experimental

Materials

Pure PE, WPE and WP utilized in this study were offered by Lukplast Ind. (ES-Brazil), as illustrated in Fig. 1. WPE was recycled from waste polyethylene products with the certain selection, such as plastic bags, plastic films, milk buckets and et al. While WP was recycled plastic without selection, which composed of a majority of polyethylene (PE) and a minority of polystyrene (PS) and polyethylene terephthalate (PET).

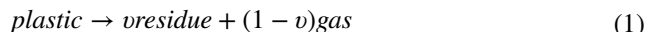
Thermogravimetric Tests

The thermogravimetric tests were using a NETZSCH STA 449F3 thermal analyzer with 60 mL/min gas flow rate of argon. Approximately 13.0 mg powder test samples were heated from room temperature to 973.15 K at four representative heating rates (i.e., 5, 10, 15, 20 K/min).

Kinetic Modeling

Pyrolysis Reaction Description

According to the literature [41,42], the pyrolysis of plastic could be described by:



where ν represents reaction stoichiometry coefficient.

Based on the aforementioned Eq. (1), this study adopted Arrhenius Law to calculate mass loss rate (MLR) during plastic pyrolysis process. Hence, MLR could be expressed as follow:

$$MLR = (1 - \nu)Af(\alpha)\exp(-E/(RT)) \quad (2)$$

where A , α , $f(\alpha)$, E , R and T represent the pre-exponential factor (1/s), the conversion rate, the dependence on the conversion rate, the activation energy (kJ/mol), the universal gas constant (equals to 8.314 J/(mol K)) and the temperature (K), respectively.

Accordingly, the mass fraction of test sample could use the following equation:

$$y = 1 - \int_0^t MLR dt \quad (3)$$

where y and t represent the mass fraction and the pyrolysis time (s), respectively.

Reaction Models

According to the literature [30], three representative reaction models, namely reaction-order model, the extended Prout–Tompkins model, and the Sestak–Berggren model 43, are possible candidates for the pyrolysis description. The expressions are listed in Table 1.

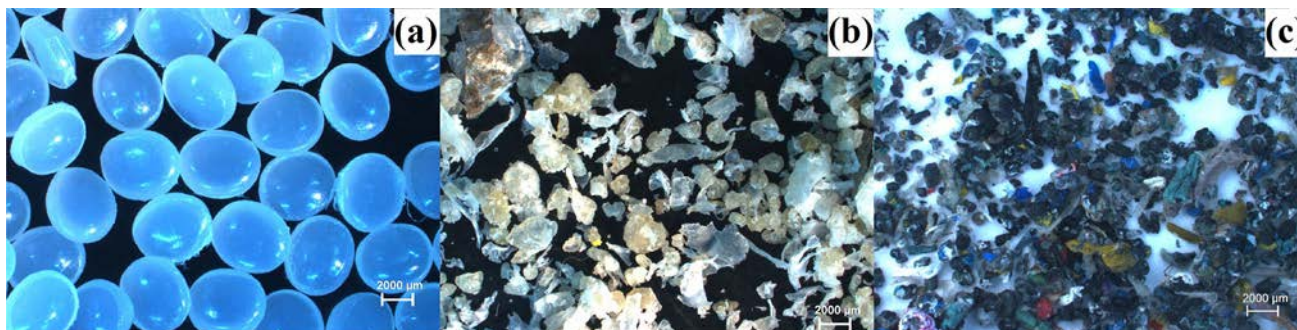


Fig. 1 Pictures of a pure PE, b WPE and c WP used in experiments

Table 1 Reaction models investigated in this study

| Reaction model | Equations |
|-------------------------------|--|
| Reaction-order model | $f(\alpha) = (1 - \alpha)^n$ |
| Extended Prout–Tompkins model | $f(\alpha) = \alpha^m \cdot (1 - \alpha)^n$ |
| Sestak–Berggren model | $f(\alpha) = \alpha^m \cdot (1 - \alpha)^n \cdot [-\ln(1 - \alpha)]^p$ |

α , $f(\alpha)$ and n represent the conversion rate, the dependence on the conversion rate and the reaction order. m and p are the exponents which applied in different reaction models, respectively

Table 2 Isoconversional methods adopted in this study

| Method | Equations |
|----------|---|
| KAS | $\ln\left(\frac{\beta}{T^2}\right) = -\frac{E}{RT} + const$ |
| Friedman | $\ln\left(\beta \frac{d\alpha}{dT}\right) = -\frac{E}{RT} + const$ |
| AIC | $\Phi(E) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E, T_i)/\beta_i}{I(E, T_j)/\beta_j}$ with $I(E, T_i) = \int_0^{T_i} \exp\left(-\frac{E}{RT}\right) dT$ |

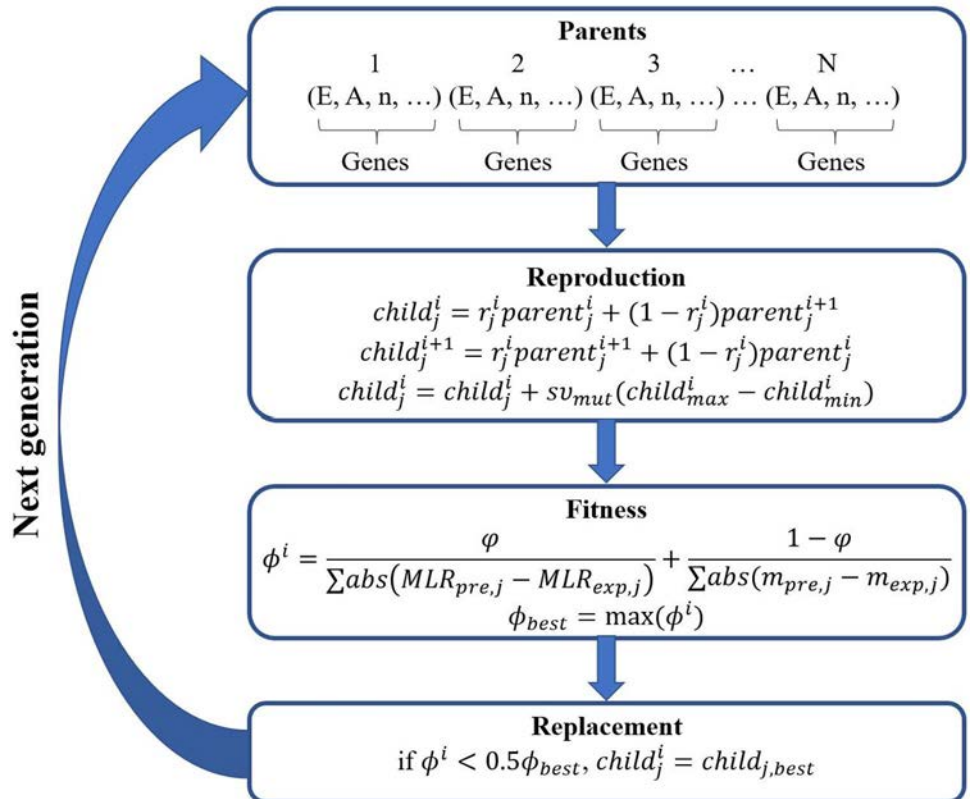
β , E , T and R represent the heating rate (K/min), the activation energy (kJ/mol), temperature (K) and universal gas constant (equals to 8.314 J/(mol K)), respectively

Isoconversional Methods

In this study, three representative isoconversional methods, as listed in Table 2, were adopted for investigating the activation energy of plastic pyrolysis, namely one integral method (KAS) [28], one differential method (Friedman) [27] and AIC method [30].

Genetic Algorithm

The genetic algorithm adopted in this study is described in Fig. 2. In each generation, there are N individuals with specific genes, such as the activation energy E , the pre-exponential factor A , the reaction order n and et al. These individuals serve as parents. Subsequently, N parents could generate N children. This procedure is known as reproduction, also accompanied by mutation. The arithmetic expressions were illustrated in Fig. 1, in which i and j denote the number of individual and gene; r_j^i is a random number varied from 0 to 1; ν_{mut} is the possibility of mutation, which equals to 0.05 41; and s is a random number varied from -0.5 to 0.5 42. The next procedure is to calculate the fitness of each individual. The fitness is calculated by experimental and predicted MLR and mass fraction. The fitness is served as the target function. Additionally, φ denotes the weight coefficient, which equals to 0.5 [42]. Furthermore, the best individual, which had the maximum fitness value, was selected.

Fig. 2 GA schematic diagram

Lastly, offspring is undergoing selection based on the value of fitness. Individuals, of which fitness values lower than half of the maximum value fitness, would be replaced by the best individual in this generation. This process is called replacement. Therewith, the next inheritance will repeat the above processes.

In this study, the number of individuals and generations are 500 and 200, respectively. The GA was coded in Matlab. In addition, ordinary differential equation ode23s was adopted to calculate the predicted mass loss rates (MLR) and mass fractions.

Results and Discussions

Thermogravimetric Analysis

Figure 3 illustrates the experimental MLR and TG (relative mass loss) curves of pure PE, WPE and WP at different heating rates during the pyrolysis process under argon atmosphere. The test samples were performed under the same experimental treatment, which heated from room temperature to 973.15 K. In general, the shape of MLR and TG curves remained unchanged regardless of the variation of the heating rate. Moreover, the peak values of MLR of PE, WPE and WP increase as the heating rate increases. For instance, as depicted in Fig. 3a, the peak value of MLR of PE increased from 0.2296 to 0.8751 wt%/s when the heating rate increased from 5 to 20 K/min. Additionally, a significant lateral shift to higher temperature occurred when the heating rate increased in the MLR and TG curves. It may be caused by the pyrolysis mechanism transformation when the heating rate increased [20,44].

Figure 4 demonstrates the onset temperature T_o , the end temperature T_e and the maximum degradation temperature T_m in the PE MLR curve at 5 K/min under argon atmosphere. T_o , T_e and T_m were proposed for evaluating the plastic pyrolysis process [20]. As listed in Table 3, due to the pyrolysis mechanisms transformation [20,44], T_o , T_e and T_m of PE, WPE and WP increased with the heating rate. For instance, the onset temperature T_o of PE, WPE and WP increased from 699 to 719 K, 700 to 725 K and 697 to 723 K gradually when the heating rate increased from 5 to 20 K/min. By comparison, WP has the highest T_e and T_m , while PE has the lowest ones. As regards to T_o , there is no obvious

regularities among PE, WPE and WP at different heating rates. However, the differences value between T_o and T_e are nearly constant, around 60 K, despite of the variation of the heating rate.

In consideration of the MLR maximum value, the pyrolysis processes of PE, WPE and WP are relatively fast under argon atmosphere. For example, the maximum MLR of WPE could come up to 0.9142 wt%/s at 20 K/min. Besides, the maximum values of MLR of PE, WPE and WP varied from 0.2296–0.8751 wt%/s, 0.2233–0.9142 wt%/s and 0.1912–0.7784 wt%/s at the heating rates 5–20 K/min, respectively. It could be regarded that WPE underwent a relatively faster pyrolysis process, while WP underwent a relatively slower pyrolysis process under argon atmosphere.

The TG curves of PE, WPE and WP, which depicted in Fig. 3, indicated that they were decomposed to gaseous products (under the experimental environment) during the pyrolysis process. After PE, WPE and WP were heated from room temperature to 973.15 K, the mass fractions of the residue at different heating rates are listed in Table 4. Plastic pyrolysis products could be divided into char, wax/oil and gases [2]. Moreover, the distributions of the products are affected by the heating rates [45]. Therefore, the residues were different at different heating rates of pure PE, WPE and WP. When the pyrolysis processes finished, there were no residue of pure PE remained when the heating rates were 10 and 15 K/min. However, it existed 0.03 and 0.90 wt% residue of pure PE at 5 and 20 K/min, respectively. The values are negligible compared to the original weight. Therefore, it could be considered that pure PE can be decomposed thoroughly after the pyrolysis process under argon atmosphere [20,21]. In the case of WPE, a minor amount of residue remains after the pyrolysis process. However, a larger amount residue remained after WP pyrolysis process. As demonstrated in Table 4, it still remained around 2.15 wt% residue at the end of WP thermal degradation process under argon atmosphere.

Degradation Kinetics by the Isoconversional Methods

Three isoconversional methods were adopted for calculating the activation energy E of pure PE, WPE and WP by using four sets of TG data at different heating rates. As exhibited in Table 5, the activation energy values of pure PE, which

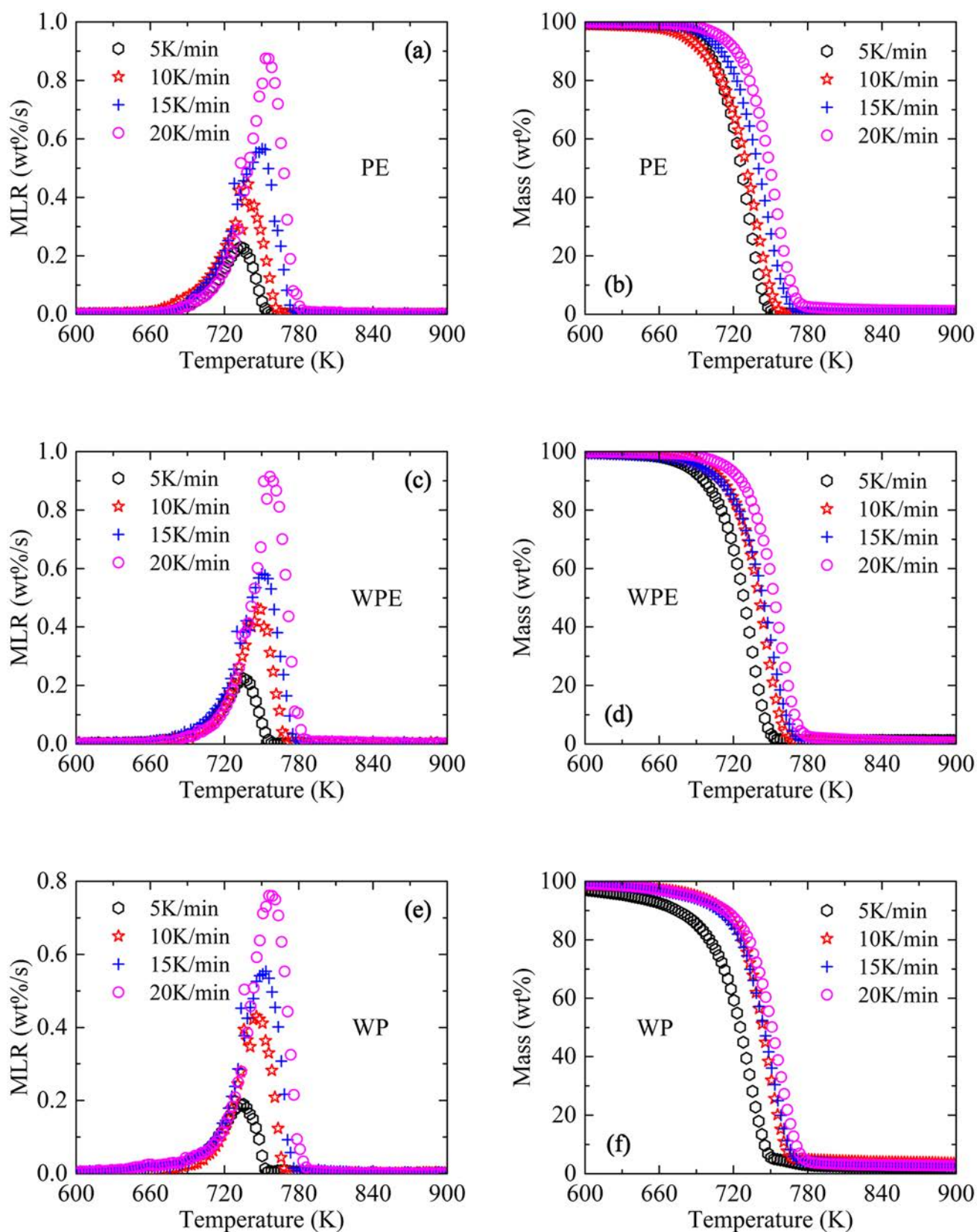


Fig. 3 Experimental MLR and TG curves at 5, 10, 15 and 20 K/min in argon: **a** MLR curves of PE; **b** TG curves of PE; **c** MLR curves of WPE; **d** TG curves of WPE; **e** MLR curves of WP; **f** TG curves of WP

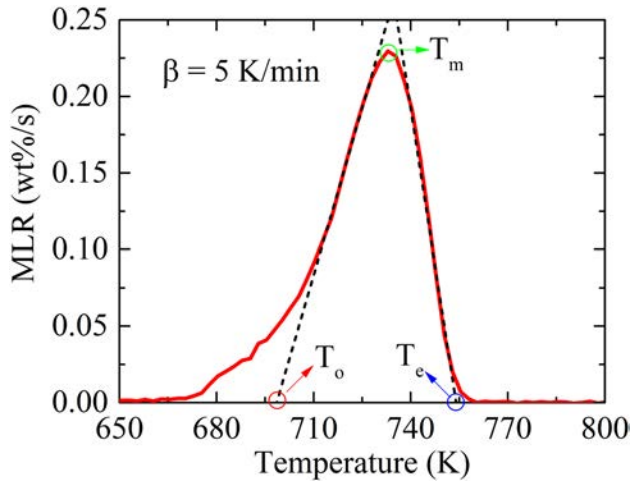


Fig. 4 T_o , T_e and T_m from MLR curve of PE at 5 K/min in argon

Table 3 Onset, end and maximum degradation temperatures and maximum MLR of PE, WPE and WP in argon

| Material | Heating rate (K/min) | T_o (K) | T_e (K) | T_m (K) | MLR_{max} (wt%/s) |
|----------|----------------------|-----------|-----------|-----------|---------------------|
| PE | 5 | 699 | 754 | 733 | 0.2296 |
| | 10 | 699 | 764 | 739 | 0.4451 |
| | 15 | 707 | 773 | 750 | 0.5664 |
| | 20 | 719 | 777 | 753 | 0.8751 |
| WPE | 5 | 700 | 756 | 735 | 0.2233 |
| | 10 | 711 | 768 | 747 | 0.4617 |
| | 15 | 711 | 776 | 750 | 0.5820 |
| | 20 | 725 | 780 | 757 | 0.9142 |
| WP | 5 | 697 | 757 | 735 | 0.1912 |
| | 10 | 714 | 770 | 748 | 0.4442 |
| | 15 | 716 | 775 | 753 | 0.5538 |
| | 20 | 723 | 781 | 756 | 0.7784 |

Table 4 The mass fractions of the residue at different heating rates of pure PE, WPE and WP

| Residue (wt%) | Heating rate (K/min) | | | |
|---------------|----------------------|------|------|------|
| | 5 | 10 | 15 | 20 |
| PE | 0.02 | 0 | 0 | 0.9 |
| WPE | 1.15 | 0.31 | 0.19 | 0.49 |
| WP | 1.08 | 3.16 | 2.1 | 2.26 |

Table 5 Calculation results of activation energy E of pure PE by KAS, Friedman and AIC methods

| Conversion | KAS (kJ/mol) | Friedman (kJ/mol) | AIC (kJ/mol) |
|---------------|--------------|-------------------|--------------|
| 0.1 | 236.67 | 239.97 | 237.00 |
| 0.2 | 250.12 | 266.66 | 250.43 |
| 0.3 | 260.39 | 260.24 | 260.70 |
| 0.4 | 266.85 | 249.27 | 267.15 |
| 0.5 | 265.02 | 255.90 | 265.32 |
| 0.6 | 268.30 | 257.03 | 268.61 |
| 0.7 | 270.58 | 271.33 | 270.88 |
| 0.8 | 272.91 | 276.17 | 273.21 |
| 0.9 | 263.12 | 197.59 | 263.43 |
| Average value | 261.55 | 252.68 | 261.86 |

Table 6 Calculation results of activation energy E of WPE by KAS, Friedman and AIC methods

| Conversion | KAS (kJ/mol) | Friedman (kJ/mol) | AIC (kJ/mol) |
|---------------|--------------|-------------------|--------------|
| 0.1 | 177.68 | 208.35 | 178.04 |
| 0.2 | 215.85 | 245.45 | 216.17 |
| 0.3 | 234.80 | 264.89 | 235.11 |
| 0.4 | 240.37 | 241.46 | 240.67 |
| 0.5 | 254.52 | 257.79 | 254.81 |
| 0.6 | 257.34 | 271.78 | 257.62 |
| 0.7 | 258.96 | 254.77 | 259.23 |
| 0.8 | 260.94 | 258.39 | 261.22 |
| 0.9 | 257.31 | 217.88 | 257.59 |
| Average value | 239.75 | 246.75 | 240.05 |

Table 7 Calculation results of activation energy E of WP by KAS, Friedman and AIC methods

| Conversion | KAS (kJ/mol) | Friedman (kJ/mol) | AIC (kJ/mol) |
|---------------|--------------|-------------------|--------------|
| 0.1 | 126.75 | 162.39 | 127.20 |
| 0.2 | 174.64 | 215.20 | 175.02 |
| 0.3 | 213.99 | 285.69 | 214.32 |
| 0.4 | 228.82 | 285.04 | 229.14 |
| 0.5 | 241.26 | 267.45 | 241.57 |
| 0.6 | 244.28 | 257.55 | 244.60 |
| 0.7 | 251.43 | 244.72 | 251.74 |
| 0.8 | 254.55 | 274.89 | 254.86 |
| 0.9 | 258.38 | 254.81 | 258.70 |
| Average value | 221.57 | 249.75 | 221.91 |

were calculated by KAS, Friedman and AIC methods, are varied with the different conversion rates. However, the differences of the activation energy values are almost negligible particularly when the conversion rate varied from 0.3 to 0.9. In addition, the activation energy is relatively lowered when the conversion rate is under 0.2. This is because that the initial degradation is relatively facilitated due to the presence of weak link sites intrinsic of PE [46,47]. Furthermore, the values of PE activation energy calculated by KAS and AIC were very close. While Friedman method calculated PE activation energy values were very different from KAS and AIC. This is consistent with the results in the work of Das et al. [20]. And it indicated that the activation energy values calculated by the KAS and AIC were more convincing to a certain extent. The low-density PE activation energy value calculated by Encinar et al. [45] was 285 kJ/mol. It is close to the calculated average value of pure PE activation energy

in this work. However, in the works of Das et al. [20], Xu et al. [48] and Wang et al. [26], the low-density PE activation energy values calculated by KAS were 162–242, 174.46 and 130.04–193.10 kJ/mol, respectively. The calculated results of activation energy in different literatures varied to a large extent. It may be caused by the different sources of the raw material and the varying processes of manufacturing [48].

The activation energy of WPE and WP were calculated by the same three isoconversional methods as its of pure PE. The results were listed in Table 6 and Table 7 separately. Hence, the calculated activation energy of pure PE, WPE and WP at different conversion rates by KAS, Friedman and AIC methods were plotted in Fig. 5. It is noticeable that the differences of activation energy, between the KAS and AIC methods, could be nearly neglected. It might be noticed that the activation energy of pure PE is larger than the one of WPE and WP. It indicates that the WPE and WP are more

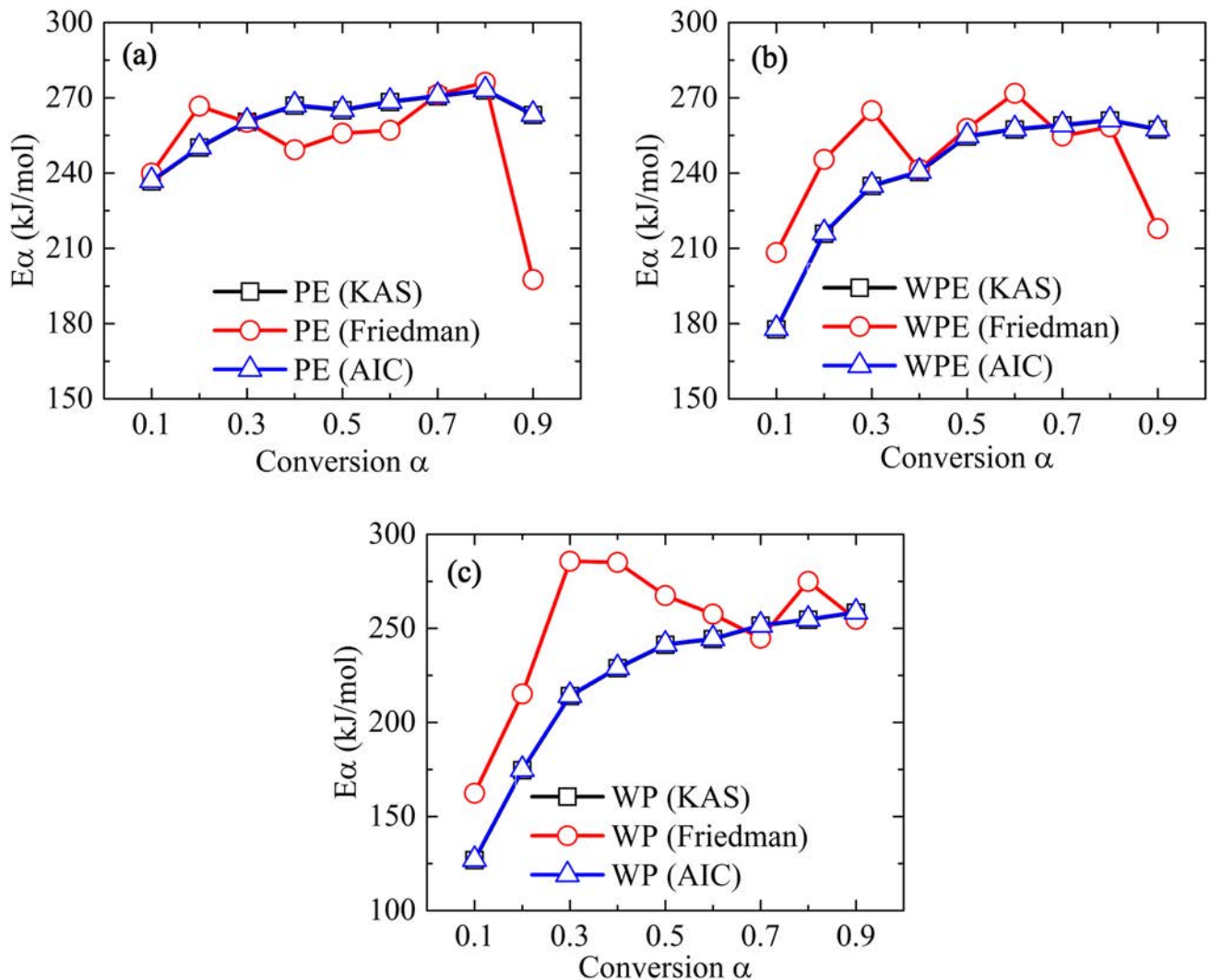


Fig. 5 The calculated activation energy of pure PE, WPE and WP by different isoconversional methods

Table 8 Optimized values of PE pyrolysis kinetic parameters by adopting reaction-order, extended Prout–Tompkins and Sestak–Berggren models

| Parameters | Optimized values | | |
|----------------------------|------------------|-------------------------|-----------------|
| | Reaction-order | Extended Prout–Tompkins | Sestak–Berggren |
| lnA (ln(s ⁻¹)) | 34.52 | 31.78 | 31.23 |
| E (kJ/mol) | 241.55 | 221.21 | 217.86 |
| n | 0.58 | 1.08 | 1.12 |
| m | – | 0.30 | 0.29 |
| p | – | – | 0.07 |

ignitable, whereas pure PE is relatively less ignitable [26]. Once again, we can notice the decrease of the value differences of activation energy of pure PE, WPE and WP with the conversion rate.

Favorable Reaction Model Selection

In order to determine which reaction model could describe the PE pyrolysis process with accuracy, three representative reaction models were adopted in this study, i.e. reaction-order, extended Prout–Tompkins and Sestak–Berggren models. Hence, the different reaction models coupled with GA were investigated separately for obtaining the optimal pyrolysis kinetic parameters of pure PE. Consequently, the optimized values of PE pyrolysis kinetic parameters by adopting reaction-order, extended Prout–Tompkins and Sestak–Berggren models are listed in Table 8. The optimized values of activation energy were 241.55, 221.21 and 217.86 kJ/mol, which were calculated with reaction-order, extended Prout–Tompkins and Sestak–Berggren models, respectively. In comparison, the activation energy values of PE calculated by KAS, Friedman and AIC methods were 261.55, 252.68 and 261.86 kJ/mol, respectively. The GA optimized activation energy of reaction-order model is close to the value determined by the isoconversional methods.

Accordingly, the predicted MLR and TG curves were plotted in Fig. 6, which with the GA optimized values of PE by adopting reaction-order, extended Prout–Tompkins and Sestak–Berggren models at the different heating rates. It could be perceived that the predicted MLR and TG curves by using of three reaction models coupled with GA were promisingly consistent with the experimental ones.

Moreover, the R-squared values between experimental and predicted data of PE by adopting different reaction models were listed in Table 9. The predicted mass fraction was more precise than the predicted MLR in all three reaction models. The average R-squared value of mass fraction and MLR were ~0.998 and ~0.971, respectively. The overall average R-squared value gradually increased in reaction-order, extended Prout–Tompkins and Sestak–Berggren models. However, the increased value was almost negligible. The R-squared values of MLR and mass fraction had no obvious differences among different reaction models. To be more exact, the reaction-order and the extended Prout–Tompkins models were more accurate in the prediction of mass fraction. Whereas the Sestak–Berggren model could describe the MLR with a greater precision. In consideration of the activation energy, the GA optical value with the reaction-order was in agreement with the value calculated by using isoconversional methods. Although the activation energy calculated by isoconversional methods has no mechanistic significance and could not be utilized for extensive academic conclusions [49]. The activation parameters are possible to obtain using isoconversional methods and could provide a guidance in plastic recycling industry [21]. So we decide to use that as a base value. Therefore, the reaction-order model coupled with GA was selected to conduct the polyethylene pyrolysis kinetic modelling. Hence, GA coupled with the reaction-order model was adopted to investigate the pyrolysis processes of WPE and WP.

Kinetic Parameters Calculated by GA

According to the previous subsection discussion, GA coupled with the reaction-order model was adopted for calculating the optimal pyrolysis kinetic parameters, i.e., the pre-exponential factor A, the activation energy E and the reaction order n of pure PE, WPE and WP. As demonstrated in Table 10, the optimized values of pyrolysis kinetic parameters lnA, E and n are 34.52 ln(s⁻¹), 241.55 kJ/mol and 0.58 of PE; 33.84 ln(s⁻¹), 239.82 kJ/mol and 0.51 of WPE; and 33.06 ln(s⁻¹), 234.51 kJ/mol and 0.71 of WP, respectively. The value of calculated activation energy of PE is the largest. Moreover, the value of calculated activation energy of WP is the smallest. It is consistence with the results calculated by the KAS and AIC methods. Furthermore, the differences of calculated E by using of GA and isoconversional methods are relatively small. It indicates the reliability of

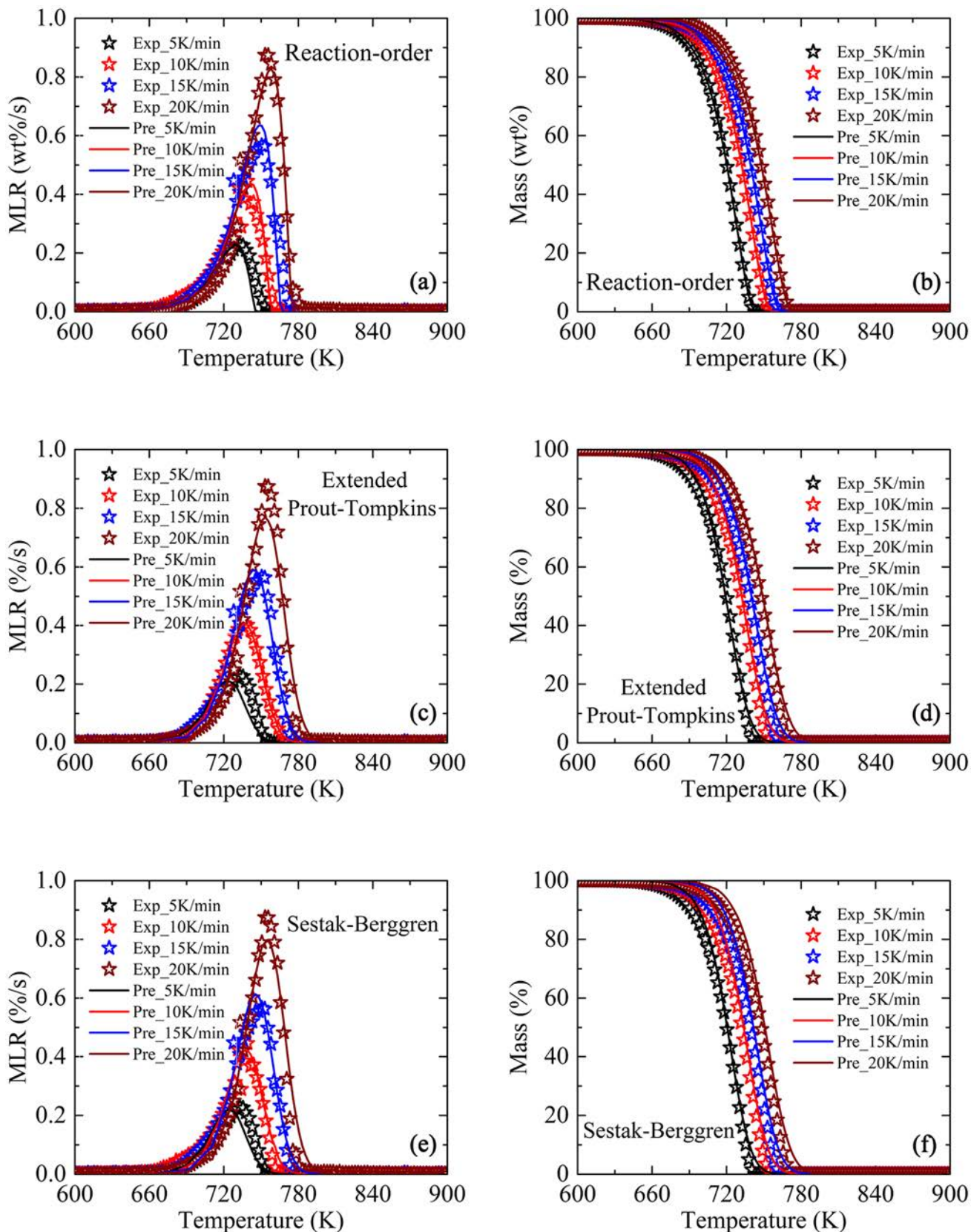


Fig. 6 Experimental and predicted MLR and TG curves at 5, 10, 15 and 20 K/min of pure PE by adopting reaction-order, extended Prout–Tompkins and Sestak–Berggren models in argon

Table 9 The R-squared values between experimental and predicted data of pure PE by adopting reaction-order, extended Prout–Tompkins and Sestak–Berggren models

| Heating rate (K/min) | Reaction-order | | Extended Prout–Tompkins | | Sestak–Berggren | |
|-----------------------|----------------|--------|-------------------------|--------|-----------------|--------|
| | Mass | MLR | Mass | MLR | Mass | MLR |
| 5 | 0.9948 | 0.9645 | 0.9949 | 0.9533 | 0.9966 | 0.9617 |
| 10 | 0.9992 | 0.9696 | 0.9982 | 0.9713 | 0.9968 | 0.9648 |
| 15 | 0.9995 | 0.9615 | 0.9997 | 0.9832 | 0.9992 | 0.9827 |
| 20 | 0.9990 | 0.9871 | 0.9996 | 0.9759 | 0.9991 | 0.9760 |
| Average value | 0.9981 | 0.9707 | 0.9981 | 0.9709 | 0.9979 | 0.9713 |
| Overall average value | 0.9844 | | 0.9845 | | 0.9846 | |

GA optimized values of PE, WPE and WP pyrolysis kinetic parameters.

Figure 7 illustrates the experimental and predicted MLR and TG curves of PE, WPE and WP at different heating rates under argon atmosphere. The predicted MLR and mass fraction were calculated by Eq. (2) and (3), respectively. Due to the kinetic parameters were all calculated by GA, the variables were just the temperature and the pyrolysis time. The temperature was only determined by the heating rate within the specific pyrolysis time. Therefore, the MLR and mass fraction at different heating rates could be calculated subsequently. It indicated that a high degree of consistency between experimental and predicted data was obtained. Additionally, the R-squared values between experimental and predicted data at different heating rates were listed in Table 11. The R-squared values of WPE mass fraction are greater than 0.999 at each heating rate. However, the R-squared values of MLR of WPE are relatively lower, which the average value is around 0.980. Moreover, in the cases of PE and WP show the same tendency as WPE. In summary, the predicted PE, WPE and WP pyrolysis kinetic parameters are relatively reliable and accurate. Furthermore, GA coupled with TGA could be applied to the more

practical pyrolysis circumstances, in which have variable heating rates. This will be discussed in the future work.

Conclusion

This study investigated the pyrolysis processes of waste polyethylene (WPE), waste plastic (WP), and pure polyethylene (PE) as a reference. Based on the pure PE, WPE and WP pyrolysis thermogravimetric experimental data at heating rates from 5 to 20 K/min under argon atmosphere, this study investigated the activation energy by using of three isoconversional methods, which are KAS, Friedman and AIC methods. Three representative reaction models, i.e. reaction-order, extended Prout–Tompkins and Sestak–Berggren models, were also investigated for determining the proper model which could describe the pyrolysis process with accuracy. Accordingly, genetic algorithm (GA) coupled with the reaction-order model was adopted for calculating the optimal pyrolysis kinetic parameters of pure PE, WPE and WP. The GA predicted optimal activation energy values are 241.55, 239.82 and 234.51 kJ/mol of pure PE, WPE and WP, respectively. It was found that the calculated activation energy values by using of GA were in good agreement with that by using of isoconversional methods. Furthermore, it compared the predicted mass fraction and mass loss rate (MLR), calculated by the GA optimized parameters, with the experimental ones. According to the results, high consistencies between experimental and GA predicted data were obtained in pure PE, WPE and WP pyrolysis processes at heating rates of 5, 10, 15 and 20 K/min. Hence, it indicates that the predicted PE, WPE and WP pyrolysis kinetic parameters by using of GA are relatively reliable and accurate. Moreover, it might be applicable of genetic algorithm coupled with thermogravimetry analysis to the future industrial WPE and WP pyrolysis circumstances that have variable heating rates.

Table 10 Optimized value of pure PE, WPE and WP pyrolysis kinetic parameters by adopting reaction-order model

| Parameters | Optimized values | | |
|---------------------------|------------------|--------|--------|
| | PE | WPE | WP |
| $\ln A$ ($\ln(s^{-1})$) | 34.52 | 33.84 | 33.06 |
| E (kJ/mol) | 241.55 | 239.82 | 234.51 |
| n | 0.58 | 0.51 | 0.71 |

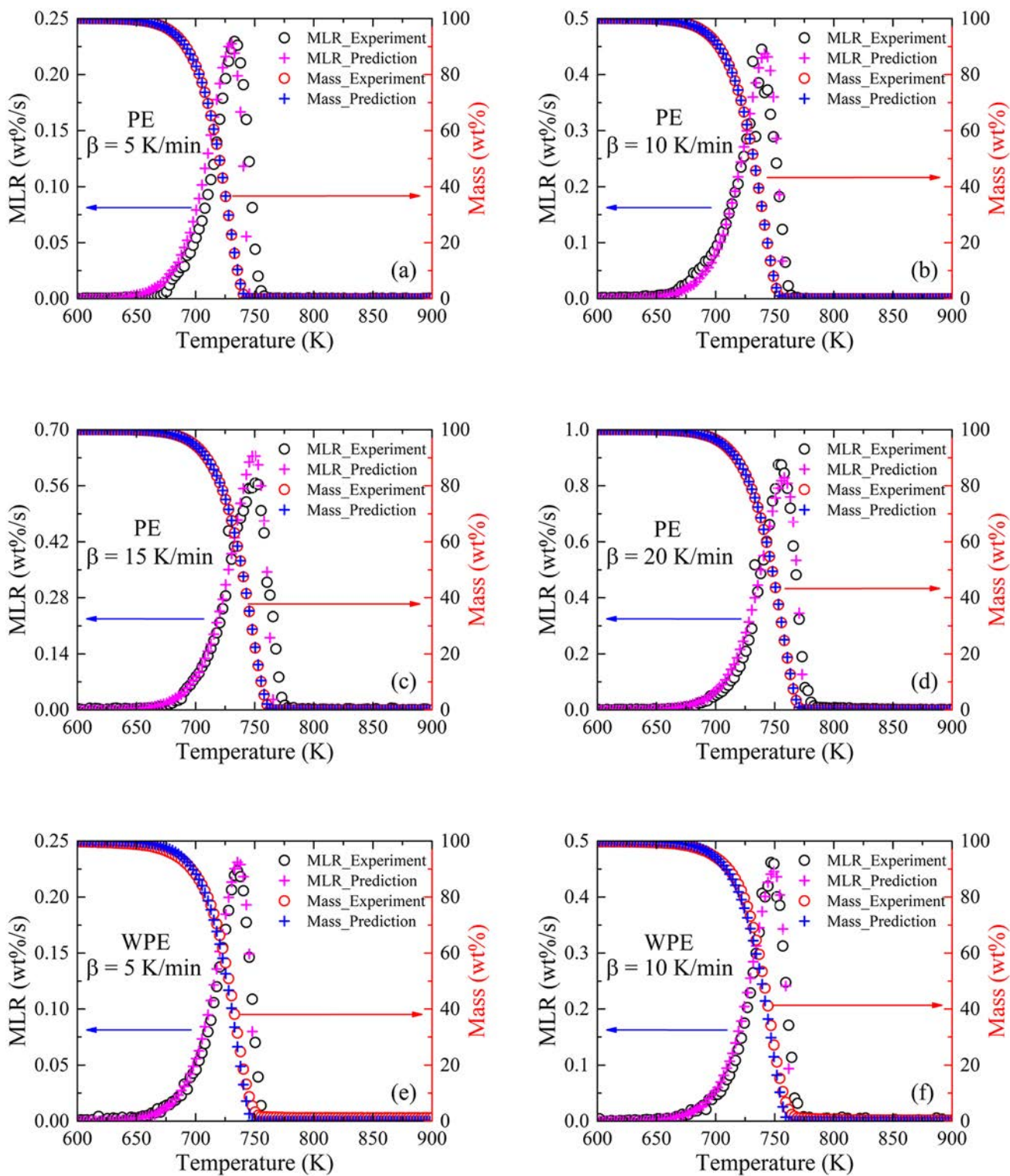


Fig. 7 Experimental and predicted MLR and TG curves at 5, 10, 15 and 20 K/min of pure PE, WPE and WP in argon

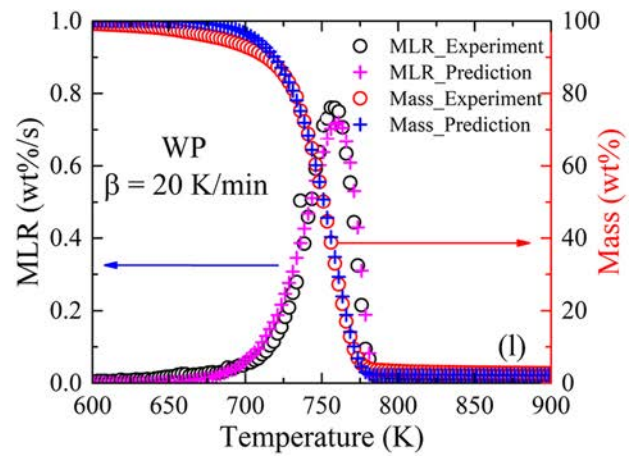
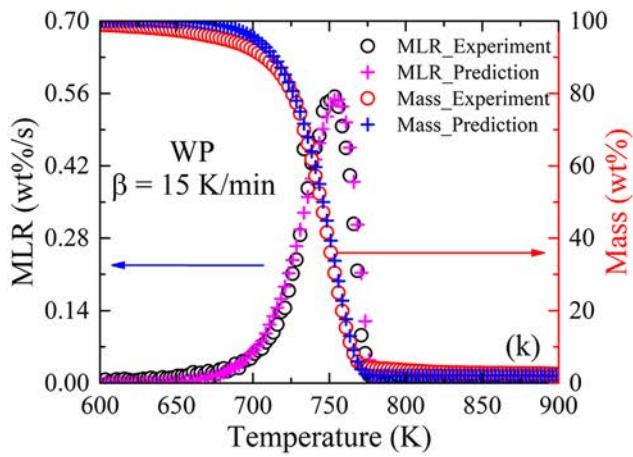
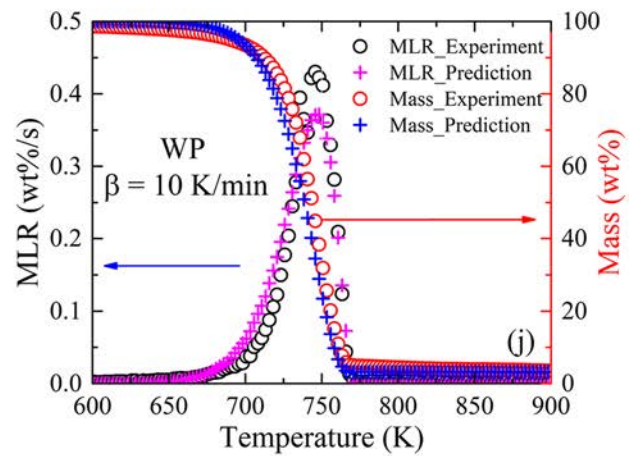
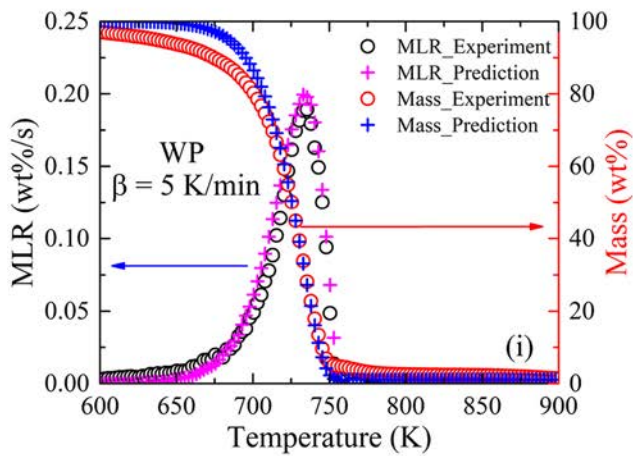
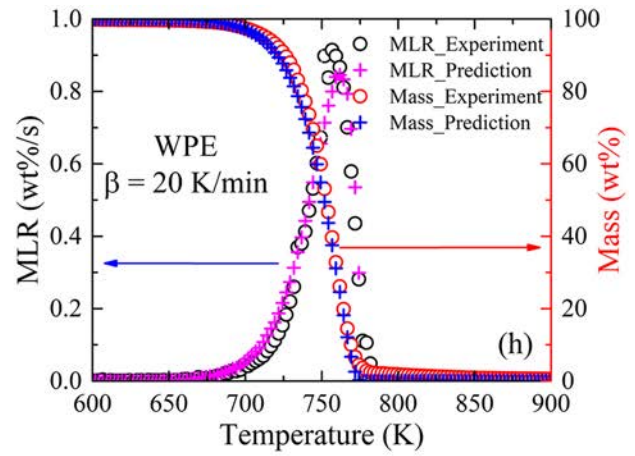
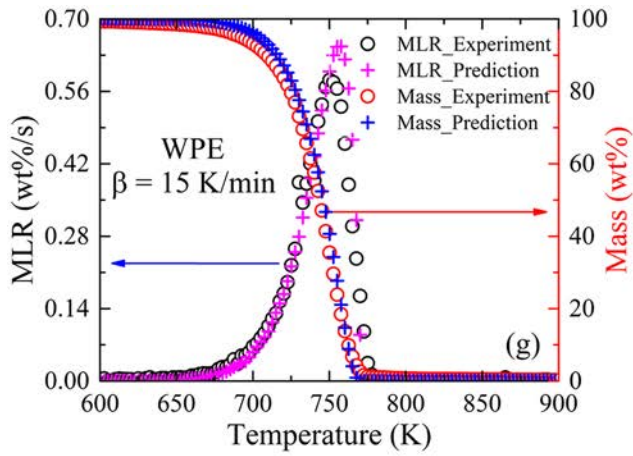


Fig. 7 (continued)

Table 11 The R-squared values between experimental and predicted data of pure PE, WPE and WP at different heating rates

| Heating rate (K/min) | PE | | WPE | | WP | |
|-----------------------|--------|--------|--------|--------|--------|--------|
| | Mass | MLR | Mass | MLR | Mass | MLR |
| 5 | 0.9948 | 0.9645 | 0.9992 | 0.9945 | 0.9966 | 0.9956 |
| 10 | 0.9992 | 0.9696 | 0.9993 | 0.9800 | 0.9966 | 0.9434 |
| 15 | 0.9995 | 0.9615 | 0.9990 | 0.9543 | 0.9990 | 0.9752 |
| 20 | 0.9990 | 0.9871 | 0.9992 | 0.9799 | 0.9992 | 0.9801 |
| Average value | 0.9981 | 0.9707 | 0.9992 | 0.9772 | 0.9979 | 0.9736 |
| Overall average value | 0.9844 | | 0.9882 | | 0.9857 | |

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Compliance with Ethical Standards

Competing interest The authors declare no competing financial interest.

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