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Model-free kinetics analysis of waste PE sample

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Abstract

Vyazovkin model-free approach is applied to study non-isothermal decomposition of waste PE sample using various temperature integral approximations such as Coats and Redfern, Gorbachev, Agrawal & Siva Subramanian and a new approximation [J. Cai, F. Yao, W. Yi, F. He, AIChE J. 52 (2006) 1554] and a new method for direct integration.

E_α dependency on α is compared with several literature data. Initial strong and increasing E_α dependency on α in case of non-isothermal decomposition is associated with initiation at the weak links. Weak but increasing E_α dependency on α in the later stages is possibly due to dependence of distribution of size of volatile products on heating rate and random scission. Weak and decreasing followed by weak but increasing function of α in case of isothermal decomposition is possibly due to existence of two opposite effects, nucleation, and distribution of size of volatile products. The sample used follows neither perfectly the LDPE trend nor the HDPE trend. Thus, it becomes mandatory to study the decomposition behaviour of any waste material before design of an incinerator and/or pyrolysis unit without using blindly the information available for standard samples. Optimum E_α dependencies from non-isothermal data at 15 K min^{-1} heating rate best predicted the isothermal data.

Keywords: Thermal decomposition kinetics; Waste PE; Non-isothermal; Isothermal; Isoconversion; Activation energy

1. Introduction

The correctness of the pyrolysis kinetics heavily depends upon reliable evaluation of activation energy from the decomposition behavior under different conditions of temperature and/or atmosphere. Thermal decomposition mechanism of polymer, a complicated phenomenon, can be described as occurring by a set of series or parallel chemical reactions via random scission mechanism, chain scission mechanism, etc., which do not follow rigorously first order kinetics. The traditional model-fitting kinetics analysis using single heating rates and single step decomposition model gives only a single set of kinetics triplet (activation energy, E; pre-exponential factor, k_0; order of reaction model, n). However, presently International Confederation of Thermal Analysis and Calorimetry (ICTAC) project, 2000 ruled out the validity of thermal kinetics analysis using single heating rate [1]. Modern model-fitting thermal kinetics analysis methods use multi-heating rates, take care of multi step reactions and incorporate possible partial diffusion, back reaction, branch reaction, etc. in the model equations [1,2]. Bockhorn et al. [3] studied thermal degradation of polyethylene (PE) and polypropylene (PP) under isothermal conditions. They evaluated the kinetics triplet by model-fitting method, proposed chain scission as possible mechanism of decomposition, and finally evaluated the rate constants for different steps of chain scission. They investigated the difference in kinetics triplet of the mixture from the single polymer decomposition kinetics triplet. In a recent paper, Faravelli et al. [4] reported a satisfactory two-phase model to describe the thermal degradation of PE polystyrene (PS) mixture. However, selection of appropriate model and initial guess of kinetics parameters are major drawback of model-fitting methods [2]. Moreover, the kinetics triplet obtained by model-fitting technique from non-isothermal condition is highly uncertain and cannot be compared with the kinetics triplet obtained from isothermal condition [5].

Alternatively, Vyazovkin model-free approach through use of isoconversion method is a trustworthy way of obtaining reliable and consistent kinetic information from non-isothermal data. It also helps to reveal the complexity of multiple reactions due to the dependencies of activation energy on the extent of conversion [5–9]. Apart from a few literatures dealing with the kinetics

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analysis using isoconversion methods for thermal decomposition of solids [5–9], Lyon [10] proposed a new series solution for integration of the Arrhenius integral, obtained during isoconversion method of analysis of the kinetics. He used single step reaction from temperature scanning experiment and applied for decomposition of low density PE (LDPE). Peterson et al. [11] studied thermal decomposition of poly (methyl methacrylate) using isoconversion method to evaluate the decomposition kinetics. Peterson et al. [12] in their subsequent research paper reported the thermal degradation kinetics of PS, PE and PP using isoconversion method. Gao et al. [13] used isoconversion method of Flynn–Wall–Ozawa method in case of high density PE (HDPE) decomposition to show the variation of activation energy, E_α with conversion, α. They recommended that random scission does not rigorously follow first order reaction and first order reaction model should not be used blindly. Vasile et al. [14] reported thermoxidative decomposition of LDPE in non-isothermal conditions and applied isoconversion method of Friedmann to analyze dependency of E_α on α. They reported continuous modifications of reaction mechanism due to competitions between the different processes involved (various decomposition paths, diffusions and volatilizations) which are all influenced differently by the temperature change during the heating. However, isothermal kinetics data are mostly needed for practical application as most of the pyrolysis reactors operate at constant temperature. The simulation of isothermal kinetics can be performed using non-isothermal data by means of modern isoconversion method of Vyazovkin model-free approach. Therefore, in our previous paper [15], we applied modern isoconversion methods of Vyazovkin model-free approach to investigate both non-isothermal and isothermal decomposition kinetics of waste PET sample using various temperature integral approximations such as Coats and Redfern; Gorbachev; Agrawal and Sivasubramanian approximation and direct integration (recursive adaptive Simpson Quadrature scheme) to analyze the thermal decomposition of PET sample. Variation of activation energy with conversion both under isothermal and non-isothermal conditions and possible involvements of mechanisms like nucleation, nuclei growth and diffusion towards such behaviour were discussed. The obtained optimum E_α dependencies derived from non-isothermal data was used to simulate the isothermal kinetics data. Thus, to the best of our knowledge, adequate information on model-free analysis of pyrolysis of waste PE samples under both isothermal and non-isothermal conditions are not available in the literature.

Therefore, in the present investigation, we applied the non-linear Vyazovkin model-free technique to study the non-isothermal decomposition of waste PE sample using a new approximation of Cai et al. [16] along with other approximation techniques of Coats and Redfern; Gorbachev; Agrawal and Sivasubramanian and a new technique of numerical integration. We also studied Friedmann isoconversion method to study the isothermal decomposition. We have shown the quantitative information on variation of E_α with α for PE sample under both non-isothermal and isothermal conditions. The results are compared with the reported results by Lyon [10]; Peterson et al. [12]; Gao et al. [13]; the qualitative trends provided by Vyazovkin [9] for complex processes involving competitive reactions, reversible reactions and reactions complicated by diffusion; reported results by the present authors [15] on PET degradation. The similarities and the differences in the results are critically analyzed and discussed.

2. Experimental

2.1. Experimental procedure and equipment

The non-isothermal and isothermal decompositions were carried out with waste coloured PE sample from poly pack. Thermal decomposition experiments were carried out in a TGA instrument of Metler TOLEDO with model no. TGA/SDTA 851^e under nitrogen atmosphere for a range of temperature 303–873 K. Nitrogen flow rate was maintained at 40–50 ml min^{-1} according to the specification of the equipment. PE samples were shredded into very small pieces and directly fed to the TGA instrument. Alumina crucible (900 μl) was used as sample holder. Experiments were conducted in dynamic condition at different heating rates of 10, 15, 20 and 25 K min^{-1}. Total mass of the sample with the corresponding experimental conditions is given in Table 1. The TGA

Table 1
Experimental conditions for TGA studies

Initial mass (mg)	Heating rate (K/min)	Temperature range (K)	$T_{w0}/T_d/T_m/T_{w\infty}$ (K)
Non-isothermal			
9.32	10	303–873	456.3/702.1/745.6/804.9
9.51	15	303–873	456.8/706.3/755/796.4
9.41	20	303–873	456.9/716.5/761.2/816.2
9.67	25	303–873	450.9/718.4/768/798.2

Initial mass (mg)	Sample temperature (K)	Total experimental time (min)	Total loss of weight (%)	$t_{w0} - t_{w\infty}$ (min)
Isothermal				
10.28	699	0–103.95	84.81	6.3–67.2
10.32	708	0–103.95	85.1	6.3–55.65
10.20	718	0–103.95	84.25	6.3–38.85

Sample name: waste coloured PE.

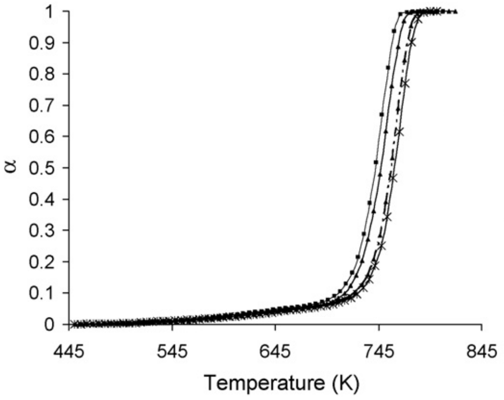

Fig. 1. Variation of conversion (α) with temperature during thermal pyrolysis of waste PE sample.

experiments were repeated thrice at 10 °C heating rate. The deviations observed are very little. However, the deviations are reported in terms of average relative deviation, ARD % $= (100/N)\sum_{i=1}^{N}\left|x_i^{\text{exp}} - x_{\text{av},i}/x_{\text{av},i}\right|$, where x_i^{exp} and $x_{\text{av},i}$ are the experimental values of the variables (temperature and normalized mass) and average values of the variables, respectively. i = no. of data points for each experiment. Results show that ARD% are 0.4–1.1 (for temperature), 1.5–4.1 (for mass). Variations of α with temperature during non-isothermal pyrolysis at different heating rates are reported through Fig. 1. Fig. 2 represents variations of α with temperature during isothermal decomposition at different target temperatures 699, 708, and 718 K. For isothermal experiments, the temperature program was optimized to reach the preset temperature of experiments within maximum of 6.2 min when the sample temperature was regulated within ±1 K of the set points (Fig. 3). Further details can be seen from our previous publications [15,17].

We also performed the differential scanning calorimetry (DSC) analysis of the PE sample under stagnant air atmosphere, using instrument DSC 821$^{\text{e}}$, to measure the melting point (Fig. 4) and percentage crystallinity. The melting point, percentage crystallinity, and purity (in terms of residue) of the sample are summarized in Table 2.

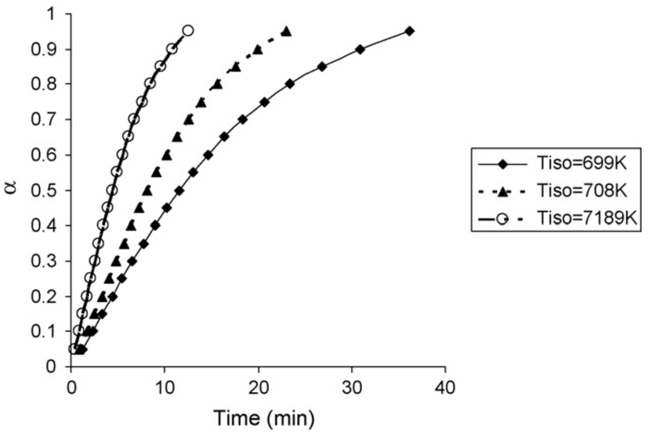

Fig. 2. Variation of conversion (α) with time during isothermal pyrolysis of waste PE sample.

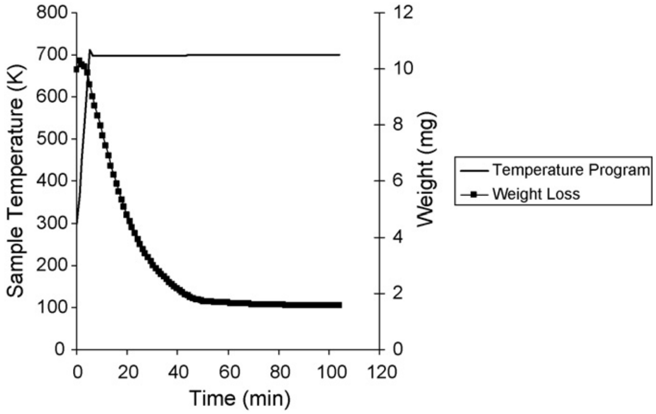

Fig. 3. Weight loss and temperature program for isothermal condition.

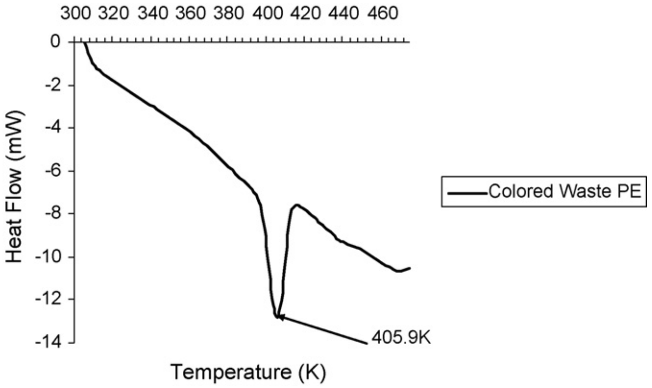

Fig. 4. DSC analysis of waste PE sample.

3. Kinetics analysis

3.1. Kinetic models and model-free kinetics analysis

The kinetic model equation combined with the Arrhenius approach of the temperature function of reaction rate constant is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_0 \exp\left(\frac{-E}{RT}\right) f(\alpha) \tag{1}$$

where t is the time (min), T the temperature (K), α the conversion of reaction $(W_0 - W)/(W_0 - W\infty)$, W_0 the initial weight of the sample (mg), W the sample weight (mg) at any temperature T, $W\infty$ the final sample weight (mg), $\mathrm{d}\alpha/\mathrm{d}t$ the rate of reaction (min^{-1}), and $f(\alpha)$ is the reaction model. k_0 is the pre-exponential factor (K^{-1}) and E is the activation energy (kJ mol^{-1}) are the Arrhenius parameters. R is the gas constant (kJ mol^{-1} K^{-1}). The reaction model may take various forms based on nucleation and nucleus growth, phase boundary reaction, diffusion, and chemical reaction [5,8,18]. However, the present investigation does not require any information of reaction model since we report here thermal decomposition kinetics of PE sample using model-free approach.

At a constant heating rate under non-isothermal conditions the explicit temporal/time dependence in Eq. (1) is eliminated

Table 2
Characteristics of waste PE sample

Sample type	Waste coloured PE
Melting point (°C)	132.4
Melting point of standard PE samples (°C) [20]	HDPE: 127–135; LDPE: 98–120
Heat of fusion ($\mathrm{J\,g^{-1}}$)	38.37
Heat of fusion, 100% crystallinity ($\mathrm{J\,g^{-1}}$)	290
Degree of crystallinity (%)	13.23
Crystallinity of standard PE samples [20]	HDPE: 80–95%; LDPE: 50–70%
Purity (residual amount after TGA experiment upto 600 °C)	Non-isothermal: 10–15%; isothermal: 15–16%

through the trivial transformation:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = k_0 \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \tag{2}$$

where, $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate ($\mathrm{K\,min^{-1}}$) and $\mathrm{d}\alpha/\mathrm{d}T$ is the rate of reaction ($\mathrm{K^{-1}}$).

3.1.1. Model-free isoconversion method for non-isothermal experiments [5–8,15]

For a set of four experiments carried out at four different heating rates (10, 15, 20 and 25 $\mathrm{K\,min^{-1}}$) the E_α can be determined at any particular value of α by finding the value of E_α for which the objective function Ω is minimized [8], where:

$$\Omega = \sum_{i=1}^{n}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{I(E_\alpha, T_{\alpha i})\beta_j}{I(E_\alpha, T_{\alpha j})\beta_i} \tag{3}$$

and

$$I(E_\alpha, T_{\alpha i}) = \int_0^{T_{\alpha i}} \exp\left(\frac{-E_\alpha}{RT}\right)\mathrm{d}T \tag{4}$$

The temperature integral can be evaluated by several popular approximations and direct numerical integration.

3.1.1.1. Numerical procedure and algorithms for model-free technique. The objective function, Ω minimization is done by numerical method in MATLAB using ‘medium-scale: Quasi-Newton line search’ algorithm. The ‘fminunc’ function for unconstrained problem is applied for the optimization.

Direct integration of temperature integral. As we understand that the temperature integral in Eq. (4) has no exact analytical solution, an alternative way to express the temperature integral is given below [16]:

$$\int_0^{T_{\alpha i}} \exp\left(\frac{-E_\alpha}{RT}\right)\mathrm{d}T = \frac{E_\alpha}{R}P(u) \tag{5}$$

where $u = E_\alpha/RT$ and:

$$P(u) = \int_u^{\infty}\frac{\exp(-u)}{u^2}\mathrm{d}u = \frac{\exp(-u)}{u} - Ei(u) \tag{6}$$

where $Ei(u) = \int_u^{\infty}\frac{\exp(-u)}{u^2}\mathrm{d}u$, exponential integral

thus,

$$I(E_\alpha, T_{\alpha i}) = \int_0^{T_{\alpha i}} \exp\left(\frac{-E_\alpha}{RT}\right)\mathrm{d}T = \frac{E_\alpha}{R}\left[\frac{\exp(-u)}{(u)} - Ei(u)\right] \tag{7}$$

The exponential integral of Eq. (7) is solved directly by a function called ‘expint’ using MATLAB.

Approximations for integration of the temperature integral. Coats and Redfern, Gorbachev, Agrawal and Sivasubramanian and a new approximation of Cai et al. [16] are used for integration of Eq. (4) to compare the results with direct integration. Details of Coats and Redfern, Gorbachev, Agrawal and Sivasubramanian approximations are already discussed in our previous paper [15].

Approximation of Cai et al. [16], a new temperature integral approximation superior to all other approximations, is as under.

$$\int_0^{T} \exp\left(-\frac{E_\alpha}{RT_{\alpha i}}\right)\mathrm{d}T = \frac{RT_{\alpha i}^2}{E_\alpha}\left[\frac{E_\alpha/RT_{\alpha i}+0.66691}{E_\alpha/RT_{\alpha i}+2.64943}\right]\times\exp\left(\frac{-E_\alpha}{RT_{\alpha i}}\right) \tag{8}$$

3.1.2. Model-free method for isothermal experiments [5–7,15]

Eq. (1) can be rearranged as:

$$g_j(\alpha) = \int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} = k_j(T_i)t \tag{9}$$

The subscript j corresponds to the reaction model selected. For each reaction model selected, the rate constants are evaluated at several temperatures, T_i, and the Arrhenius parameters are determined from the equation.

$$\ln(k_jT_i) = \ln(k_{0j}) - \frac{E_{\alpha j}}{RT_i} \tag{10}$$

Under isothermal conditions, Eqs. (9) and (10) can be combined to obtain:

$$-\ln t_{\alpha,i} = \ln\left[\frac{k_{0j}}{g_j(\alpha)}\right] - \frac{E_\alpha}{RT_i} \tag{11}$$

where E_α is evaluated from the slope of the plot $-\ln(t_{\alpha,i})$ against T_i^{-1}.

3.2. Isothermal model prediction from non-isothermal model-free analysis

The sole evaluation of E dependence is sufficient to simulate the isothermal kinetics from non-isothermal data. This is formularized [9] by Eq. (12).

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp(-E_\alpha/RT)\mathrm{d}T}{\beta \exp(-E_\alpha/RT_0)} \tag{12}$$

The time (t_α) at which a given conversion (α) will be reached at an arbitrary temperature (T_0) is to be computed by Eq. (12). Since predictions using this method can be made without knowledge of the reaction model and the pre-exponential factor, they are referred as ‘model-free predictions’.

4. Results and discussion

4.1. Non-isothermal decomposition

The non-isothermal pyrolysis yielding 85–90% weight loss starts at temperature around T_d and finishes at temperature around $T_{\mathrm{w}\infty}$ (Fig. 1). The temperature at which the conversion (α) is zero ($T_{\mathrm{w}0}$), decomposition starts (T_d), maximum weight loss rate occurs (T_m) and the end of pyrolysis step ($T_{\mathrm{w}\infty}$) takes place is reported in Table 1 for each case of the experiments. The initial weight of sample is taken at temperature, $T_{\mathrm{w}0}$ to eliminate moisture and volatile compound content. A quick thermal decomposition is observed in the range of T_d to $T_{\mathrm{w}\infty}$ (Fig. 1) and the highest decomposition rate is at around T_m reported in Table 1. After this, the sample continues decomposing smoothly and slowly till the end of experiment.

4.2. Isothermal decomposition

It is evident from non-isothermal experiment (Table 1) that the PE thermal decomposition starts in the temperature range of 697–718 K and the maximum decomposition temperature lies between 740 and 768 K depending upon the heating rate. Also at 10 K min^{-1} heating rate, the maximum decomposition temperature is 746 K. Therefore, the three different temperatures viz., 699, 708 and 718 K of isothermal experiments were chosen in between 698 and 718 K (i.e., in between start of decomposition and maximum decomposition temperatures) with an approximate interval of 10 K. A very quick fall (84–85% weight loss) (Fig. 3) is observed within 38–67 min after reaching the preset isothermal temperature (6.3 min) for each of the isothermal experiments. The initial weight, temperature, total time, percentage loss of total weight, $t_{\mathrm{w}0}$, and $t_{\mathrm{w}\infty}$ are presented in Table 1. After this quick fall, the sample continues decomposing smoothly and very slowly till the end of experiment. We have taken W_0 at $t_{\mathrm{w}0}$ when the preset temperature is reached and W_∞ at $t_{\mathrm{w}\infty}$ when weight loss is about 99.5% of total weight loss for the calculation of α (Fig. 2).

4.3. Kinetics for non-isothermal and isothermal model-free analysis

Model-free analysis technique is advantageous over model-fitting analysis when the real kinetics mechanism is unknown. A sample plot for E_α dependency on α obtained for non-isothermal decomposition for PE sample using direct numerical integration and approximation of Cai et al. [16], superior to all other approximations, is shown in Fig. 5. It is observed from the figure that initially activation energy is strong and increasing function of conversion for $\alpha \le 0.1$, then decreasing for $0.1 < \alpha < 0.15$ and then again slowly increasing with decreasing slope for $\alpha \ge 0.15$. All the approximations of Coats and Redfern, Gorbachev, Agrawal and Sivasubramanian and Cai et al. [16] used for integration of Eq. (4) showed almost similar result and similar deviations from the results with direct integration. Fig. 6 represents deviations from the results with direct integration. The average relative deviation (ARD%) [15] values are 0.04225, 0.01145, 0.00377 and 0.00104 for Coats & Redfern; Gorbachev; Agrawal and Sivasubramanian and new approximation, respectively. Therefore, the other results obtained and presented in this work are by direct integration only.

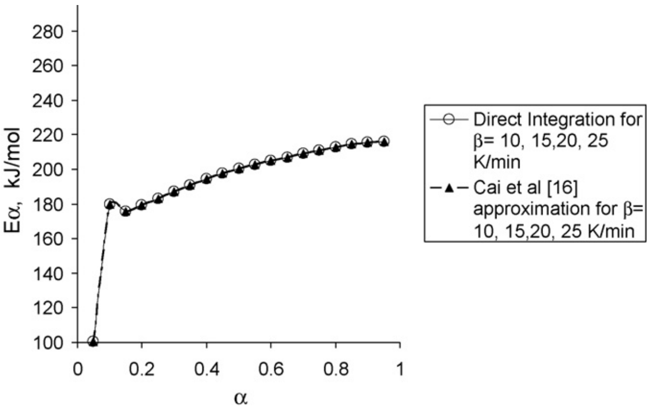

Fig. 5. Dependency of activation energy on conversion of non-isothermal decomposition of waste PE sample using model-free isoconversion technique using direct numerical integration and approximation of Cai et al. [16] to evaluate the temperature integral.

Application of model-free isoconversional method to isothermal and non-isothermal decomposition of waste PE samples to obtain E_α dependency on α is presented through Fig. 7. In case of non-isothermal decomposition of waste PE samples, similar nature was also observed for waste PET samples except a difference in slope of increase of E_α with α, which led to a cross over. The reported data of Lyon [10], Peterson et al. [12] and Gao et al. [13] are also compared with the present result through Fig. 8.

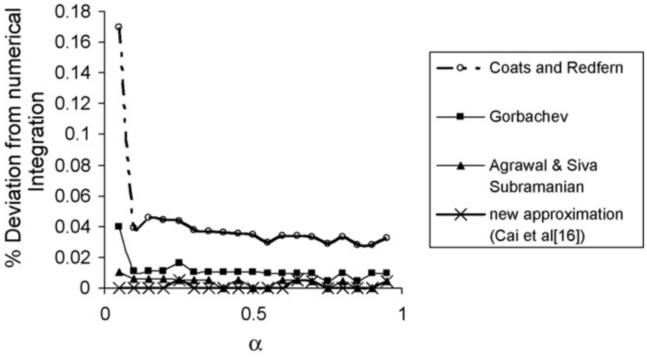

Fig. 6. Percentage deviation from direct numerical integration (The ARD% values are 0.04225, 0.01145, 0.00377 and 0.00104, respectively, for Coats and Redfern, Gorbachev, Agrawal and Subramanian and new approximation [16]).

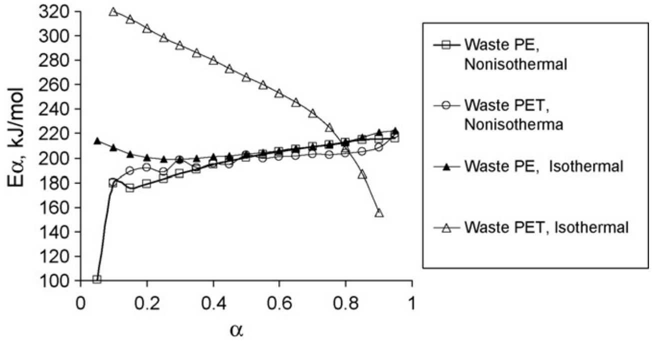

Fig. 7. Comparison of the dependency of activation energy on conversion using model-free isoconversion technique under non-isothermal (direct numerical integration) and isothermal for decomposition of waste PE and PET [15] samples.

It is observed from the figure that in all the cases except that of Lyon [10] the variation of E_α with α follows similar trend. In case of data reported by Lyon [10] for LDPE sample, E_α is almost independent of α after $\alpha \geq 0.2$. This apparent trend may possibly due to lack of sufficient data for different values of α and also due to application of new series solution for integration of the Arrhenius integral. Initial strong and increasing function of α for all the cases (Fig. 8), for $\alpha \leq 0.1$, can be attributed to the fact that the low values of E_α at low α are quite typical for degradation of polymers and usually associated with initiation at the weak links [10–12]. It is further observed that the values of E_α, $\alpha \geq 0.15$, are almost matching with that of Gao et al. [13] except at initial and final stages of decomposition but there is almost a constant difference between the present E_α values and that reported by Peterson et al. [12], Table 2 shows that the present coloured sample is a non-standard one having melting point closer to HDPE with certain amount of impurity. The lower crystallinity data in comparison to standard LDPE and HDPE sample may possibly be due to recycling for several times. The close match of our E_α values with that of Gao et al. [13] indicates that the sample is possibly a HDPE sample. But the differences in values of E_α between the present work and that of Gao et al. [13] may be due to difference in structure and molecular weight. Similarly, the constant difference between the present E_α values and that reported by Peterson et al. [12] might also be due to difference in molecular weight [12] of the samples as well chain branching.

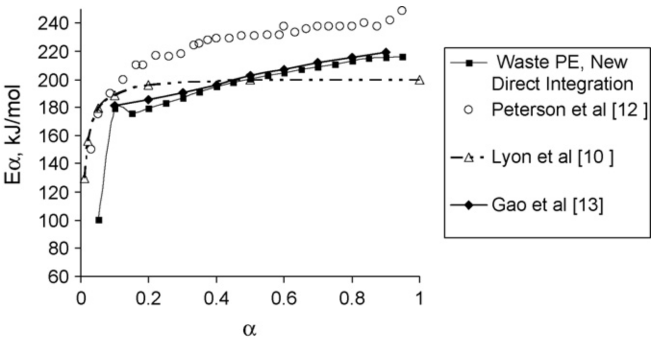

Fig. 8. Comparison between present work and the literature reported data (Lyon [10], Peterson et al. [12], and Gao et al. [13]) for variation of E_α with α.

Thus, it may be concluded here that the sample used for the present study, a non-standard sample, follows neither perfectly the LDPE trend nor the HDPE trend. In practice, while going for solid waste management, most of the waste materials happen to be a non-standard one, particularly in developing countries. Therefore, the present study reflects that it becomes mandatory to study the decomposition behaviour of the waste materials before design of an incinerator and/or pyrolysis unit and one should not use blindly the information available for standard samples.

The thermal decomposition of PE occurs via initiation, propagation (intermolecular and intramolecular hydrogen transfer and β-scission) and termination [3,4,12,13,19]. Vyazovkin [9] discussed that the shape of the increasing dependencies of E_α on α is found due to competing and some independent and consecutive reactions. The results agreed well with the thermal decomposition of polypropylene (PP) and PE samples. Again Peterson et al. [12] reported that after the weak links are consumed, the limiting step of the degradation shifts towards the degradation initiated by random scission. Therefore, higher activation energy is observed at higher conversion. But according to Gao et al. [13], PE degrades via random chain scission, which does not depend upon heating rate. Degradation temperature influences the size of the volatile products. As temperature increases, the minimum length of the fragments, which can evaporate under the prevailing conditions, increases. A higher heating rate leads to degradation at higher temperature, which results in a dependence of distribution of size of volatile products on heating rate and hence the variation of the activation energy with conversion. In our previous work [15], we discussed that in case of non-isothermal decomposition of PET sample, the two opposite effects (nuclei growth and gas diffusion) may finally make activation energy a weak function of conversion. But the difference in the slope of E_α versus α under non-isothermal condition for PE and PET sample may be due to difference in chemical structure.

E_α dependency on α presented in case of isothermal decomposition (Fig. 7) is also quite interesting. Results show that at initial stage till ($\alpha < 0.25$), E_α is weak and decreasing function of α and thereafter it is a weak but increasing function of α. Initial stage of polymer decomposition is often accompanied by melting (or softening) [18]. At this stage the thermal decomposition can be controlled by the process of formation of a gas phase inside the polymer and by nucleation and nucleus growth in a heterogeneous medium. Vyazovkin and Wight [7] have reported that concentration of nuclei at fast heating rate, which is commonly the case for isothermal system (90 K min^{-1} for the present case) is very low and the isothermal decomposition is limited by nucleation only. They also added that nucleation takes place at lower activation energy. Therefore, we may find decrease in E_α at the initial stages. Again, as discussed earlier, distribution of size of volatile products plays an important role for the increase of the activation energy with conversion. Thus the two opposite effects might have resulted in first decrease and then increase in activation energy for PE under isothermal condition. The continuous decrease in E_α with conversion in case waste PET samples has already been discussed in our previous paper [15], which says that nucleation at the initial stages and then diffusion of the

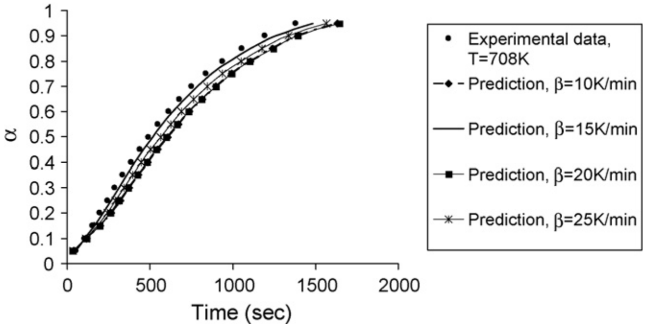

Fig. 9. Prediction at different heating rates using direct integration for isothermal data (708 K) (The ARD% values are 21.133, 5.4928, 18.674 and 12.229, respectively, for heating rates 10, 15, 20 and 25 °C $\min^{-1}$).

formed gas in the subsequent stages of the decomposition phenomenon is responsible for continuous decrease of activation energy of waste PET samples under isothermal condition.

A sample plot for the prediction of isothermal data by model-free kinetics analysis technique at 708 K is presented in Fig. 9 for four different heating rates (10, 15, 20 and 25 K $\min^{-1}$) using direct numerical integration of temperature integral. The results show that amongst the others, 15 K $\min^{-1}$ heating rate (ARD% = 5.4928) [15] very closely predicts the isothermal data.

5. Conclusion

Nonlinear model-free technique is applied to study the non-isothermal decomposition of waste PE sample using several approximations and a new technique of numerical integration. Variation of E_α with α for PE under non-isothermal condition is compared with the reported results by Lyon [10]; Peterson et al. [12]; Gao et al. [13]; the qualitative trends provided by Vyazovkin [9] for complex processes involving competitive reactions, reversible reactions and reactions complicated by diffusion and reported results by the present authors [15] on PET degradation. In addition, variation of E_α with α for PE under isothermal condition is also compared with the results by the present authors [15] on PET degradation. All the approximations used for integration of Eq. (4) showed almost similar result and similar deviations from the results with direct integration. However, the new approximation of Cai et al. is the best amongst the other three approximation methods. Initial strong and increasing E_α dependency on α in case of non-isothermal decomposition is usually associated with initiation at the weak links. Weak but increasing E_α dependency on α in the later stages is possibly due to dependence of distribution of size of volatile products on heating rate. Further, the limiting step of the degradation shifts towards the degradation initiated by random scission leading to higher activation energy at higher conversion. Weak and decreasing followed by weak but increasing function of α in case of isothermal decomposition is possibly due existence of two opposite effects viz., nucleation and distribution of size of volatile products. After comparing the present data with the literature data, it can be concluded that the sample used for the present study, a non-standard sample, neither follows perfectly the LDPE trend nor the HDPE trend. In practice, while going for solid waste management, most of the waste materials happen to be a non-standard one, particularly in developing countries. Therefore, the present study reflects that it becomes mandatory to study the decomposition behaviour of the waste materials before design of an incinerator and/or pyrolysis unit and one should not use blindly the information available for standard samples. The difference in the slope of E_α versus α and the cross-over under non-isothermal condition for PE and PET sample may be due to difference in chemical structure. Optimum E_α dependencies from non-isothermal data have shown reliable prediction of isothermal data. A 15 K $\min^{-1}$ heating rate showed the best prediction.

References

[1] J.R. Opfermann, E. Kaisersberger, H.J. Flammersheim, Thermochim. Acta 391 (2002) 119.
[2] H.J. Flammersheim, J.R. Opfermann, Thermochim. Acta 337 (1999) 141.
[3] H. Bockhorn, A. Hornung, U. Hornung, D. Schawaller, J. Anal. Appl. Pyrol. 48 (1999) 93.
[4] T. Faravelli, G. Bozzano, M. Colombo, E. Ranzi, M. Dente, J. Anal. Appl. Pyrol. 70 (2003) 761.
[5] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340/341 (1999) 53.
[6] S. Vyazovkin, Thermochim. Acta 355 (2000) 155.
[7] S. Vyazovkin, C.A. Wight, Chem. Mater. 11 (1999) 3386.
[8] S. Vyazovkin, D. Dollimore, J. Chem. Inf. Comp. Sci. 36 (1996) 42.
[9] S. Vyazovkin, Int. J. Chem. Kinet. 28 (1996) 95.
[10] R.E. Lyon, Thermochim. Acta 297 (1997) 117.
[11] J.D. Peterson, S. Vyazovkin, C.A. Wight, J. Phys. Chem. B 103 (1999) 8087.
[12] J.D. Peterson, S. Vyazovkin, C.A. Wight, Macromol. Chem. Phys. 202 (2001) 775.
[13] Z. Gao, I. Amasaki, M. Nakada, J. Anal. Appl. Pyrol. 67 (2003) 1.
[14] C. Vasile, E. Costea, L. Odochian, Thermochim. Acta 184 (1991) 305.
[15] B. Saha, A.K. Maity, A.K. Ghoshal, Thermochim. Acta 444 (2006) 46.
[16] J. Cai, F. Yao, W. Yi, F. He, AIChE J. 52 (2006) 1554.
[17] B. Saha, A.K. Ghoshal, Chem. Eng. J. 111 (2005) 39.
[18] V. Mamleev, S. Bourbigot, M. Le Bras, S. Duquesne, J. Šesták, Phys. Chem. Chem. Phys. 2 (2000) 4708.
[19] H. Bockhorn, A. Hornung, U. Hornung, Chem. Eng. Sci. 54 (1999) 3043.
[20] J.R. Fried, Polymer Science and Technology, Prentice-Hall, India, 2000, p. 291.