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Model-free method for isothermal and non-isothermal decomposition kinetics analysis of PET sample

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Abstract

Pyrolysis, one possible alternative to recover valuable products from waste plastics, has recently been the subject of renewed interest. In the present study, the isoconversion methods, i.e., Vyazovkin model-free approach is applied to study non-isothermal decomposition kinetics of waste PET samples using various temperature integral approximations such as Coats and Redfern, Gorbachev, and Agrawal and Sivasubramanian approximation and direct integration (recursive adaptive Simpson quadrature scheme) to analyze the decomposition kinetics.

The results show that activation energy (E_α) is a weak but increasing function of conversion (α) in case of non-isothermal decomposition and strong and decreasing function of conversion in case of isothermal decomposition. This indicates possible existence of nucleation, nuclei growth and gas diffusion mechanism during non-isothermal pyrolysis and nucleation and gas diffusion mechanism during isothermal pyrolysis. Optimum E_α dependencies on α obtained for non-isothermal data showed similar nature for all the types of temperature integral approximations.

Keywords: Thermal decomposition kinetics; TGA; PET; Non-isothermal; Isothermal; Isoconversion; Activation energy

1. Introduction

Plastic materials have become an important part of urban solid waste. To overcome certain demerits of recycling and incineration, researchers across the world have focused on development of value added products from waste plastics such as activated carbon, liquid fuel and gaseous product and monomer recovery [1–5]. The application of novel alternative process, pyrolysis or catalytic degradation as a means of reusing scrap tyres and waste plastics, have recently been the subject of renewed interest. The kinetics of pyrolysis of plastics is important for the proper selection of reactor, optimization of the reactor design and operating condition. The correctness of the kinetics expression heavily depends upon reliable evaluation of activation energy from the decomposition behavior under different conditions of temperature and/or atmosphere. Polymer decomposition mechanism, needless to mention, is a complicated phenomenon. The thermal decomposition of polymer can be described as occurring by a set of series or parallel chemical reactions via random scission mechanism, chain scission mechanism, etc. However, TGA is one of the widely used techniques to study the thermal decomposition of polymer. In absence of prior information about real kinetic mechanism, the reaction model can be chosen from a set of well-known reaction models to fit experimental data usually done in model-fitting techniques. In most of the reported literatures, model-fitting methods are applied to evaluate pyrolysis kinetics parameters using single heating rates and traditional reaction models. Pyrolysis study of various mixtures and individual commodity plastics including poly(ethylene terephthalate) (PET) using thermogravimetric analyzer (TGA) coupled with mass spectrometry (TG:MS) showed that plastics with different molecular structures decomposed at different temperatures [5–8]. Application of simplified kinetics model resulted in discrepancies in kinetic parameters obtained for polystyrene (PS) from isothermal and non-isothermal experiments. Therefore, detailed kinetics scheme was proposed for polystyrene (PS) and polyethylene (PE) taking into consideration of heat transport effect and complex reaction mechanism [6,7]. Pyrolysis kinetics of various substances including polyamide 6 to recover ε-carprolactam

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[8], scrap tyre using two-step reaction model and single heating rate [9], electronic packaging materials at high temperature and in oxidizing atmosphere [10], poly(vinyl chloride) [11] and PE and PS mixture [12] were reported in the literature. The non-isothermal TGA kinetics of poly(trimethyl terephthalte) (PTT) and PET under argon, air and nitrogen by Freeman-Carroll, Friedman and Chang methods to estimate the kinetics triplet [13] and PET thermal decomposition under strict pyrolysis condition and with different proportions of oxygen using TGA [14] were studied. Thermal degradation of polymer is mostly described by random scission mechanism, which does not follow rigorously first-order kinetics. Therefore, a relation for determining reaction order was established to avoid blind use of first-order kinetics [15]. In our previous paper, we used *n*th-order technique and ASTM E698 techniques to determine apparent kinetics triplet for thermal degradation of PET using TGA [16]. Non-isothermal kinetics for polymer was reported by Mamleev et al. [17]. In another paper, Mamleev and Bourbigot [18] reported cotton decomposition by modulated thermogravimetry (MTG) using single or multi heating rates and multi-step reaction mechanisms. They reported that in a number of cases it is possible that the obtained kinetics triplet describes the rate-limiting step of the decomposition process and recommended that this approach is acceptable for chemical engineering applications. Artificial neural network technique [19] and various computational methods [20] were also applied to study thermal decomposition kinetics. Thus, the traditional model-fitting kinetics analysis using single heating rates and single step decomposition model gives only a single set of kinetics triplet, which is estimated after minimizing deviation between simulated data and experimental data. However, presently International Confederation of Thermal Analysis and Calorimetry (ICTAC) project, 2000 ruled out the validity of thermal kinetics analysis using single heating rate [21]. Modern model-fitting thermal kinetics analysis methods uses multi-heating rates, takes care of multi step reactions and incorporates possible partial diffusion, back reaction, branch reaction, etc. in the model equations [21,22]. But still the selection of appropriate model and initial guess of kinetics parameters are major drawback of model-fitting method [22]. 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 [23].

On the other hand, use of isoconversion methods, i.e., Vyazovkin model-free approach is a trustworthy way of obtaining reliable and consistent kinetic information from both non-isothermal and isothermal data. It can also help to reveal the complexity of multiple reactions due to the dependencies of activation energy on the extent of conversion [23–27]. A few literatures dealt with the kinetics analysis using isoconversion methods such as thermal decomposition kinetics of solid like 1,3,5,7-tetraanitro-1,3,5,7 tetrazocine and ammonium dinitramide [23], ammonium perchlorate [24,25], calcium carbonate [24], triphenylphosphine oxide [26] and desolvation kinetics of drag solvate, sulfameter (5-methoxy sulfadiazine and dioxolane) [28].

Polymer decomposition phenomenon, as mentioned earlier, involves several steps with different activation energies occurring at different temperature regions. So, the activation energy, E is expected to be a function of temperature and the extent of conversion (α).

Isothermal kinetics data are mostly needed for practical application as most of the pyrolysis reactors operate at constant temperature. So, the simulation of isothermal kinetics can be performed using non-isothermal data by means of modern isoconversion methods, i.e., Vyazovkin model-free approach. In the present work we have applied model-free technique to investigate both non-isothermal and isothermal decomposition kinetics of waste PET samples using various temperature integral approximations such as Coats and Redfern, Gorbachev, and 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 behavior are discussed. The obtained optimum E_α dependencies derived from non-isothermal data is used to simulate the isothermal kinetics data. The simulation result agrees well with the experimental data.

2. Experimental

2.1. Experimental procedure and equipment

The non-isothermal and isothermal decompositions were carried out with samples from waste PET soft drink bottles from M/s Coca Cola. 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. PET samples were shredded into very small pieces (Mess size: −40 + 60) and directly fed to the TGA instrument. Total mass of sample taken was 7–10 mg for each run of the experiments for non-isothermal case. Alumina crucible (70 μl from non-isothermal and 900 μl for isothermal case) was used as sample holder. The experiments were repeated thrice at heating rate of 10 K min^{-1} to confirm the repeatability and authenticity of the generated data. Experiments were conducted in dynamic condition at different heating rates of 5, 10, 15, and 25 K min^{-1}. Total mass of the sample with the corresponding experimental conditions is given in Table 1. Variations of conversion (α) with temperature during non-isothermal pyrolysis at different heating rates are reported through Fig. 1. Fig. 2 represents variations of conversion (α) with temperature during isothermal decomposition at different target temperatures. Four different temperatures viz. 685, 693, 703, and 711 K were maintained to study the isothermal decomposition (Fig. 2). 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).

Table 1
Experimental conditions for TGA studies

Sample Name	Non-isothermal			
	Initial mass (mg)	Heating rate (K/min)	Temperature range (K)	$T_{w0}/T_d/T_m/T_{w\infty}$ (K)
Coca-Cola	7.96	5	303–873	622.01/639.4/703.03/790.42
	8.25	10	303–873	625.51/655.43/715.05/786.64
	9.45	15	303–873	623.08/664.57/723.599/788.69
	9.60	25	303–873	623.82/671.76/737.81/792.12

Sample Name	Isothermal			
	Initial mass (mg)	Sample temperature (K)	Total experimental time (min)	Total loss of weight (%)
Coca-Cola	45.99	684.8	0–84.3	83.03
	52.49	692.9	0–94.4	82.47
	42.16	702.9	0–94.4	83.92
	29.64	710.9	0–94.6	86.22

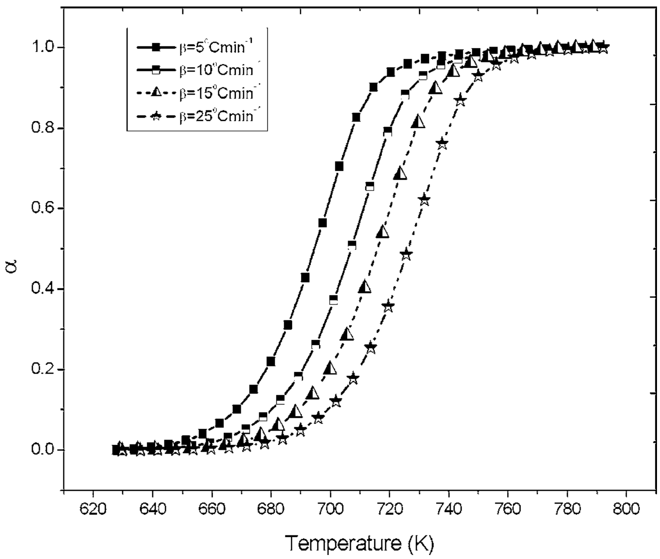

Fig. 1. Variation of conversion (α) with temperature during thermal pyrolysis of waste PET samples.

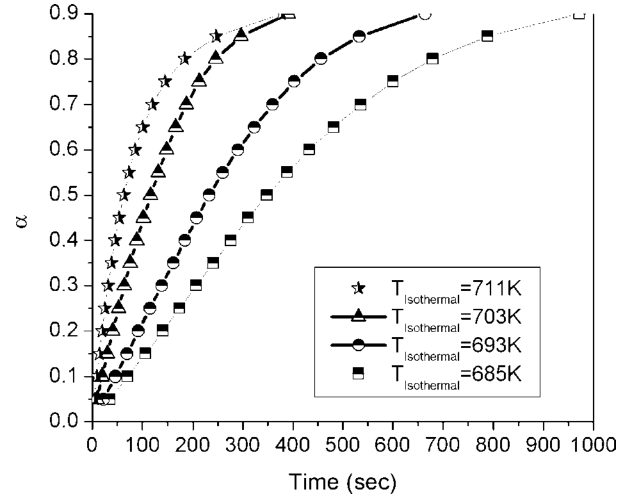

Fig. 2. Variation of conversion (α) with time during isothermal pyrolysis of waste PET samples.

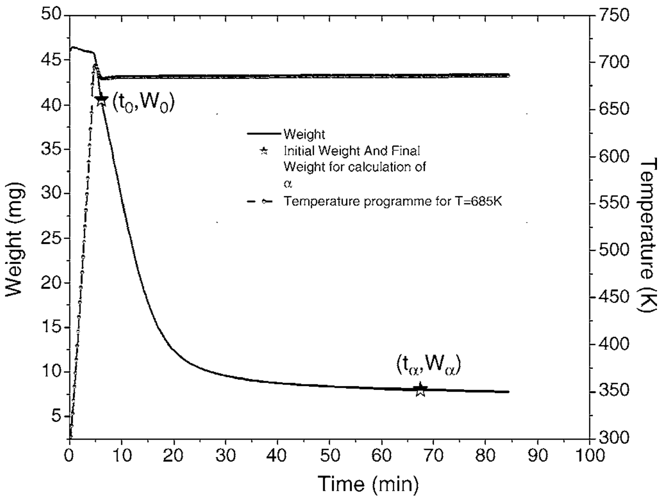

Fig. 3. Weight loss and temperature programme for isothermal condition.

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

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

where t is 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_∞ the final sample weight (mg), $d\alpha/dt$ the rate of reaction (min^{-1}), and $f(\alpha)$ is the reaction model. k_0, the pre-exponential factor (K^{-1}) and E the activation energy (kJ mol^{-1}) are the Arrhenius parameters. R is the gas constant ($\text{kJ mol}^{-1}\,\text{K}^{-1}$). The reaction model may take various forms based on nucleation and nucleus growth, phase boundary reaction, diffusion, and chemical reaction [17,23,26]. However, the present investigation does not require any information of reaction model since we report here thermal decomposition kinetics of PET sample using model-free approach.

At a constant heating rate under non-isothermal conditions the explicit temporal/time dependence in Eq. (1) is eliminated 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 (K min^{-1}) and $\mathrm{d}\alpha/\mathrm{d}t$ is rate of reaction (K^{-1}).

Follows below a brief discussion of the model-free technique used to obtain E_α, activation energy as a function of α.

3.1.1. Model-free isoconversion method for non-isothermal experiments [23–26]

For a set of four experiments carried out at four different heating rates (5, 10, 15, and 25 °C min^{-1}) the activation energy can be determined at any particular value of α by finding the value of E for which the objective function Ω is minimized [26], where

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

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. The numerical integration of Eq. (4) was carried out by a function called ‘quadv’ using recursive adaptive Simpson quadrature. Several popular approximations such as Coats–Redfern, Gorbachev, and Agrawal and Sivasubramanian, discussed subsequently, are also used for integration of Eq. (4) to compare the results with direct integration.

Coats and Redfern [29] first approximated the integral by the relation:

$$\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \frac{RT^2}{E}\left(1-\frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right) \tag{5}$$

Gorbachev [27] suggested a more accurate approximation as

$$\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \frac{RT^2}{E}\left(\frac{1}{1+\frac{2RT}{E}}\right)\exp\left(-\frac{E}{RT}\right) \tag{6}$$

Gorbachev approximation [29] is better than Coats and Redfern approximation for E ranging from 40 to 250 kJ mol^{-1} over the temperature range 300–1000 K.

Agrawal and Sivasubramanian [29] improved the temperature integral by the relation:

$$\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \frac{RT^2}{E}\left[\frac{1-\frac{2RT}{E}}{1-5\left(\frac{RT}{E}\right)^2}\right]\exp\left(-\frac{E}{RT}\right) \tag{7}$$

This approximation is proved to be superior to the other two approximations for E ranging from 40 to 250 kJ mol^{-1} over the temperature ranges 300–1000 K [29].

3.1.2. Model-free method for isothermal experiments [23–25]

Eq. (1) can be rearranged as

$$g_j(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = k_j(T_i)t \tag{8}$$

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:

$$\ln(k_j(T_i)) = \ln(k_{0j}) - \frac{E_{\alpha j}}{RT_i} \tag{9}$$

Under isothermal conditions, Eqs. (8) and (9) can be combined to obtain:

$$-\ln t_{\alpha,i} = \ln\left[\frac{k_{0j}}{g_j(\alpha)}\right] - \frac{E_\alpha}{RT_i} \tag{10}$$

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 [27] by Eq. (11):

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT_0}\right)\mathrm{d}T}{\beta \exp\left(\frac{-E_\alpha}{RT_0}\right)} \tag{11}$$

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. (11). 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_{w0} to eliminate moisture and volatile compound content. A quick thermal decomposition is observed in the range of T_d to $T_{w\infty}$ (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 to the end of experiment.

4.2. Isothermal decomposition

It is evident from non-isothermal experiment (Table 1) that the PET thermal decomposition starts in the temperature range of 639–672 K and the maximum decomposition temperature lies between 703 and 738 K depending upon the heating rate. Also at 10 K min^{-1} heating rate, the universal heating rate, the maximum decomposition temperature is 715 K. Therefore, the four different temperatures viz. 685, 693, 703, and 711 K of isothermal experiments were chosen in between 672 and 715 K (i.e., in between start of decomposition and maximum decomposition temperatures) with an approximate interval of 10 K. A very quick fall (82–85% weight loss) (Fig. 3) is observed within 62.5–67 min after reaching the preset isothermal temperature (6–6.2 min) for each of the isothermal experiments for different temperature. The initial weight, temperature, total time and percentage loss of total weight are presented in Table 1. After this quick fall, the sample continues decomposing smoothly and very slowly to the end of experiment. We have taken W_0 at t_0 when the preset temperature is reached and W_∞ at t_∞ when weight loss is about 99.5% of total weight loss for the calculation of α, conversion (Fig. 3). The experiment at temperature 685 K was repeated thrice to test the repeatability.

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 conversion obtained for non-isothermal decomposition for PET sample using Agrawal and Sivasubramanian approximation is shown in Fig. 4. For the other approximations (Coats–Redfern and Gorbachev) exactly similar nature is obtained (not reported here). We compared the optimal activation energy obtained by direct numerical integration and by using various approximation techniques. This is reported in terms of percentage deviation of E_α obtained by Agrawal and Sivasubramanian approximation (Fig. 5) from direct numerical integration using recursive adaptive Simpson quadrature scheme. All the approximations of temperature integral have all most same deviation from the results of recursive adaptive Simpson quadrature scheme. The average relative deviation (ARD) is defined as

$$\text{ARD}\,(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{E_{\alpha,i}^{\text{DI}} - E_{\alpha,i}^{j}}{E_{\alpha,i}^{\text{DI}}}\right| \tag{12}$$

where $E_{\alpha,i}^{\text{DI}}$ and $E_{\alpha,i}^{j}$ respectively, are the activation energies calculated by direct integration method (recursive adaptive Simpson quadrature scheme) and jth approximations of temperature integral, respectively. N is the number of data points. The ARD values are 10.81, 10.82, and 10.83 for Coats and Redfern, Gorbachev, and Agrawal and Sivasubramanian approximation, respectively. Application of model-free isoconversional method to isothermal and non-isothermal decomposition of waste PET samples to obtain E_α dependency on α is compared through Fig. 6. It is observed from the figure that that activation energy is weak but increasing function of conversion, though there are some fluctuations at the initial stages of conversions under non-isothermal condition. But activation energy is a strong and continuously decreasing function of conversion in case of isothermal condition. These may be explained as follows. According to Mamleev et al. [17], initial stage of polymer decomposition is often accompanied by melting (or softening). At this stage the thermal decomposition can be controlled by the process of for-

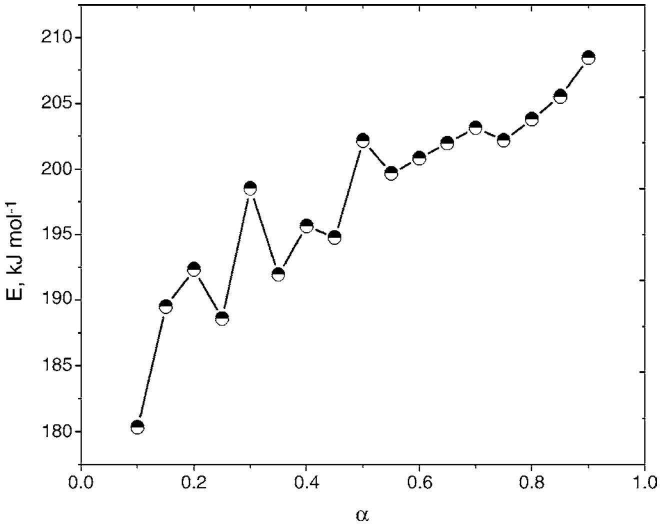

Fig. 4. Dependency of activation energy on conversion of non-isothermal decomposition of waste PET samples using model-free isoconversion technique and Agrawal and Sivasubramanian approximation method to evaluate the temperature integral.

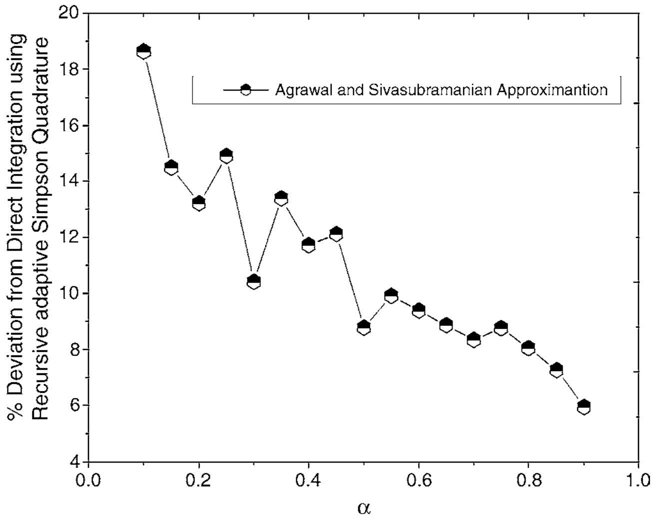

Fig. 5. Comparison of direct integration method and approximation relations used in model-free kinetics analysis.

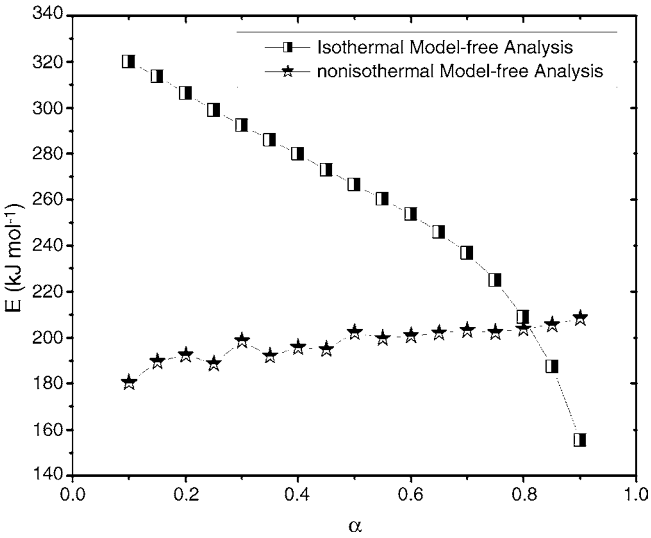

Fig. 6. Dependency of activation energy on conversion using model-free isoconversion technique for non-isothermal (Agrawal and Sivasubramanian approximation) and isothermal decomposition of waste PET samples.

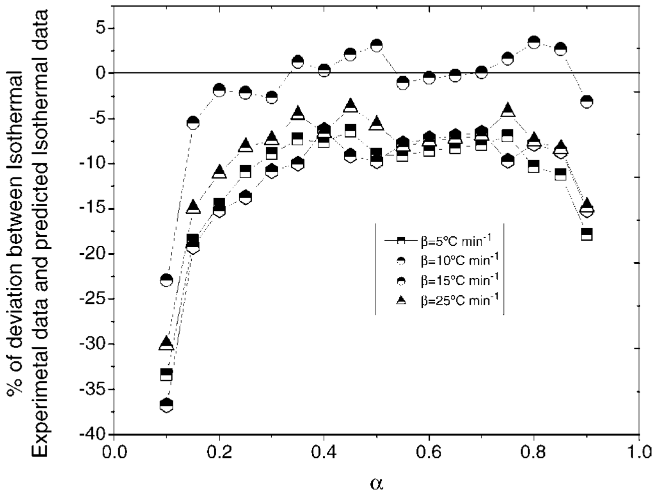

Fig. 7. Percentage deviation from experimental data for isothermal (685 K) prediction at different heating rates using Agrawal and Sivasubramanian approximation (The ARD values are 11.59, 1.51, 11.80 and 9.24, respectively, for heating rates 5, 10, 15, and 25 °C min^{-1}).

mation of a gas phase inside the polymer and by nucleation and nucleus growth in a heterogeneous medium. Further, Vyazovkin and Wight [25] 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. But in case of non-isothermal decomposition, it is limited by nuclei growth since the heating rate is low (5–25 K min^{-1} in the present case). They also added that nucleation and nuclei growth takes place at lower and higher activation energies, respectively. Therefore, we may find decrease and increase in activation energies for isothermal and non-isothermal cases, respectively, at the initial stages (Fig. 6). In addition, it is also reported by Vyazovkin and Wight [25], Vyazovkin [27] and Flammersheim and Opfermann [22] that diffusion of the formed gas plays an important role to reduce the activation energy in the subsequent stages of the decomposition phenomenon. Therefore, in case of isothermal decomposition we can observe continuous decrease of activation energy during the course of decomposition (Fig. 6). But in case of non-isothermal decomposition, the two opposite effects (nuclei growth and gas diffusion) may finally make activation energy a weak function of conversion. It may further be observed in case of isothermal decomposition that at the later stage of the decomposition phenomenon, the activation energy quickly falls with conversion. This may possibly be attributed to the fact that at the later stage formation of porous solid residue makes the diffusion faster leading to more decrease in activation energy.

However, the optimum E_α dependencies from non-isothermal data have shown reliable prediction of isothermal data. A sample plot for the prediction of isothermal data by model-free kinetics analysis technique at 684 K is presented in Fig. 6 for different heating rates using Agrawal and Sivasubramanian approximation during numerical integration of temperature integral. The corresponding percentage deviations from experimental data are shown in Fig. 7. The results show that 10 °C min^{-1} heating rate (ARD = 1.51) better predicts the isothermal data for all isothermal temperatures. ARD is defined as

$$\mathrm{ARD}\,(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{t_{\alpha,i}^{\mathrm{exp}} - t_{\alpha,i}^{j}}{t_{\alpha,i}^{\mathrm{exp}}}\right| \qquad (13)$$

where $t_{\alpha,i}^{\mathrm{exp}}$ and $t_{\alpha,i}^{j}$ are the experimental times and times simulated by model-free method from non-isothermal experiment (Eq. (11)), respectively, to reach the conversion, α.

5. Conclusion

Reliable evaluation of kinetics parameters is very important for pyrolysis of polymer to optimize the reactor design and operating conditions required during its recycling. Model-free method is advantageous over model-fitting method since it evaluates the accurate activation energies without reaction models. In the present study, model-free method is used to evaluate the optimum activation energy of decomposition of waste PET under non-isothermal condition. Optimum E_α dependencies from non-isothermal data have shown reliable prediction of isothermal data. Since, most of the pyrolysis reactors/units operate under isothermal conditions, the optimum activation energy can be used to design a recycle reactor for PET. The model-free isoconversion method of analysis shows that activation energy is a weak but increasing function of conversion in case of non-isothermal decomposition and strong and decreasing function of conversion in case of isothermal decomposition. Variation of E_α with α indicates possible existence of nucleation, nuclei growth and gas diffusion mechanism during non-isothermal pyrolysis and possible existence of nucleation and gas diffusion mechanism during isothermal pyrolysis. Optimum E_α dependencies on α obtained for non-isothermal data showed similar nature for all the types of approximations (Coats and Redfern, Gorbachev, and Agrawal and Sivasubramanian approximations) used in the present study.

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