

Hybrid genetic algorithm to find the best model and the globally optimized overall kinetics parameters for thermal decomposition of plastics

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Abstract

Model-fitting methods that are exercised till date for evaluating the optimum overall pyrolysis kinetics parameters usually applied traditional gradient base optimization techniques but associated with major drawback of attaining global optimum due to uncertainties in selection of initial guess. To overcome such uncertainties and drawbacks, we have, applied the modern evolutionary optimization method (hybrid genetic algorithms (HGA) technique) for 15 models to attain the globally optimum kinetics parameters using the experimental thermogravimetric analysis (TGA) data and we did compare the experimental and simulated data to expect the possible mechanism to occur during pyrolysis. As case studies, we used thermal decomposition of waste polyethylene terephthalate (PET), waste low-density polyethylene (LDPE) and polypropylene (PP). The suitability of the models is also tested using the AIC_c score. Nucleation and growth model with reaction order, $n = 2/3$ is the best suited one and it also predicted the experimental TGA data successfully. The n th order model also shows good AIC_c score and well predicted the experimental TGA data.

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1. Introduction

Polymer decomposition phenomena can be described by a set of series or parallel chemical reactions via random scission mechanism, chain scission mechanism, etc. thermogravimetric analysis (TGA) is widely used technique to study such decomposition of polymer. Pyrolysis kinetics 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 behaviour under different conditions of temperature and/or environment. In most of the reported literatures, model-fitting methods are applied to evaluate pyrolysis kinetics parameters using single heating rates and traditional reaction models, but 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, 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 [2–6]. Still the selection of appropriate model [1–11], oversimplified approximation of temperature integral [4], and initial guess of kinetics parameters are major drawbacks of model-fitting methods [3]. Recently, Vyazovkin model-free kinetics technique has extensively been applied for many complex reaction processes to obtain reliable and consistent kinetics information about the overall process [12–21]. Apart from this, isoconversion method presents a compromise between the single-step Arrhenius kinetic treatments and the prevalent occurrence of processes whose kinetics are multi-step or non-Arrhenius [18–19]. However, information on activation energy is useless without a method of calculation of kinetics curves. For description of multistage processes, the

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use of model-fitting methods is unavoidable [7]. Since polymer decomposition is a complicated process, serious doubts arise about an accurate description of decomposition kinetics by using simplified equations expressing a rate of the process only via mass loss [9]. Therefore, 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 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 [1–11]. It is worth mentioning that a good fit of experimental results is only one criterion, but it should not be the unique one [10]. Further analysis involving infrared or mass spectroscopy, morphology study using SEM or TEM during decomposition can be useful in order to obtain more information about processes involved.

In view of these, application of genetic algorithm (GA) or hybrid genetic algorithm (HGA) to overcome the above-mentioned drawback of model-fitting method for the estimation of kinetics parameters has attracted interest in chemical engineering, chemistry, and other fields [22–27]. GA, based on natural selection, repeatedly modifies a population of individual solutions. Over successive generations, the population “evolves” toward an optimal solution. GA is considered to have better global optimizing properties than other heuristic optimization techniques, especially, in the case of discontinuous, non-differentiable, stochastic, and highly non-linear problems having large search spaces with many local extrema [22–31].

Therefore, in the present work, we have reported pyrolysis kinetics of polypropylene (PP), low-density polyethylene (LDPE) and polyethylene terephthalate (PET) for different heating rates employing the HGA technique to get the globally optimum overall kinetics parameters (activation energy, E ; pre-exponential factor, k_0 ; reaction model) [7–9] using direct integration technique of temperature integral. In this approach, GA is used to provide initial guess for the local optimization

algorithm (LOA), the direct search method used in the present work. Fifteen different physico-chemical models available from literatures are used coupled with HGA to find out the best one that predicts the experimental data well. In addition to that, Akaike’s Information Criteria (AIC) [11,32] is also applied to choose the most appropriate reaction model. The 15 reaction models used are based on nucleation and growth, phase boundary reaction, diffusion, power law and chemical reaction models with different values of the order of the reaction, n [2–9,13,15]. Thus, applying HGA (possibly first time in polymer decomposition) in the present work, we tried to establish the reaction mechanism involved during thermal decomposition of plastic samples mentioned above and correspondingly reported the globally optimized kinetics parameters. The present work exploits the advantages of GA to overcome the limitation of model-fitting methods generally used to find the kinetic parameters, where initial guess of kinetics parameters are the major drawbacks.

2. Experimental [6,11,17,20,21]

The non-isothermal decompositions were carried out for waste PET soft drink bottles, waste LDPE, and PP (polypropylene homopolymer (PPHP), trade name: Koylene ADL, Grade AS030N) supplied by Indian Petrochemicals Corporation Limited, Vadodara, India, with melt flow index 3.0. Experiments were carried out in a TGA instrument of Mettler TOLEDO with model no. TGA/SDTA 851^e under nitrogen environment for a range of temperature 303–875 K. Nitrogen flow rate was maintained at 40–50 ml min⁻¹ according to the specification of the equipment. All samples were shredded into very small pieces and directly fed to the TGA instrument. Thermal decomposition experiments were conducted in dynamic condition at different heating rates. The experiments were repeated three times at a heating rate of 10 K min⁻¹, to confirm the repeatability and authenticity of the generated data for all cases. The deviations observed are very little. However, the deviations are reported in

Table 1
Experimental conditions for TGA studies

Sample	Non-isothermal experiments				
	Initial mass (mg)	Heating rate (K min ⁻¹)	Temperature range (K)	Residue (%)	$T_{w0}/T_d/T_m/T_{w\infty}$ (K)
Waste	7.76	5	303–873	2.02	551.1/621.3/734.2/805.5
LDPE	8.43	10	303–873	1.92	551.3/634.3/748.4/800.4
	11.19	15	303–873	2.29	549.0/648.2/754.0/800.4
	8.66	20	303–873	2.35	549.4/646.8/763.3/802.5
	10.96	25	303–873	1.23	576.5/680.2/770.4/809.6
	Waste	7.80	5	303–873	11.59
PET	8.12	10	303–873	13.56	623.2/653.2/710.4/785.1
	9.36	15	303–873	14.84	623.1/661.4/720.6/782.7
	9.52	25	303–873	14.13	623.8/671.8/734.8/786.1
	PP	19.77	5	303–873	1.49
PP	20.32	10	303–873	0.88	526.9/670.0/723.07/749.8
	20.67	15	303–873	0.51	527.8/684.6/731.4/777.6
	19.78	20	303–873	0.73	527.5/684.8/736.8/770.2
	19.41	25	303–873	0.70	527.1/696.6/742.9/785.7

Table 2
Characteristics of samples (LDPE, PET and PP)

Sample type	Melting point (°C)	Melting point of standard PE samples [33] (°C)	Heat of fusion (J g ⁻¹)	Heat of fusion, 100% crystallinity (J g ⁻¹)	Degree of crystallinity (%)	Crystallinity of standard PE samples [33] (%)	Purity (residual amount after TGA experiment up to 600 °C) (%)
Waste LDPE	128.7	LDPE: 98–120	38.37	290	23.95	LDPE: 50–70	Non-isothermal: 1–2
Waste PET	246.55	PET: 267	46.85	115	40.74	–	10–15
PP	175.69	PP: 165–171	62.38	190	32.83	82	0.67–1.4

terms of average relative deviation,

$$\text{ARD} (\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{x_i^{\text{exp}} - x_{\text{av},i}}{x_{\text{av},i}} \right|,$$

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, and i is the number of data points for each experiment. Results show that ARD% is 0.009–0.021, 0.051–0.119, 0.005–0.019 (for temperature), 0.09–0.257, 0.865–2.457, and 0.041–0.1579 (for mass) of waste PET, waste LDPE, and PP, respectively. Further details of the experimental procedure are described in our published literatures [6,11,17,20–21]. Experimental conditions for TGA studies are given in Table 1. Properties of the polymers used for the present study are presented through Table 2.

3. Kinetics analysis

3.1. Multi-heating rates model-fitting method for non-isothermal experiments [1–11]

The kinetics model equations combined with the Arrhenius approach of the temperature function of reaction rate is expressed as:

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

where t is time (given in min), T the temperature (given in K), α the conversion of the reaction [$\alpha = (W_0 - W)/(W_0 - W_\infty)$, where W_0 is the initial weight of the sample, W the sample weight at any temperature T and W_∞ is the final sample weight all sample weight given in milligrams], $d\alpha/dt$ the rate of reaction (expressed in units of min⁻¹), and $f(\alpha)$ is the reaction model. The terms k_0 , which represents the pre-exponential factor (expressed in units of K⁻¹), and E , which is the activation energy (expressed in units of kJ mol⁻¹), are the Arrhenius parameters. R is the universal gas constant (expressed in units of 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 [2–9,13,15]. In the present investigation, we have applied 15 such well-known models for estimating the best fitted overall kinetics parameters (pre-exponential factor, k_0 ; activation energy, E) except n th order reaction model, where we have obtained the best fitted kinetics triplet (order of chemical reaction, n ; pre-exponential factor, k_0 ; activation energy, E) using

single-step and multi-heating rates for all the three types of polymers.

At a constant heating rate under non-isothermal conditions the explicit temperature/time [11,13], dependence in Eq. (1) is eliminated through the trivial transformation

$$\beta \frac{d\alpha}{dT} = k_0 \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (2)$$

where $\beta = dT/dt$ is the heating rate (K min⁻¹) and $d\alpha/dT$ is rate of reaction (K⁻¹).

For each step Eq. (2) can be integrated as

$$\begin{aligned} g(\alpha) &= \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{k_0}{\beta}\right) \int_0^T \exp\left(\frac{-E}{RT}\right) dT \\ &= \left(\frac{k_0}{\beta}\right) I(E, T) = x \end{aligned} \quad (3)$$

and

$$I(E, T) = \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

For example, the n th order and first order kinetic model equation can also be solved by substituting $k_0/\beta = \exp(\tilde{K}_0)$, where $K_0 - \ln(\beta) = \tilde{K}_0$ and $k_0 = \exp(K_0)$ and transforming Eq. (3) as follows.

For $n \neq 1$,

$$\alpha = 1 - [(\exp(\tilde{K}_0))I(E, T)(n+1) + 1]^{1/(n-1)} \quad (5)$$

$$\text{For } n = 1, \quad \alpha = 1 - \exp[-(\exp(\tilde{K}_0))I(E, T)] \quad (6)$$

The temperature integral (Eq. (4)) can be evaluated by several popular approximations and direct numerical integration as reported in our recent publications [11,17,20–21]. We used the technique of direct numerical integration [20–21] for the same, where the temperature integral takes the form

$$I(E, T) = \int_0^T \exp\left(-\frac{E}{RT}\right) dT \frac{E}{R} \left[\frac{\exp(-u)}{u} - Ei(u) \right] \quad (7)$$

where $u = E/RT$ and $Ei(u) = \int_u^\infty (\exp(-u)/u) du$.

Details of development of Eq. (7) and numerical procedure have been discussed in our recent publication [20].

Akaike's Information Criteria [11,32], discussed below, is also applied to choose the appropriate reaction model.

$$\text{AIC} = N \ln\left(\frac{\text{SS}}{N}\right) + 2K \quad (8)$$

where N is number of data points, K the number of parameters plus one and SS is sum of square of the difference between the calculated mass and experimental mass.

The corrected AIC for small number of data points is obtained from

$$AIC_c = AIC + \frac{2K(K+1)}{N-K-1} \quad (9)$$

The model with the lower AIC_c score is the model more likely to be correct [11,32].

3.2. Multi-parameter optimization

The objective function most frequently used in case of multiple heating rates of TGA curves to calculate optimum values of $\Delta(E, K_0, n)$ for total J data points and total L heating rates by minimization of square of deviation between experimental mass [$M_{Exp}(T)$] and calculated mass [$M_{Cal}(T)$] is given by Eq. (10).

$$\Delta(E, K_0, n) = \sum_{l=1}^L \left[\sum_{j=1}^J [M_{Exp,l,j} - M_{Cal,l,j}] \right]^2 \quad (10)$$

where j and l denote the data point and heating rate, respectively.

The values of $M_{cal}(T)$ calculated for each single value of $\alpha_{l,j}$ are as follows:

$$M_{Cal,l,j} = M_{Exp,l,0} - \alpha_{l,j}(M_{Exp,l,0} - M_{Exp,l,\infty}) \quad (11)$$

where $M_{Exp,l,0}$ is the initial is point and $M_{Exp,l,\infty}$ is the final point of l th heating rate. However, in the present work, all models except n th order reaction model involved two parameters optimization since in those models E, K_0 values are optimized for different fixed values of n .

The calculated optimum values are completely dependent on the model used and can greatly differ for different models for all traditional model-fitting kinetics analysis techniques [7–11]. Moreover, this multi-parameter optimization strongly depends on the initial guess values of the parameters [2,3,11] leading to possibility of achieving false minima, thus, resulting in unreliable values of the parameters. Therefore, in the present work, hybrid genetic algorithm, discussed later, in MATLAB using ‘fminsearch’ as hybrid local search method in GA toolbox, is used for the objective function [Eq. (10)] minimization. Here, GA is used to provide initial guess values of the kinetics triplet (activation energy, pre-exponential factor and reaction order) for the local optimization algorithm, the direct search method.

3.3. The structure of a hybrid genetic algorithm [22–31]

GA employs a probabilistic approach and has better global optimizing properties but shows poor convergence to optimality. Whereas, HGA using a typical basic GA with elitist strategy to reach near gradient or/direct-based search method shows faster convergence to global optima. Therefore, often GA is hybridized using a LOA to improve its performance as a global optimization technique while overcoming the limitations of poor conver-

gence and weak exploitation capabilities. The various kinds of hybridizations using LOA can be classified into three types.

3.3.1. Pre-hybridization [30]

Here the initial population of GA is generated using an LOA reducing the solution space for GA and improving the efficiency. Such an approach seems to be well suited to the specific problem they addressed and does not seem to be suitable for general optimization.

3.3.2. Organic-hybridization [30]

In this case, an LOA is used as one of the operators of GA for improving each member of the population in each generation. Though the organic-hybridization is computationally more efficient than a GA, it offers little assurance of global minima and also lacks proper convergence criteria.

3.3.3. Post-hybridization [30]

In this case, GA is used to provide an initial design for LOA. This kind of hybridization seems to be the best way of combining the best characteristics of the two approaches as no compromise is made on the global and local optimizing characteristics.

3.4. Structure of HGA used for the present work [31]

In the present work, we have used post-hybridization method, i.e. GA coupled with LOA. We have used the default initial population size (20), the default creation function ‘Uniform’ to create a random initial population with a uniform distribution, the stochastic options from the GA toolbox that chooses parents for the next generation, Gaussian function for mutation, scattered function for the next generation, forward migration option for the movement of individuals between subpopulations, default value of migration fraction (0.2) for migration of individuals between subpopulation, value of interval as 20, i.e. migration between subpopulations takes place every 20 generations, multidimensional unconstrained non-linear minimization function ‘fminsearch’ as the hybrid function that uses the final point from the genetic algorithm as its initial point, and specified only the number of generation as stopping criteria.

The optimized kinetics triplet obtained by the above-configured HGA showed pretty good prediction of the experimental TGA decomposition data. However, further improvement on the HGA configuration can be made through optimization of configuration through several runs, for present cases we have consider 20 runs for each model and we have taken most appropriate values of triplets/doublets from those runs.

4. Results and discussion

4.1. Pyrolysis kinetics analysis

Pyrolysis of the PP and LDPE samples were carried out at five different heating rates (5, 10, 15, 20, and 25 K min⁻¹) and of PET sample was carried out at four different heating rates (5, 10, 15, and 25 K min⁻¹). The temperature at which $\alpha = 0$ (T_{w0}), the temperature at which decomposition starts and $\alpha \approx 0.1$ (T_d),

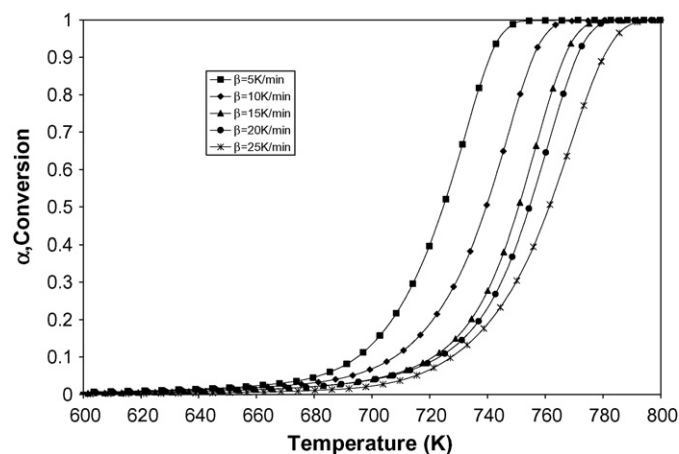


Fig. 1. Variation of conversion (α) with temperature during non-isothermal pyrolysis of waste LDPE sample at multiple heating rates.

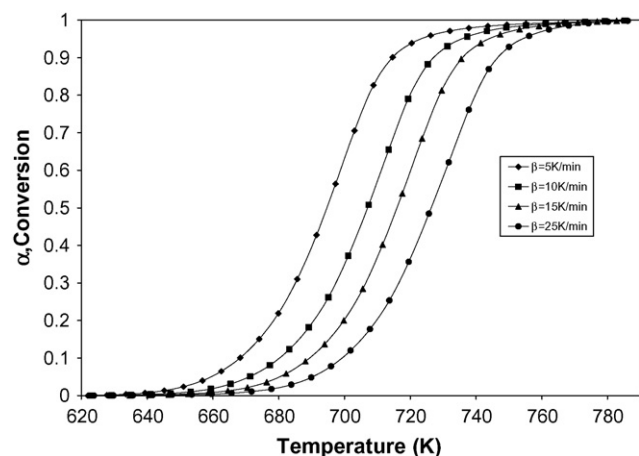


Fig. 2. Variation of conversion (α) with temperature during non-isothermal pyrolysis of waste PET sample at multiple heating rates.

the temperature at which the maximum weight loss rate occurs (T_m), and the temperature at the end of the pyrolysis step ($T_{w\infty}$) are reported in Table 1 for each case of experiments. Figs. 1–3 represent α versus T curves for pyrolysis of LDPE, PET and PP,

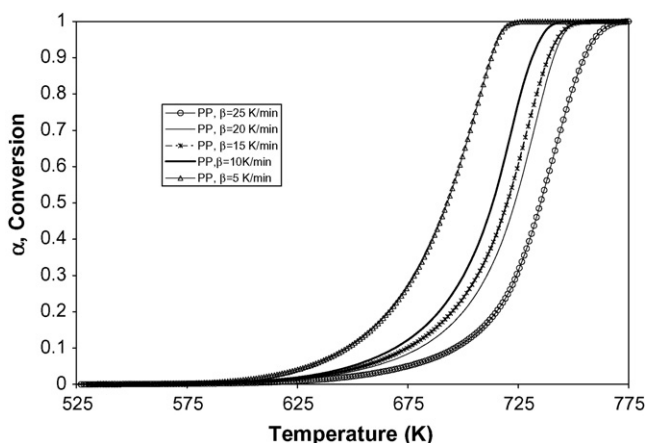


Fig. 3. Variation of conversion (α) with temperature during non-isothermal pyrolysis of PP sample at multiple heating rates.

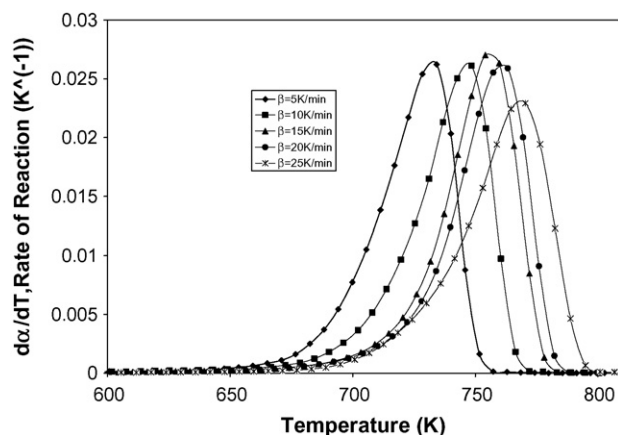


Fig. 4. Variation of rate of decomposition ($d\alpha/dT$) with average temperature during non-isothermal pyrolysis of waste LDPE sample at multiple heating rates.

respectively, at several heating rates. It is observed from the figures that the curves show constant pattern behaviour at different heating rates. A quick thermal decomposition is observed in the range of T_d to $T_{w\infty}$ (Figs. 1–3) and the highest decomposition rate is observed at $\sim T_m$ (Figs. 4–6), as reported in Table 1. After this quick increase, the solid continues to decompose smoothly and slowly until the end of the experiment. Higher heating rate finishes the decomposition phenomenon faster. The thermal decomposition behaviour of all of samples is almost similar, except for a difference in T_m . The constant pattern behaviour is attributed to the fact of similar reaction mechanism, which is the basis of multi-heating rate approach for kinetics analysis [7–21]. Figs. 4–6 represent the $d\alpha/dT$ versus T (derivative thermogravimetric) curves for pyrolysis of waste LDPE, waste PET, and PP, respectively, at several heating rates. We can clearly notice the single peak in all the curves. This is because we had approximated it as a single-step reaction taking place and found out the single-step overall kinetics triplet (E , K_0 and n) for pyrolysis of all three plastics by GA coupled with LOA, fminsearch (HGA) applying all 15 models as mentioned in Table 3 using multi-heating rates. It is worth mentioning here that the single peaks that are observed in Figs. 4–6 do not necessarily indicate

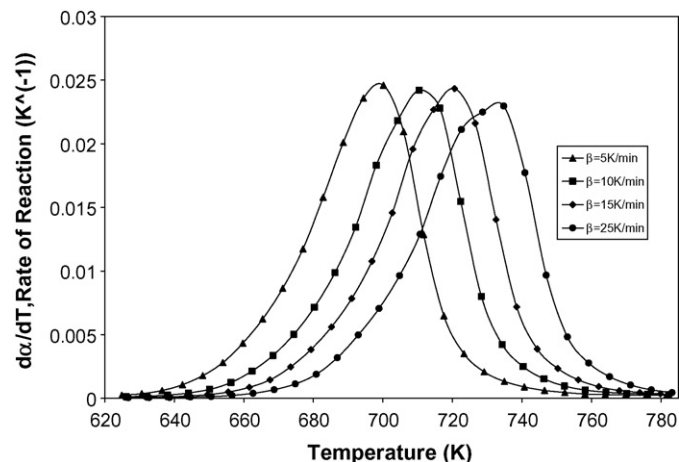


Fig. 5. Variation of rate of decomposition ($d\alpha/dT$) with average temperature during non-isothermal pyrolysis of waste PET sample at multiple heating rates.

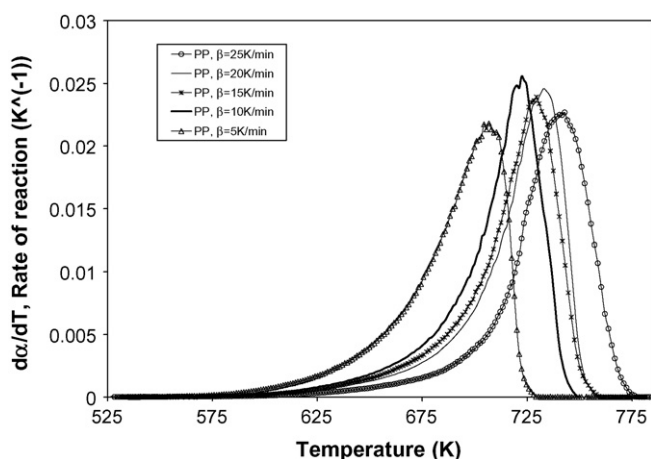


Fig. 6. Variation of rate of decomposition (da/dT) with average temperature during non-isothermal pyrolysis of PP sample at multiple heating rates.

a single-step reaction that is occurring during pyrolysis. The initial guesses are taken from the GA. The kinetics triplet data and the standard deviations, obtained from HGA based on 15 best data points for all the models and all types of plastics used are reported through Tables 3–5.

4.2. Prediction of experimental TGA data

As already discussed, AIC_c scores help to identify the better reaction model for pyrolysis study. Lower the AIC_c scores for a reaction model, more correct is the model representing the system [11,32]. Therefore, the kinetics triplets (Tables 3–5) obtained by HGA method employed in the present study are used in simulation to calculate the ACI_c scores for all the 15 models considered. The AIC_c scores for all the models and the integral form of all kinetics models are presented in Table 6. It is observed from Table 6, for all the three plastics used, that the AIC_c score is minimum for nucleation and growth model with $n = 2/3$. The n th order and first order models also show encouraging

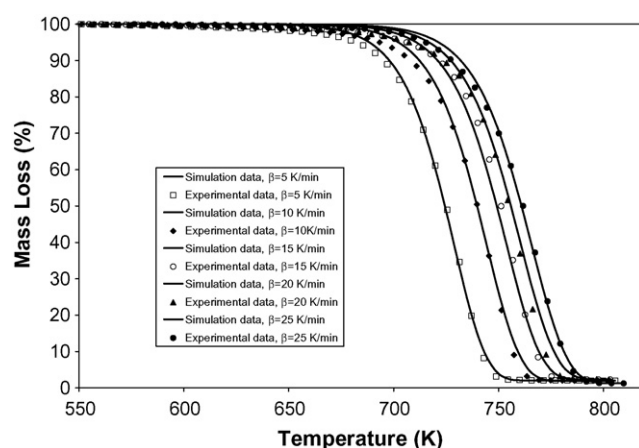


Fig. 7. Comparison between simulated (using HGA predicted kinetics triplet) and experimental mass loss during non-isothermal pyrolysis of LDPE at five different heating rates for nucleation and growth ($n = 2/3$) model (experimental data and simulated data).

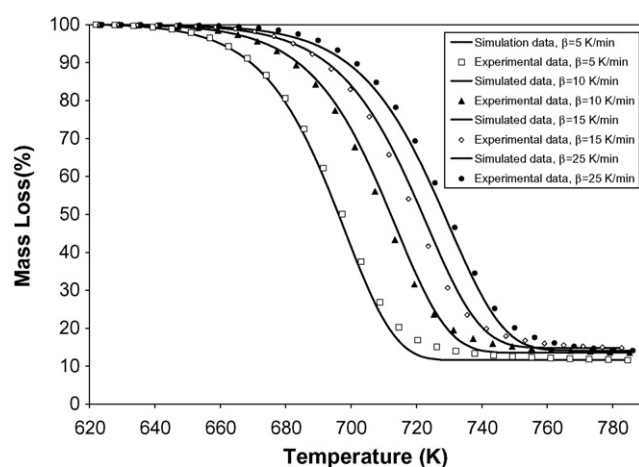


Fig. 8. Comparison between simulated (using HGA predicted kinetics triplet) and experimental mass loss during non-isothermal pyrolysis of PET at four different heating rates for nucleation and growth ($n = 2/3$) model (experimental data and simulated data).

Table 3
Average values of kinetic parameters for waste LDPE

Kinetic models	Order	E (kJ mol^{-1})	S.D. in E (kJ mol^{-1})	K_0	S.D.
Nucleation and growth	$n = 1/4$	148.14	$5.16\text{E}-06$	23.01	$3.75\text{E}-15$
	$n = 1/3$	151.44201	$2.77\text{E}-06$	23.53623	$7.40\text{E}-15$
	$n = 1/2$	166.67	0	26.02636	$7.42\text{E}-15$
	$n = 2/3$	189.06	$2.94\text{E}-14$	29.70	0
Phase boundary	$n = 1$ (plate)	69.17697	0	8.56174	0
	$n = 2$ (cylinder)	88.0816	0	11.46703	$3.61\text{E}-15$
	$n = 3$ (sphere)	106.76425	$1.59\text{E}-14$	14.38751	0
Diffusion	$n = 1$ (plate)	161.35968	0	22.8995	$7.35\text{E}-15$
	$n = 1/4$	7.06097	0	-3.00337	0
Power law	$n = 1/3$	12.37652	0	-1.84356	0
	$n = 1/2$	24.86678	$3.71\text{E}-15$	0.6511	$1.16\text{E}-16$
	$n = 3/2$	115.36091	$4.41\text{E}-14$	16.20774	$2.58\text{E}-06$
	$n = 1$, 1st order	246.2922	$2.93609\text{E}-06$	39.045	$4.8349\text{E}-07$
Chemical reaction	$n = 2$, 2nd order	337.9255	$5.83201\text{E}-14$	54.5665	$7.29001\text{E}-15$
	$n = n$, n th order ^a	242.425	0.1680986	38.385	0.02892788

^a $n = 0.949$, S.D. = 0.002917.

Table 4
Average values of kinetic parameters for waste PET

Kinetic models	Order	E (kJ mol ⁻¹)	S.D. in E (kJ mol ⁻¹)	K_0	S.D. in K_0
Nucleation and growth	$n = 1/4$	134.8427	0	21.7678	7.29E-15
	$n = 1/3$	137.9391	2.92E-14	22.2816	1.0935E-14
	$n = 1/2$	152.231	5.83E-14	24.728	3.65E-15
	$n = 2/3$	173.3451	3.08E-05	28.3564	0
Phase boundary reaction	$n = 1$ (plate)	51.49	9.96E-07	5.79	1.74E-07
	$n = 2$ (cylinder)	71.05	1.06E-06	9.01	1.82E-07
	$n = 3$ (sphere)	87.50	1.32E-06	11.70	2.20E-07
Diffusion	$n = 1$ (plate)	119.777	2.95E-14	16.7591	3.69E-15
Power law	$n = 1/4$	4.7957	1.82E-15	-3.4669	4.56E-16
	$n = 1/3$	9	1.78E-18	-0.0025	4.46E-19
	$n = 1/2$	85.53	1.32E-06	11.70	2.26E-07
	$n = 3/2$	18.6717	2.24E-05	-0.3978	1.139E-16
Chemical reaction	$n = 1$, 1st order	227.0584	5.83201E-14	37.5614	1.458E-14
	$n = 2$, 2nd order	309.8936	5.83201E-14	52.3226	1.458E-14
	$n = n$, n th order ^a	225	0.029018	37.2	0.004936

^a $n = 0.969$, S.D. = 0.004693.

scores. But, according to the AIC_C criteria, the nucleation and growth model with $n = 2/3$ is likely to be the best of all the 15 models for the all the polymers (LDPE, PET and PP) used in the present study. Thus, the pyrolysis kinetics equation was simulated using globally optimized kinetics triplet for all the three reaction models (nucleation and growth model with $n = 2/3$, first order and n th order reaction model) to predict the experimental TGA data. Figs. 7–9 show prediction of the experimental TGA data by nucleation and growth model with $n = 2/3$ for different heating rates. It is observed from the figures that nucleation and growth ($n = 2/3$) model successfully predicted the experimental TGA data particularly for LDPE and PET samples. In case of PP samples, it is observed that there is a significant deviation between experimental and predicted (nucleation and growth model ($n = 2/3$)) data. From the agreement of nucleation and growth model ($n = 2/3$), particularly for waste LDPE and waste

PET samples, it is worth mentioning that an initial stage of polymer degradation is often accompanied by melting (or softening). At this stage, the thermal degradation 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 [9].

Since, n th order and first order models also show encouraging AIC_C scores, we compare the predictions of n th order and first order models with experimental data and nucleation and growth model predictions and report through Fig. 10. It is a sample plot for waste LDPE. Similar behaviour are observed for waste PET and PP samples also and therefore not presented in the present study. Figure shows that though nucleation and growth model with $n = 2/3$ is marginally better than n th order and first order models, they also closely predict the experimental TGA data. This fact is also supported by the AIC_C scores as discussed above. Therefore, suitability of both the nucleation

Table 5
Average values of kinetic parameters for waste PP

Kinetic models	Order	E (kJ mol ⁻¹)	S.D. in E (kJ mol ⁻¹)	K_0	S.D. in K_0
Nucleation and growth	$n = 1/4$	122.031	0	19.4421	3.66E-14
	$n = 1/3$	123.0691	0	19.6025	3.65E-15
	$n = 1/2$	131.9114	0	21.1064	3.65E-15
	$n = 2/3$	146.6868	2.916E-14	23.6383	7.29E-15
Phase boundary reaction	$n = 1$ (plate)	61.48	7.29E-15	7.6349	9.11E-16
	$n = 2$ (cylinder)	85.3717	2.92E-14	11.6102	1.82E-15
	$n = 3$ (sphere)	104.5035	0	14.7527	0
Diffusion	$n = 1$ (plate)	146.1213	0	21.3854	0
Power law	$n = 1/4$	132.9115	260.7238	17.35658	42.14982
	$n = 1/3$	127.2946	240.1613	16.8	38.82339
	$n = 1/2$	20.8227	0	0.0468	2.14E-17
	$n = 3/2$	104.3377	1.46E-14	15.0636	3.65E-15
Chemical reaction	$n = 1$, 1st order	186.6747	5.831E-14	30.48	3.65E-15
	$n = 2$, 2nd order	247.31	2.92E-14	41.4	1.46E-14
	$n = n$, n th order ^a	181.4567	0.061891	29.53	0.012581

^a $n = 0.9039$, S.D. = 0.004667.

Table 6

The equation for calculation of kinetics parameters and AIC_c results of LDPE, PET and PP samples

Kinetic models	Kinetic functions, integral of kinetics function and calculation of α where, $x = (k_0/\beta t)I(E_i, T_{i,t})$	Order	Model no.	AIC _c values LDPE	AIC _c values PET	AIC _c values PP
Nucleation and growth	$f(\alpha) = (1/n)(1-\alpha)(-\ln(1-\alpha))$	$n = 1/4$	1	-195.903	-101.895	1006.2
	$g(\alpha) = n(1-\alpha)^{(n-1)/n}$	$n = 1/3$	2	-321.217	-165.638	542.29
	$\alpha = 1 - \exp(-x^{1/n})$	$n = 1/2$	3	-620.52	-312.951	-433.58
		$n = 2/3$	4	-850.068	-421.609	-1150.03
Phase boundary reaction	$f(\alpha) = n(1-\alpha)^{(n-1)/n}$	$n = 1$ (plate)	5	348.5874	201.9599	2777.814
	$g(\alpha) = [1 - (1-\alpha)^{1/n}]$	$n = 2$ (cylinder)	6	198.5402	122.8186	1906.95
	$\alpha = 1 - (1-x)^n$	$n = 3$ (sphere)	7	84.85229	68.24294	1227.18
Diffusion	$f(\alpha) = 1/\alpha$	$n = 1$ (plate)	8	141.4932	112.4871	1785.18
	$g(\alpha) = \alpha^2/2$ $\alpha = (2x)^{1/2}$					
Power law	$f(\alpha) = (1/n)\alpha^{1-n}$	$n = 1/4$	9	-	-	-
	$g(\alpha) = \alpha^n (0 < n < 2)$	$n = 1/3$	10	-	-	-
	$\alpha = x^{1/n}$	$n = 1/2$	11	524.0944	-	-830.97
		$n = 3/2$	12	216.5771	144.3685	-830.97
Chemical reaction	$f(\alpha) = (1-\alpha)$	$n = 1$, 1st order	13	-541.103	-294.404	-675.54
	$g(\alpha) = -\ln(1-\alpha)$ $\alpha = 1 - \exp(-x)$					
	$f(\alpha) = (1-\alpha)^n$ $g(\alpha) = [1/(1-\alpha)^{n-1} - 1]/(n-1)$ $\alpha = 1 - [1 + (n-1)x]^{1/(1-n)}$	$n = 2$, 2nd order $n = n$, nth order	14 15	-299.036 -557.949	-194.547 -294.955	381.7632 -830.97

and growth model and chemical reaction models for all the three samples indicates that both the mechanism (nucleation, growth and diffusion and chemical reaction) significantly controls the decomposition phenomena. Therefore, as opined by Marcilla et al. [10], a good fit of experimental results is not only the criterion to decide upon the decomposition mechanism. Further studies including infrared or mass spectroscopy, morphology study using SEM or TEM during such decomposition is very much needed to conclude upon the actual reaction mechanism that controls the decomposition behaviour of polymer samples. It may be further added here that the proposed models may not fully describe particularly the decomposition phenomena of PP

samples. Though we have taken up single-step kinetics from the single peak of derivative thermogravimetric curves, it may be possible that more steps are involved in the reaction, which may possibly be taken care of by a new and different model. Therefore, further studies in this direction may help to estimate the more accurate kinetics expression for thermal decomposition of PP.

Table 7 summarizes the optimum model and the optimum kinetics parameters for all the polymers used in the present study along with the literature published data on the kinetics parameters of thermal degradation of waste LDPE, waste PET, and PP using different techniques. From the table, it is observed that most of the reported studies are based on first order model. We

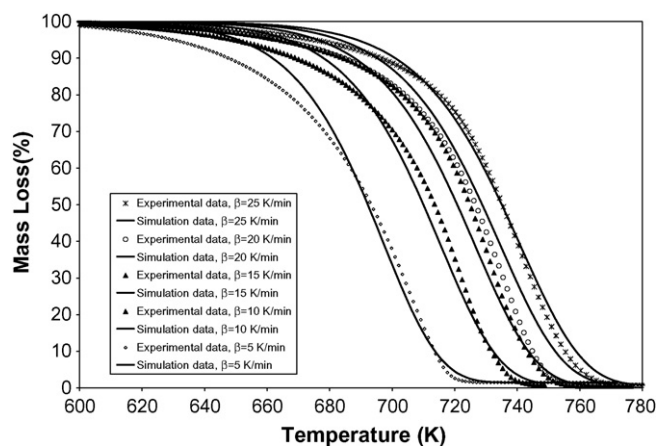


Fig. 9. Comparison between simulated (using HGA predicted kinetics triplet) and experimental mass loss during non-isothermal pyrolysis of PP at five different heating rates for nucleation and growth ($n = 2/3$) model (experimental data and simulated data).

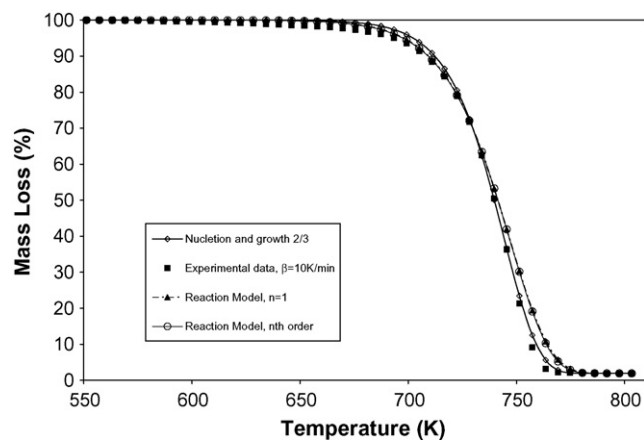


Fig. 10. Comparison of (mass loss vs. temperature) curves of different models having very less AIC_c scores with experimental values for LDPE and at 10 K/min.

Table 7
Present work and literature reported kinetics parameters (N₂ atmosphere)

Polymer	E (kJ mol ⁻¹)	$\ln(k_0)$	n	Method	Reference
Waste	322.3	54.76	1.724	n th-order model	[6]
PET	162.15	26.37	1	ASTM E698	[6]
	256.4	36.88	1.05	n th-order model	[34]
	271.6	41.98	1.09	n th-order model	[35]
	269.35	44.94	1	SDMT-multiple heating rate	[11]
	242	–	1	First-order model	[36]
	180–210	–	–	Isoconversion model-free method	[17]
	173.3451	28.3564	2/3	Nucleation and growth	Present work
Virgin	238.7	18.00	1.15	n th-order model	[37]
PET	259.34	43.077	1	SDMT-multiple heating rate	[11]
	220 ± 10	30.297	1	First-order model	[38]
PP	244 ± 8	35.7 ± 1.3	1	First-order model	[39]
	237 ± 7	32.1 ± 1.3	1	Random-chain dissociation model	[39]
	216	30.909	1	First-order model	[40]
	214.5	28.198	1	Random-chain dissociation model	[40]
	(138.1 ± 3.8) ^a	(26.7099) ^a	1	Method of Ozawa, Flynn and Wall	[41]
	43.9	24.8664	0.90	n th-order model	[42]
	150–250	–	–	Isoconversion method	[19]
	146.69	23.64	2/3	Nucleation and growth	Present work
LDPE	221	31.0944	1	First-order model	[39]
	234.5	30.518	1	Random-chain dissociation model	[39]
	241 ± 10	34.6 ± 1.7	1	First-order model	[40]
	244 ± 12	32.2 ± 2.1	1	Random-chain dissociation model	[40]
	(214.2, 238.9, 200) ^a	(24.58, 32.71, 25.476) ^b	–	Three-reaction model (Flexible Simplex Optimization Method)	[43]
	272	–	0.14	Freeman and Carroll's Method	[44]
	49.3	27.81334	0.63	n th-order model	[42]
	150–240(200) ^c	–(26.039) ^c	–	Isoconversion method	[19]
	192–263	–	–	Integral method	[45]
	201.5	–28.1257 ± 0.0185	0.55	Isoconversional method by Flynn	[46]
	189.05815	29.69583	2/3	Nucleation and growth	Present work

^a At 10% weight-loss and values of E increase with the extent of degradation.

^b Three step mechanism is assumed.

^c Almost constant for $\alpha > 0.2$ (130–200).

have, through the present work, shown that first order and n th order models well describe the thermal decomposition behaviour of the samples used. At the same time, we have also established here that the nucleation and growth model with $n = 2/3$ is better suited for describing the thermal degradation kinetics of all the plastic samples used in the present study.

5. Conclusion

Pyrolysis studies of PP, waste LDPE, and waste PET are conducted at different heating rates to evaluate the kinetics parameters. The constant pattern behaviour of the TG curves for all three polymers at different heating rates possibly suggests existence of similar reaction mechanism. We have approximated the whole process of pyrolysis as single step and accordingly found out the globally optimum overall kinetics parameters employing hybrid genetic algorithm and using 15 different decomposition models reported in the literatures. The suitability of the models is tested using the AIC_c score. Results show that nucleation and growth model with reaction order, $n = 2/3$ is the best suited one and it also predicted the experimental TGA data successfully. However, n th order model also shows

good AIC_c score and well predicted the experimental TGA data. Thus, though apparently it seems that nucleation and growth model controls the decomposition of plastic samples used in the present study, further investigation in detail including infrared or mass spectroscopy, morphology study using SEM or TEM during such decomposition is very much essential to conclude upon the actual reaction mechanism that controls decomposition of polymers considered. This is particularly so for PP samples where the present reaction models also have shown significant deviation from the experimental TGA data and it may be possible that more steps are involved in the reaction, which may possibly be taken care of by a new and different model.

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