



# Thermal degradation kinetics of plastics and model selection



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## ABSTRACT

The thermal decomposition behaviour of high and low-density polyethylene (LDPE and HDPE), polypropylene (PP), poly(lactic acid) (PLA) were investigated under inert condition by dynamic thermogravimetric analysis (TGA) in the temperature range of 303–973 K at seven different heating rates. Determination of distributed activation energy at various stages of degradation process and their implication in degradation process was investigated with the help of isoconversational methods. Reaction models ( $f(\alpha)$ ) were predicted using Criados masterplots. Corresponding values of pre-exponential factors were calculated using compensation effect. A comparative study of various isoconversational methods/models like Friedman, Kissinger-Akahira-Sunose, Ozawa-Flynn and Wall (OFW), Starink and advance isoconversational method (AIC) was discussed and reliability of all these methods was examined. Reconstruction of the conversion profiles for different thermal history was performed and compared with experimental data to select the appropriate model.

## 1. Introduction

Waste plastic is one of the major contributors to the municipal solid waste. India generates 5.6 million tons of plastic waste annually [1]. Most of the commercial plastics are non-biodegradable and responsible for various environmental and ecological problems. With the increase of human population and development activities, the plastic consumption is also increasing at a higher rate. Landfilling and incineration, two most commonly used waste disposal techniques are not sustainable enough because of the lack of available land for dumping and harmful emissions respectively. Pyrolysis of waste plastic can transform solid waste into a wide range of valuable chemicals and hydrocarbon compounds [2]. Designing and implementation of the pyrolysis process for complex materials like plastics depends primarily on kinetic analysis. The precision of the pyrolysis kinetics heavily depends upon the reliable evaluation of the kinetic triplets, activation energy ( $E_a$ ), pre-exponential factor ( $A_a$ ) and reaction model ( $f(\alpha)$ ). Degradation of plastics includes all changes related to chemical structure and physical properties due to external stresses. The mechanism of thermal degradation of plastics is complex in nature. Thermal degradation involves the occurrence of molecular scission which leads to the changes in molecular weight distribution of the material. This phenomenon is decisive for recycled plastics because they suffer a continuous change in temperature [3,4]. Heating any organic or inorganic solid results in many physico-chemical phenomena like melting, sublimation, polymorphic transformation, desolvation or degradation, etc [5]. TGA provides the pathway to determine the macroscopic kinetics of these

processes. The microscopic kinetic accounts for simultaneously occurring multistep phenomena and requires computational methods. Isoconversational methods recommended by the International Confederation for Thermal Analysis Calorimetry (ICTAC) are able to capture the complexity involved in the process of thermal degradation of solid [6–11]. Isoconversational methods use the thermal degradation data at different temperature program and calculate the distribution of activation energy as reaction/process progresses [12]. The variable activation energy explains the complexity of the thermal degradation process at various stages of conversion process. In general single activation energy is comprehensively corresponding to gas phase reactions, whereas any condensed phase or solid phase reactions the activation energy becomes a function of temperature dependent properties of reaction media such as progress of reaction. Variable activation energy gives more mechanistic approach of complex reactions link to the energy barrier of individual steps, diffusion through solid matrix and secondary reactions etc [13].

The aim of the current study is to compare the quantitative aspects of the thermal decomposition process for four different plastics low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and polylactic acid (PLA), which are mainly used for packaging purpose. Five different isoconversational models, namely Friedman (FR) [13], Ozawa Flynn and Wall (OFW) [14,15], Kissinger Akahira and Sunose [16], Starink [17] and advance isoconversational models (AIC) [18] are considered. The broader aspects of the study are to understand the complex degradation reaction mechanism under pyrolysis condition and the applicability of the various isoconversational

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Nomenclature			
$a$	$1/RT_\alpha$	LDPE	Low density polyethylene
$A$	Pre-exponential factor ( $\text{min}^{-1}$ )	OFW	Ozawa-Flynn-Wall
$A_\alpha$	Distributed pre-exponential factor with conversion ( $\text{min}^{-1}$ )	PE	Polyethylene
AIC	Advance isoconversional method	PLA	Polylactic acid
$b$	$\ln((d\alpha/dt)_\alpha)$	PP	Polypropylene
DSC	Differential scanning calorimetry	$R$	Universal gas constant ( $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ )
DTG	Differential thermal gravimetric	$T$	Temperature (K)
$E$	Activation energy ( $\text{kJ/mol}$ )	$T_\alpha$	Distributed temperature with conversion (K)
$E_\alpha$	Distributed activation energy with conversion ( $\text{kJ/mol}$ )	$T_o$	Onset degradation temperature (K)
$f(\alpha)$	Reaction mechanism	$T_e$	End degradation temperature (K)
$g(\alpha)$	Integral form of rate equation	$T_m$	Peak temperature (K)
HDPE	High density polyethylene	$t$	Time (min)
$i$	Various temperature program (ranging from $1-n$ , $n$ being the total number of temperature program)	$t_\alpha$	Time corresponding any particular conversion ( $\alpha$ )
$j$	Suffix represents the temperature program other than $i^{\text{th}}$ program, $i \neq j$	TGA	Thermal gravimetric analysis
$J$	Symbol represents integral function	$W$	Weight of sample at any temperature during degradation (mg)
IKP	Invariant kinetic parameter	$W_o$	Initial weight of the sample (mg)
KAS	Kissinger-Akahira-Sunnose	$W_\infty$	Residual weight, (mg)
		$\alpha$	Conversion
		$Z(\alpha)$	$f(\alpha) \times g(\alpha)$
		$\Phi$	Minimization function of $E_\alpha$

methods and their limitations. Selection of material is totally based on their availability in plastic waste stream except PLA, which is chosen because of its growing presence in medical field and food packaging, which also have complex molecular structure due to presence of oxygen which may create complexity in the post-consumer disposal processes like pyrolysis and combustion.

Isoconversional methods were employed to evaluate the decomposition kinetics of HDPE [19], PS and PE [20], PP [21], tyre rubber [22], biomass [23,24], coal [25], cellulose [26], and polymer composites [27,28] etc. Most of the previous studies able to utilize the way of measuring distributed activation energy and their applications. However, a few studies have captured the essence of kinetic triplet ( $E$ ,  $A$  and  $f(\alpha)$ ), which represent the whole understanding of any reaction. The current study successfully demonstrates the variable activation energy ( $E_\alpha$ ) with the extent of the progress of the reaction for LDPE, HDPE, PP and PLA and also at the same time considers the possibility of a distributed pre-exponential factor (frequency factor) ( $A_\alpha$ ). Distributed pre-exponential factor ( $A_\alpha$ ) actually compensate a logarithmic linear relationship with the variable activation energy, which ultimately helps to reconstruct the degradation plot and can further help to verify the calculated kinetic parameters. The kinetic parameters were obtained by applying various isoconversional methods to experimental TGA data and were examined critically. The presented results and methodology will be applicable for selecting appropriate strategies for analysis of kinetic parameters from TGA, particularly for the study of degradation kinetic of plastics, biomass, coal and composites.

## 2. Materials and methods

### 2.1. Materials

LDPE, HDPE, and PP were procured from Haldia Petrochemicals Limited, India and PLA was obtained from Nature Works®. Physical properties of plastic samples like density, glass transition temperature and melting point are reported in Table 1. The material received were in pellet form of size around 3–5 mm. The collected materials were manually cut to make 1–2 mm average particle size before subjected to TGA analysis.

### 2.2. Methods

The thermal degradation study was carried out using TGA (NETZSCH 209 F1 TG) equipment in the inert environment ( $\text{N}_2$  gas) with a flow rate of 60 ml/min (40 ml/min as purge and 20 ml/min as protective gas) at seven heating rates, 5, 10, 15, 20, 30, 40, 50 K/min in the temperature range of 303–973 K. The heating rates were chosen in the range of 5 K/min to 50 K/min taking consideration of both slow pyrolysis and fast pyrolysis scenario. Industrially all these heating rates are applicable, directly or indirectly. Generally, the rate of heat absorption for any material is subjected to the thermal conductivity and the available surface area of the material. Industrially, very high heating rate and uniform distribution of heat can be achieved by using fluidised bed pyrolyser. The kinetic parameters obtained with chosen heating rates captured both slow and fast pyrolysis processes and help in accurately extrapolate the profiles for both lower and higher heating rates. Constant  $\text{N}_2$  flow rate, particle size (1–2 mm) and initial weight (6–7 mg) were maintained for all the experiments. Differential Scanning Calorimetry (DSC) [make of Metler-Toledo with temperature range  $-30^\circ\text{C}$ – $200^\circ\text{C}$  (from ambient to  $-30^\circ\text{C}$  then to  $200^\circ\text{C}$  and finally bring the temperature to ambient) with a program of constant heating rate of  $5^\circ\text{C}/\text{min}$ ] was used to determine the melting points while densities and glass transition temperatures were provided by the manufacturer (Table 1).

### 2.3. Processing of TGA data

The decomposition profiles at seven different heating rates obtained from the TGA are shown in Fig. 1. TGA registers the change in mass of the sample with temperature (or time) at the specified gas environment and heating rate under a certain temperature range. Weight loss data then converted into conversion,  $\alpha = (W_o - W)/(W_o - W_\infty)$ .

**Table 1**  
Physical properties of materials.

Plastics	Density (g/cc)	Glass transition temperature (K)	Melting point (K)
LDPE	0.934	148	$384 \pm 2$
HDPE	0.950	193	$405 \pm 1$
PP	0.9	263	$441 \pm 1$
PLA	1.25	$330 \pm 3$	$443 \pm 1$

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