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Unveiling the Dynamics of Thermal Degradation: A Kinetic Approach

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ABSTRACT

Thermal degradation is a complex process that is of paramount importance in various scientific and industrial fields, ranging from polymer chemistry and materials science to environmental engineering and food technology. Understanding the kinetics of thermal degradation is crucial for optimizing processes, predicting product lifetimes, and ensuring the safety of materials and products. The present study provides a concise overview of recent research efforts in the field of kinetic studies on thermal degradation, highlighting key findings and trends.This review encompasses a wide range of materials and compounds, including polymers, organic molecules, and biological substrates. It discusses the various techniques employed for studying thermal degradation kinetics, such as thermogravimetric analysis, differential scanning calorimetry, and model-free approaches. Notably, the review emphasizes the importance of multi-step degradation processes and the need for advanced mathematical modeling to accurately describe the underlying mechanisms.Key findings from recent studies include the identification of activation energy barriers, the determination of reaction mechanisms, and the elucidation of degradation pathways. The impact of environmental factors, such as oxygen concentration and humidity, on thermal degradation kinetics is also discussed. Furthermore, the review highlights the role of additives, stabilizers, and catalysts in influencing degradation rates and product outcomes.

Keywords: Thermal degradation, kinetics, reaction mechanism, thermogravimetry, thermal analysis, polymer degradation.

INTRODUCTION

Thermal degradation, a fundamental chemical process, plays a pivotal role in a multitude of scientific and industrial domains. Whether it's the stability of polymers in industrial applications, the shelf life of food products, the behavior of organic molecules under various conditions, or the safety of materials in extreme environments, understanding the kinetics of thermal degradation is paramount. This paper provides a foundational overview of the field of kinetic studies on thermal degradation, highlighting its significance and the key factors that make it a subject of enduring interest and investigation.

The study of thermal degradation kinetics is essential for several reasons. First, it is crucial in the design and optimization of manufacturing processes, where temperature and time play critical roles in determining the quality and properties of the final products. For example, in the polymer industry, understanding the kinetics of thermal degradation is essential to control processing conditions and ensure the longevity of materials. Another significant application of kinetic studies on thermal degradation is predicting the lifetimes and durability of materials and products. This is especially relevant in fields like automotive engineering, where the longevity of components exposed to high temperatures is of utmost importance. By characterizing the rate of degradation, engineers can estimate when a product might fail, allowing for timely maintenance or replacement[1,2].

The safety implications of thermal degradation cannot be understated. In chemical processes, the build-up of heat can trigger rapid and potentially catastrophic reactions. Understanding the kinetics of thermal degradation is essential for risk assessment and ensuring the safe handling of materials. Additionally, in the context of environmental sustainability, knowledge of how materials degrade under different conditions is crucial for assessing the impact of waste disposal and developing more eco-friendly products. Thermal degradation affects a wide variety of materials, ranging from synthetic polymers and organic compounds to natural substances and biological materials. Each of these materials may exhibit unique degradation patterns and pathways, necessitating a comprehensive approach to kinetic studies[3,4].

The field of kinetic studies on thermal degradation relies on a diverse array of analytical techniques. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and other thermal analysis methods are employed to study the behavior of materials under varying temperature regimes. These techniques help researchers elucidate the underlying mechanisms governing thermal degradation [5-7].Many materials undergo multi-step degradation processes, making the study of kinetics more challenging. It often involves the identification of intermediate products, reaction pathways, and the determination of activation energy barriers, which vary at different stages of degradation [8].The influence of environmental factors, such as oxygen concentration, humidity, and pressure, on thermal degradation kinetics is a critical area of investigation. These factors can significantly impact the rate and nature of degradation reactions, adding complexity to the field.

THERMAL DEGRADATION

Thermal degradation, a fundamental concept in chemistry and materials science, refers to the process in which materials, compounds, or substances undergo chemical and physical changes when exposed to elevated temperatures. This phenomenon occurs in various contexts, ranging from the decomposition of organic matter to the transformation of polymers and the aging of materials. Understanding the mechanisms, factors, and consequences of thermal degradation is critical in numerous scientific disciplines and industrial applications [9]. In this in-depth exploration, we will delve into the intricacies of thermal degradation.

The Mechanisms of thermal degradation

Thermal degradation processes are complex and typically involve a combination of chemical and physical changes [10,11]. The specific mechanisms at play depend on the nature of the material, the temperature, and other environmental factors. Some of the common mechanisms include:

Pyrolysis: Pyrolysis is a decomposition process in which a substance is heated in the absence of oxygen, resulting in the breakdown of chemical bonds and the formation of smaller, often volatile, compounds. This process is commonly observed in the thermal degradation of organic materials like wood, plastics, and biomass.

Oxidation: In the presence of oxygen, thermal degradation can lead to oxidation reactions. These reactions result in the formation of oxidized products, which can change the physical and chemical properties of the material. Oxidation processes are prevalent in the thermal degradation of metals, fuels, and organic compounds.

Depolymerization: Polymers, such as plastics, can undergo depolymerization during thermal degradation. High temperatures can break the long polymer chains into smaller fragments, altering the material's properties and potentially releasing harmful substances.

Decomposition: Decomposition reactions involve the breakdown of a substance into simpler compounds or elements. These reactions can lead to the release of gases, such as carbon dioxide, carbon monoxide, or water vapor, and are crucial in processes like combustion.

Cross-linking: In some cases, thermal degradation can result in the formation of cross-links between molecules or polymer chains, leading to the hardening or strengthening of materials. This is observed in the curing of certain materials like thermosetting plastics.

Factors affecting thermal degradation

Several factors influence the rate and extent of thermal degradation [12-14]:

Temperature: Temperature plays a central role in thermal degradation kinetics. Higher temperatures generally accelerate degradation processes, as they provide more energy to overcome activation energy barriers. The Arrhenius equation quantifies this temperature dependence.

Presence of Oxygen: The availability of oxygen greatly influences the degradation pathway. In the absence of oxygen (as in pyrolysis), materials undergo different reactions than in the presence of oxygen, where oxidation reactions predominate.

Time: The duration of exposure to high temperatures is a crucial factor. Prolonged heating can lead to more extensive degradation, resulting in a change in material properties or even complete disintegration.

Pressure: For some materials, variations in pressure can affect degradation behavior, particularly when gases are involved.

Catalysts: Certain materials or compounds act as catalysts, either promoting or inhibiting thermal degradation reactions. Catalysts can significantly alter the kinetics of degradation.

Practical applications and significance

Understanding thermal degradation is vital in various fields and applications [15-17]:

Polymer Industry: The polymer industry relies on a deep understanding of thermal degradation to design materials with specific properties, ensure product stability, and optimize processing conditions.

Food Processing: The knowledge of thermal degradation kinetics is used in cooking, pasteurization, sterilization, and shelf-life determination in the food industry.

Pharmaceuticals: Stability testing, drug formulation, and determining shelf-life are critical applications in the pharmaceutical sector.

Energy Sector: The design and optimization of fuel combustion processes and power generation systems depend on understanding thermal degradation processes to maximize efficiency and minimize emissions.

Materials Science: Material aging, durability, and reliability are closely linked to thermal degradation behavior. Understanding degradation processes aids in developing long-lasting materials and predicting maintenance needs.

Environmental Impact: The study of thermal degradation is also essential in assessing the environmental impact of materials and substances, particularly in waste management and pollution control.

ADVANCED ANALYTICAL TECHNIQUES

Several advanced techniques and instruments are used to study thermal degradation[18-21]**(Table 1)**, including:

Differential scanning calorimetry (DSC)

DSC measures the heat flow associated with thermal transitions and degradation reactions, providing valuable information on thermal stability. The DSC curve represents plot of heat flow per unit time versus time or temperature. There are two types of DSC systems in common use (a) Power-compensated DSC (b) Heat-flux DSC. In power-compensated DSC, the temperatures of the sample and reference are controlled independently by separate, identical furnaces. The temperatures of samples and reference are made identical by varying power input to the two furnaces; energy required to do this is the measure of enthalpy or heat capacity changes in the sample relative to the reference. In heat-flux DSC, both the sample and reference are heated by single furnace. The temperature difference is recorded and is related to the enthalpy change in the sample by calibration experiments.

Applications of DSC: The applications may be divided roughly into two categories:
(i) Physical changes and measurements:

- Melting point and heat of fusion of materials
- Crystalline phase transition
- Liquid crystalline transitions
- Heat capacity
- Glass transition temperature in polymers
- Purity measurements in pharmaceuticals, insecticides, pure organics and Metals

(ii) Chemical Reactions:

- Kinetic studies of wood/wood composites/polymers
- Synthesis of compounds at high temperature
- Study of superconductors
- Polymer cure
- Degradation of wood

Thermogravimetric analysis (TGA)

TGA measures changes in sample weight as a function of temperature or timein a specified atmosphere, offering insights into decomposition and volatilization processes. It is of two types:

Isothermal thermogravimetry: In this technique the change in mass of the sample is monitored as a function oftime at constant temperature.

Non-isothermal/dynamic thermogravimetry: In this technique the change in mass of the sample is monitored as a function oftime or temperature while the temperature of the sample is raised at a given heating rate.

Derivative thermogravimetric analysis (DTG)

In order to enhance the steps in the TG, derivative thermogravimetry (DTG) traceis frequently drawn. In DTG, the plot of the rate of mass change with time or temperatureis drawn. DTG measures the amount and rate (velocity) of change in the mass of a sampleas a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidativestabilities of materials as well as their compositional properties. The information obtainedby the technique consists of:-

(i) The number of stages of breakdown, **(ii)** A quantitative measure of the mass loss in any stage

(iii) The threshold temperatures and temperatures of maximum rate of mass loss forthe processes occurring and

(iv) Maximum mass loss rate (MMLR) was measured to corresponding peak in DTG maxima.

It is especially useful for the study of polymeric materials, including wood, cellulose, lignocellulosic material, biomass, thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints. The technique is particularly useful for the following types of measurements:

- Evaluation of flame retardants in polymers
- Proximate analysis of fuels and other similar materials
- Compositional analysis of multi-component materials or blends
- Thermal stabilities of cellulosic material
- Inert and reactive gas analysis
- Oxidative stabilities
- Decomposition kinetics
- Degradation of cellulose and modified cellulose

Table 1. Thermal methods, property which can be studied and uses of techniques

Technique	Observed property	Results
Thermogravimetry (TG/TGA)	Mass	Decomposition, dehydration, Oxidation
Differential thermal analysis (DTA)	Temperature difference	Phase changes, reactions
Differential scanning Calorimetry (DSC)	Power difference	Heat capacity, phase changes, reactions, calorimetry
Evolved gas analysis (EGA)	Gases	Decompositions, catalyst and surface reactions
Thermogravimetric-mass Spectroscopy (TGMS)	Mass, Gases	Decompositions, surface reactions, type of gas evolved

Differential thermal analysis (DTA)

DTA is a technique in which the temperature difference between the sample and referenceis monitored against time or temperature while the temperature of the sample isprogrammed in a specified atmosphere. This was developed by ceramists and mineralogists for studying the phenomenon occurring when materials are heated. If thesample and reference temperatures are Ts and Tr respectively, then the graph between (Ts-Tr) (along Y-axis) and the system temperature (along X-axis) is plotted. The curve soobtained is called the DTA curve. Reference material generally used is α-alumina (Al_2O_3). The following two types of peaks/signals are obtained in DTA curves:

(i) An endothermic peak or an endotherm is a peak where the temperature of sample falls below that of reference material temperature i.e. (Ts-Tr) is negative.

(ii) An exothermic peak or an exotherm is a peak where the sample temperature rises above reference material temperature i.e. (Ts-Tr) is positive.

This method is sensitive to endothermic and exothermic processes including phase transitions, dehydration, and decomposition, redox, or solid-state reactions. If neither the sample nor the reference compound undergoes a thermal reaction over the temperature range involved, a continuous recording of the difference between the temperature of the sample and the reference or furnace temperature should result in a baseline which is parallel to the temperature axis. The DTA technique can be used as a *finger print* for identification purposes, for example, in the study of clays where the structure similarity of different forms renders diffraction experiments difficult to interpret.

Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS is used to identify and quantify the volatile products of thermal degradation reactions, helping researchers understand reaction pathways [22].

THEORETICAL APPROACH OF THERMAL DEGRADATION KINETICS

Thermal degradation is a complex and multifaceted phenomenon with profound implications for a wide range of industries and scientific disciplines. Its study involves understanding the underlying mechanisms, factors that influence degradation, and the development of advanced techniques for analysis. Study of thermal degradation kinetics is critical for product development, process optimization, environmental protection, and the advancement of materials science. As we continue to explore and utilize high-temperature environments, the field of thermal degradation remains central to innovation and progress.

To study the kinetics of thermal degradation, various mathematical models and methods are employed. These models aim to describe how the rate of degradation changes with time and temperature, offering insights into the underlying mechanisms and helping researchers predict and control the behavior of materials and substances when exposed to elevated temperatures. Here are some commonly used models and methods for studying thermal degradation kinetics. Each of these models and methods provides a unique perspective on the kinetics of thermal degradation, making them applicable to various materials, processes, and research goals. The choice of model or method depends on the specific system being studied and the level of detail required to understand the degradation behavior[23-26].

Arrhenius kinetics

The Arrhenius equation is a fundamental model in thermal degradation kinetics. It describes the temperature dependence of reaction rates based on the activation energy (E_a) and the pre-exponential factor (A):

Equation 1

$$k = A.e^{-\frac{E_a}{RT}}$$

Where, k: Reaction rate constant, A: Pre-exponential factor, E_a: Activation energy, R: Gas constant and T: Absolute temperature.

By measuring the reaction rate at different temperatures, one can determine E_a and A, providing information about the temperature sensitivity of the degradation process.

First-order kinetics

The first-order kinetic model assumes that the rate of thermal degradation is directly proportional to the remaining amount of the material. It is described as:

Equation 2

$$R = -\frac{d[A]}{dt} = k[A]$$

Where, R: Rate of degradation,$[A]$: Concentration or amount of material remaining and k: First-order rate constant. The first-order model is widely used for its simplicity and applicability to a range of degradation processes [27].

nth-order kinetics

nth-order kinetics generalize the first-order model, allowing for more complex reactions. The rate of degradation is expressed as a power of the concentration of the remaining material:

Equation 3

$$R = -\frac{d[A]}{dt} = k[A]^n$$

Where, n: reaction order (n = 1 for first order) and other variables as previously defined. Higher values of n represent more complex reactions. For example, second-order kinetics (n = 2) are common for polymer degradation [28].

Parallel reactions

In situations where multiple degradation reactions occur simultaneously, researchers use a model that considers the individual contributions of each reaction. The overall rate of degradation is the sum of the rates of these parallel reactions. This model helps explain complex systems where different pathways contribute to overall degradation.

Model-free methods

Some methods do not assume a specific kinetic model but instead focus on analyzing the rate of degradation as a function of temperature [29,30]. Examples include the Kissinger method and the Flynn-Wall-Ozawa (FWO) method. These approaches use differential scanning calorimetry (DSC) or thermogravimetric analysis (TGA) data at different heating rates to calculate activation energy without specifying a kinetic model.

Catalytic kinetics

When catalytic materials are involved, the kinetics of thermal degradation can be influenced significantly. The study of catalytic degradation kinetics involves the characterization of catalytic sites, their activity, and how they affect the degradation rate [31].

Advanced techniques

Techniques such as isothermal or non-isothermal analysis using DSC, TGA, or thermogravimetric analysis Fourier-transform infrared (TG-FTIR) spectroscopy allow for real-time monitoring of thermal degradation processes and provide valuable data for kinetic analysis [32,33]. Isoconversional methods, like the Kissinger-Akahira-Sunose (KAS) method, are also employed to determine kinetic parameters by measuring degradation at various heating rates [34].

KINETIC METHODS OF ANALYSIS

International Confederation for Thermal Analysis and Calorimetry (ICTAC) focused on extensive comparison of various methods for computational kinetic parameters and concluded that single heating rate methods are not reliable and “model free” multiple heating rate programs are recommended for computation of kinetic parameters [35,36]. The “model free” multiple heating rate methods include Kissinger [37], Friedman [38], Ozawa-Flynn-Wall (O-F-W) [39,40] and modified Coats-Redfern [41,42].

Kinetic analysis by single heating rate methods

Freeman and Carroll method:[43]Thermal degradation reaction of a solid materialis represented as:
Equation 4

$$A(Solid) \xrightarrow{Heat} B(Solid) + C(Gas)$$

The rate of disappearance of reactant A from the mixture is
Equation 5

$$-\frac{dW}{dT} = K_1 W^n = R_T$$

Where W= Weight fraction of reactant A;K$_1$= Specific rate constant$(K_1 = A.e^{-\frac{E}{RT}})$ andn= Order of reaction.
Equation for calculating activation energy is given by
Equation 6

$$\Delta log R_T = n\Delta log W - \frac{E}{RT}\Delta\left(\frac{1}{T}\right)$$

The plot of $\Delta \log R_T$ vs.$\Delta \log W$ should give a straight line whose slope yielded the value of n. Its other rearrangement equation gives the value of E is represented as:
Equation 7

$$\frac{\Delta log R_T}{\Delta log W} = n - \frac{E}{2.303R}\left[\frac{\Delta\left(\frac{1}{T}\right)}{\Delta log W}\right]$$

Plot of $\frac{\Delta log\, R_T}{\Delta log W}$vs.$\left[\frac{\Delta\left(\frac{1}{T}\right)}{\Delta log W}\right]$should be linear. The slop of this line gives the value ofE and its intercept is the order of reaction.

Broido Method [44]**:** When a solid substance is heated in vacuum, it undergoes pyrolysis in which some of the pyrolysis products are volatile; the progress of reaction is determined by continuous weighing of the sample. W_t, the weight at any time t, is related to the fraction of number of initial reactant molecules not yet decomposed, y, by the equation
Equation 8

$$y = \frac{N}{N_o} = \frac{W_t - W_\infty}{W_o - W_\infty}$$

If the thermal degradation is carried out isothermally, the reaction rate is given by
Equation 9

$$\frac{dy}{dt} = -K_1 y^n$$

In which n is the order of reaction. If the rate constant K_1 changes with absolute temperature according to Arrhenius equation.
Equation 10

$$K_1 = ze^{\frac{-E}{RT}}$$

If pyrolysis is non-isothermal, then the temperature T is a linear function of time t, i.e.,
Equation 11

$$T = T_o + \beta T$$

Where,β is the linear heating rate. Equations 9, 10 and 11 may combined to give
Equation 12

$$\frac{dy}{y^n} = -\frac{z}{\beta}e^{\frac{-E}{RT}}.dT$$

For such a reaction, TG curve is represented by an equation integrated from a temperature
T_o at which y = 1. Therefore,
Equation 13

$$\int_y^1 \frac{dy}{y^n} = \frac{z}{\beta}\int_{T_o}^{T} e^{\frac{-E}{RT}}.dT$$

Horowitz and Metzger [45] applied the following approximation to the right-hand side equation 13.
Equation 14

$$e^{\frac{-E}{RT}} \approx \left(\frac{T_m}{T}\right)^2 e^{\frac{-E}{RT}}$$

T_m is temperature of maximum reaction rate.
Substituting Eq. 14 in Eq. 13, get
Equation 15

$$\ln\left[ln\frac{1}{y}\right] = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln\left[\frac{R}{E}.\frac{z}{\beta}.T_m^2\right]$$

This is the most accurate equation of many integrated equations, for the pyrolysis of cellulose obtained by Broido.

Kinetic analysis by multiple heating rate methods

Kinetic investigation of thermal degradation gives useful information for theoptimization of the consecutive treatment of polymer material in order to avoid or at leastcontrol thermal degradation. As the thermal degradation of a polymeric substrate follows various mechanisms, therefore the application of single heating rate model-fitting methods seems to be unjustified as they yield a single value for the entire process. Therefore, we have applied here multiple-heating rate model-free methods like Kissinger [37],Friedman [38], Ozawa-Flynn-Wall [39.40] and modified Coats-Redfern method [41,42]. In general, the thermal degradation reaction of a solid substance can be simplyshown as:

$$A(Solid)\xrightarrow{Heat}B(solid)+C(Gas)$$

Where, A is the starting material, B and C are the different products during the disappearance of A. In the thermogravimetric measurements the degree of conversion (α)(decomposition) can be calculated as follows:
Equation 16

$$\alpha=\frac{W_o-W_t}{W_o-W_f}$$

Here, α is the degree of conversion or degree of decomposition or the fraction reacted. $W_o$is the initial mass, W_t is the mass at any time t and W_f is the final mass of sample.

All the kinetic studies assumes that the isothermal rate of conversion,$\frac{d\alpha}{dt}$, is alinear function of a temperature dependent rate constant, k, and a temperature-independentfunction of conversion, α, that is:
Equation 17

$$\frac{d\alpha}{dt}=\mathrm{k\,f\,(\alpha\,)}$$

In case of polymer degradation, it is usual to assume that the rate of conversion isproportional to the concentration of material which has yet to react:

Equation 18

$$f(\alpha)=(1-\alpha)^n$$

Where n is the order of the reaction. This function has received the greatest use in polymer degradation kinetics, where a solid material is decomposing to give gaseous reaction products. The temperature dependence of the rate constant is expressed by Arreheniusequation:
Equation 19

$$k=A.e^{-\frac{E}{RT}}$$

Here, A is the pre-exponential factor, assumed to be independent of temperature. E is theenergy of activation, T is the absolute temperature and R is the gas constant. Thecombination of above three equations gives the following relationship.
Equation 20

$$\frac{d\alpha}{dt}=A(1-\alpha)^n.e^{-\frac{E}{RT}}$$

This forms the basis of subsequent analytical procedures used to derive kineticparameters from TG data.

Kissinger method [37]: It involves observing the temperature values, Tm, at the maxima of the firstderivative mass loss curves (DTG). Since the maximum mass loss occurs when
Equation 21

$$\frac{d\left(\frac{d\alpha}{dt}\right)}{dt}=0$$

So, by using equation 20, we get
Equation 22

$$\frac{E\beta}{RT_m^2}=An(1-\alpha)^{n-1}.e^{\frac{-E}{RT_m}}$$

Where, β is linear rate of heating,$\beta = \frac{dT}{dt}$.Kissinger then assumes that the product$n(1-\alpha)^{n-1}$ is independent of β and very nearly equal to unity for a first order reactionsuch that the following expression can be derived:
Equation 23

$$\frac{d\left(\ln\left(\frac{\beta}{T_m^2}\right)\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R}$$

Therefore, the activation energy, E, can be obtained from a plot of $\ln\left(\frac{\beta}{T_m^2}\right)$against $1/T_m$ for a particular stage of decomposition since the slope of such line is givenby -E/R.

Friedman method [38]: This method is probably the most general of the derivative techniques and is basedon the intercomparison of the rates of weight loss,$\frac{d\alpha}{dt}$, for a given fractional weight loss,α, determined using different linear heating rates, β.
According to equation 20:
Equation 24

$$\frac{d\alpha}{dt} = A(1-\alpha)^n.e^{-\frac{E}{RT}}$$

Taking natural logarithm both sides, we have
Equation 25

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta.\frac{d\alpha}{dt}\right) = lnA + nln(1-\alpha) - \frac{E}{RT}$$

The values for activation energy of degradation over a wide range of weight losscould be obtained by plotting ln(dα/dt) against 1/T for a constant α value. In addition to E, the values of n and log A can be determined from a plot of E/RT_o against ln(1-α) where$1/T_o$ is the temperature at which ln(dα/dt) = 0. Friedman calculation is applicable to allpoints on TGA curve while, in Kissinger's method only the point of maximum rate inweight loss is used.

Ozawa-Flynn-Wall (O-F-W) method [39,40]: In differential methods, to determine kinetic parameters the relationship betweendα/dt and T is utilized. However, in the integral methods i.e. O-F-W, the kineticparameters are determined from the standard TGA curve. According to equation 20:
Equation 26

$$\frac{d\alpha}{dt} = A(1-\alpha)^n.e^{-\frac{E}{RT}}$$

or
Equation 27

$$\frac{d\alpha}{(1-\alpha)^n} = A.e^{-\frac{E}{RT}}.dt$$

Now, using standard rate of heating,$\beta = \frac{dT}{dt}$

Equation 28

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{1}{\beta}A.e^{-\frac{E}{RT}}.dT$$

On integrating and applying initial condition α=0 at T = T_o the following expression isobtained:
Equation 29

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{1}{\beta}\,A\int_{T_o}^{T} e^{-\frac{E}{RT}}.dT$$

Essentially this technique assumes that A,$(1-\alpha)^n$ and E are independent of T whileA and E are independent of α, wherein the variables given in the equation 29 may beseparated and integrated to give in logarithmic form:

Equation 30

$$\log g(\alpha) = \log(\frac{AE}{R}) - \log(\beta) + \log\left(p\left(\frac{E}{RT}\right)\right)$$

Where, $p = e^{-\frac{x}{x(x+2)}}$ and $x = \frac{E}{RT}$

Using Doyle's approximation for the integral which alloys for E/RT greater than20, then log (p (E/RT)), may be expressed as:
Equation 31

$$\log\left(p\left(\frac{E}{RT}\right)\right) = -2.315 - 0.4567\left(\frac{E}{RT}\right)$$

So, equation becomes:
Equation 32

$$\log(\beta) = \log\left(\frac{AE}{R}\right) - \log g(\alpha) - 2.315 - 0.4567\left(\frac{E}{RT}\right)$$

Therefore, the activation energy, E, can be obtained from a plot of log β against1/T for a fixed degree of conversion since the slope of such line is given by-0.4567E/R. The pre-exponential factor, A, can be obtained from the equation:
Equation 33

$$A = \beta\left(\frac{E}{RT^2}\right).e^{\frac{E}{RT}}$$

Coats-Redfern (modified) method [41,42]: The modified Coats-Redfern method is a multi-heating rate application of the Coats and Redfern equation, producing a model-free approach similar to those of O-F-W[39,40] and Friedman [38].
Equation 34

$$\ln\left[\frac{\beta}{T^2\left(1-\frac{2RT}{E}\right)}\right] = \ln\left[-\frac{AR}{E\ln(1-\alpha)}\right] - \frac{E}{RT}$$

In this method, $\ln(\beta/T^2)$ is plotted against 1/T which gives slope -E/R of line atany degree of conversion. Using the value of slope of each line, E can be calculated corresponding to each conversion. If the value of E varies with extent of conversion, then results should be interpreted in terms of multi-step reaction mechanisms [43].

CONCLUSIONS

Kinetic studies on thermal degradation provide invaluable insights into the behavior of materials and compounds under elevated temperatures [46-48]. This research area continues to evolve, with ongoing efforts to develop more accurate models, explore novel analytical techniques, and address the environmental implications of thermal degradation [49-52]. The knowledge gained from these studies has broad implications for product development, quality control, and sustainability in various industries. The study of kinetic processes in thermal degradation is a multidisciplinary field that combines chemistry, materials science, engineering, and environmental science. As industries strive for greater efficiency, safety, and sustainability, a comprehensive understanding of the kinetics of thermal degradation is indispensable. This research not only deepens our understanding of fundamental chemical processes but also has far-reaching implications for product development, quality control, and environmental responsibility in today's complex and interconnected world. This represents a dynamic and vital field of research with far-reaching implications for a wide range of industries and scientific disciplines. The journey through the intricacies of thermal degradation kinetics has revealed valuable insights and challenges. In the era of environmental consciousness, kinetic studies have become crucial for assessing the impact of materials on the environment, including their degradation products [53-55]. This research informs decisions on sustainable materials and waste disposal strategies.

Advances in analytical techniques, such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), have enhanced our ability to dissect thermal degradation processes. Mathematical models and computational approaches are continually evolving to provide more accurate descriptions of complex degradation pathways [56-58].Many materials exhibit multi-step degradation processes, which require a deeper understanding of intermediate products and reaction mechanisms. Unraveling these complex pathways remains an ongoing challenge. The influence of environmental factors, such as oxygen concentration, humidity, and pressure, on thermal degradation kinetics cannot be underestimated. These factors significantly affect degradation rates and the nature of degradation reactions, adding layers of complexity to the research[59].

This field continues to evolve and expand as it addresses the growing demands of modern industries and environmental stewardship. The insights gained from this research have not only deepened our understanding of fundamental chemical processes but have also contributed to safer, more efficient manufacturing practices and sustainable product development. As technology and materials advance, kinetic studies will remain an invaluable tool for maintaining product quality, ensuring safety, and safeguarding our environment. The future of this field is promising, with ongoing efforts to refine analytical techniques and models, ultimately leading to more informed and responsible decision-making in various industries.

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