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Polypropylene pyrolysis kinetics under isothermal and non-isothermal conditions: a comparative analysis

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Abstract: The kinetics of polypropylene pyrolysis has been studied under isothermal and non-isothermal conditions using Arrhenius and Kissinger–Akahira–Sunose (KAS) equations. Under isothermal conditions, applying first order kinetic model, activation energy (*E*a) and pre-exponential factor (*A*) were investigated and observed as 119.7 kJ mol^{-1} and 1.2×10^{10} min^{-1}, while in case of non-isothermal kinetics using Kissinger–Akahira–Sunose method, the average *E*a and *A* were found to be 91.23 kJ mol^{-1} and 2.3×10^{7} min^{-1}, respectively. A comparison among the isothermal and non-isothermal reactions was made on the basis of kinetics parameters. The results from both the methods showed trivial variation in kinetic parameters of the pyrolysis reaction which may be due to two major reasons. Firstly, the selection of the kinetic model applied and secondly the inconsistency due to various experimental conditions used which can be reduced at optimized conditions. As the disposal of plastic materials need reliable kinetics information to model their decomposition reactions, therefore, the kinetics data thus obtained from pyrolysis reaction of model polypropylene will help in the utilization of polypropylene waste as energy source on industrial scale.

Keywords: activation energy; frequency factor; kinetic analysis; polypropylene; thermal decomposition.

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1 Introduction

Plastic is an essential part of our daily life and is extensively used for domestic and commercial activities due to its durability and resistance to degradation [1]. The production of plastics has increased many folds worldwide due to its demand in the local market. As the consumption increases, the production of waste also increases and this waste comes from different sources including automotive, agriculture, construction and daily life use [2]. Waste from plastics has an adverse impact on environment due to its non-degradable nature [3]. Efforts are on for the last many years to dispose them of safely, and many research groups are involved worldwide for the solution of this problem [4–7].

Previously land filling and incineration were frequently used for this purpose; however, these practices were now abandoned due to their ill effects on health and environment as land filling results in contamination of soil and water, whereas incineration leads to formation of hazardous smoke [8–10]. The best method is to recycle the waste under control environment [11–13]. Currently different techniques are being used for disposal and recycling of plastic materials. These consist of mechanical, thermo-chemical and biological recycling. Mechanical method is environmentally friendly however; the process is not economical because high energy is required for the cleaning, categorization, shipping and additive used in the yield of final product [14]. Using mechanical recycling method, polymer technologists made many efforts for the reuse of waste plastic materials; however, the products obtained from the reprocessing of the plastic waste are generally of low quality and have less market value as compared to those made from virgin polymers [15].

These days the majority of research work is focused on the introduction of biodegradable polymers; however, this method is not much efficient because the plastic materials will degrade only if they are disposed of in suitable conditions [16]. Another method used is chemical recycling, in which the plastic waste is treated with chemicals to convert it into valuable products and monomers, however, this method is also not very effective [17]. An alternate option is thermal degradation; however, this method is associated with some disadvantages as it requires more energy in the form of heat and sometimes little or no useful products are produced [18]. Therefore, the ultimate option is thermo-catalytic pyrolysis in which the required products can be obtained at lower temperature using a suitable catalyst [19, 20]. The foremost thing in this process is the selection of a suitable catalyst and this can be identified by studying the kinetics of the catalyzed reaction vis-a-vis reduction in activation energy and degradation temperature [21–23].

The main goal of a kinetic study of a reaction is to find out kinetic parameters and in this connection thermal analysis can be proved very successful especially

in case of solid-state reactions [24]. The procedure involves decomposing the sample under isothermal and non-isothermal conditions. The kinetic parameters under isothermal conditions are calculated applying Arrhenius equation, whereas under non-isothermal conditions, the kinetic parameters are determined using Kissinger–Akahira–Sunose equation and various other equations [25–27]. The kinetics of polypropylene decomposition has been widely studied using both isothermal and non-isothermal methods; however, no report is available on comparative kinetic study of polypropylene under isothermal and non-isothermal conditions. This reality forced us to investigate decomposition of polypropylene as the data collected from these studies demonstrate many factors influencing kinetics parameters. Therefore, the major objective of this work is to study the kinetics of pyrolysis of polypropylene under isothermal and non-isothermal conditions using Arrhenius and Kissinger–Akahira–Sunose equations. Kinetic parameters determined from both the methods will be compared and variation if any in *E*a and *A*-factor of the pyrolysis reaction will be explained in terms of the kinetic model applied and complexity of the reaction in the solid phase. The kinetic data thus obtained from pyrolysis reaction will help in the utilization of polypropylene waste as energy source on industrial scale.

2 Materials and methods

Poly(propylene) isotactic, was purchased from Aldrich and used without any further treatment. Thermogravimetric analysis was performed on TG/DTA (Perkin Elmer, USA). N_2 at a purge rate of 20 mL/min was utilized to ensure inert environment during the run. An accurately weighed 6 ± 0.3 mg of sample was decomposed in each experimental run. Under isothermal conditions, thermogravimetric analysis was performed at 243, 255, 267, 280 and 290 °C as function of time whereas under non-isothermal conditions experiments were performed at heating rates of 5, 10, 15 and 20 °C/min in temperature range from 25 to 600 °C. The data thus obtained was used for kinetic analysis using Arrhenius and Kissinger–Akahira–Sunose equations.

2.1 Kinetic study

Under isothermal conditions the kinetics of pyrolysis of a substance is expressed as:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α shows conversion in the range $0 \le \alpha \le 1$, k rate constant, t time, and $f(\alpha)$ is dependent upon the reaction model used. According to Arrhenius equation k is expressed in the form;

$$k = Ae^{-Ea/RT} \tag{2}$$

where A is frequency factor, Ea, activation energy, T, absolute temperature and R gas constant. Substituting Eq. (2) in 1 we get

$$\frac{d\alpha}{dt} = Ae^{-Ea/RT} f(\alpha) \tag{3}$$

where α is expressed in terms of loss in mass of sample as

$$\alpha = (w_o - w_o)/(w_\circ - w_f) \tag{4}$$

where w_o, w and w_f are the initial, actual and final mass of the sample, respectively.

And $f(\alpha) = (1-\alpha)^n$, where n is the order of reaction.

The Eq. (3), in final form can be written as

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{5}$$

and

$$\frac{d\alpha}{(1-\alpha)^n} = kdt \tag{6}$$

Integrating Eq. (6), the following expression is obtained

$$kt = -\ln(1-\alpha) \quad \text{for } n = 1 \tag{7}$$

and

$$kt = \left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] \quad \text{for } n \neq 1 \tag{8}$$

As in accord with the findings of other researchers, a reaction order of 1 is assumed for pyrolysis of plastic materials [28]. Therefore, Eq. (7) is applied in this work for calculation of kinetic parameters of polypropylene pyrolysis under isothermal conditions.

In case of non-isothermal kinetics Kissinger–Akahira–Sunose (KAS) model free method as given in Eq. (9) [29, 30] is used to investigate kinetic parameters of polypropylene degradation.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AR}{Eag(\alpha)}\right] - \frac{Ea}{RT} \tag{9}$$

Where β is heating rate and all other terms have their respective meanings. Ea and A can be determined from the slope and intercept of the plot $\ln(\beta/T^2)$ versus $1/T$, respectively [5].

3 Results and discussion

3.1 Isothermal kinetics

The plots of $-\ln(1-\alpha)$ versus time were constructed as presented in Figure 1. From the best linear fits of plots, it can be deduced that the pyrolysis of polypropylene follows first order kinetics, and this agrees well with a reported study [31]. The rate

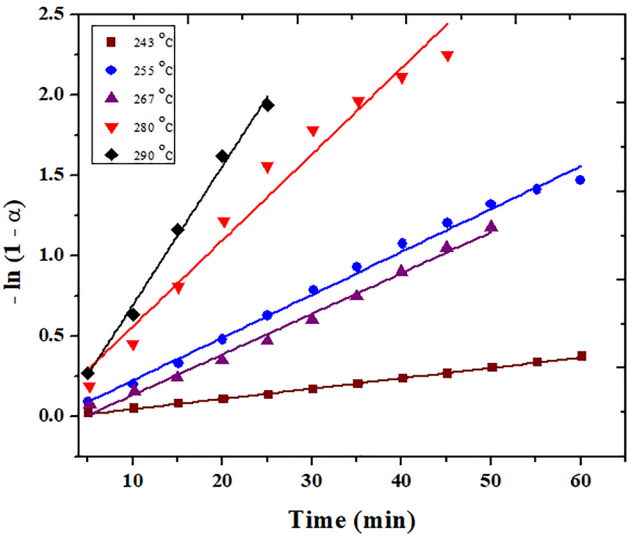

Figure 1: Plots of –ln(1–α) versus t at different temperatures for calculation of rate constant for decomposition of polypropylene.

constant values at different temperatures were calculated from the slopes of the plots of –ln(1–α) versus time.

Taking natural logarithm of Eq. (2), we get:

$$\ln k = \ln A - E\mathrm{a}/RT \tag{10}$$

Thus, plotting ln$k$ versus $1/T$ gives a straight line with slope equivalent to Ea and intercept equal to ln$A$. Figure 2 shows the plot of ln$k$ versus $1/T$. For polypropylene degradation Ea determined from the slope of the curve was observed as 119.70 kJ mol^{-1}. The intercept of the plot gives the frequency factor with a value of 1.2×10^{10} min^{-1}. Table 1 shows order of reaction, Ea, A and R^2 values. The R^2 value shows that the fit is of high-quality. Encinar and González [32] investigated the isothermal kinetic study of polypropylene degradation in inert environment. The Ea value was found as 169.35 kJ mol^{-1}, which is higher than observed in our case.

3.2 Non-isothermal kinetics

Thermal analysis of polypropylene was performed at heating rates of 5, 10, 15 °C/min from 25–600 degree centigrade and the DTG are depicted in Figure 3. It can be seen from the figure that by increasing heating rates, maximum

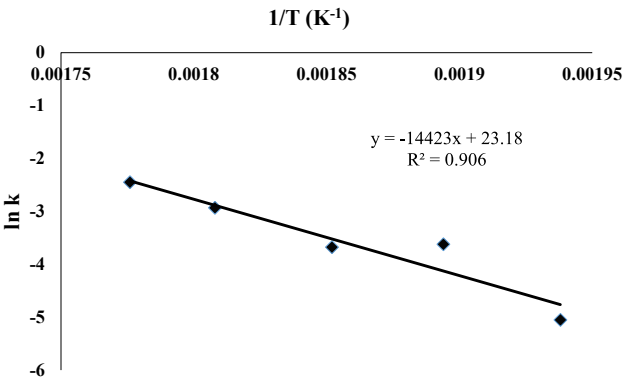

Figure 2: Arrhenius plot for decomposition of polypropylene.

Table 1: Kinetics parameters obtained from pyrolysis of polypropylene using Arrhenius equation.

Method	Sample	Reaction order	*Ea* (kJ/mol)	*A* (min^{-1})	R^2
Isothermal	Polypropylene	1^{st}order	119.7	1.20×10^{10}	0.906

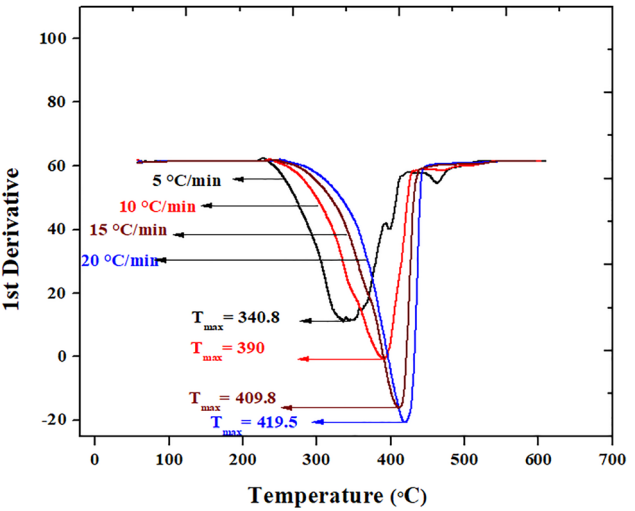

Figure 3: DTG of polypropylene in nitrogen atmosphere at different heating rates.

temperature for the degradation also increases. This shows that at low heating rate the equilibrium is attained rapidly while in the case of high heating rate the equilibrium is attained slowly and accordingly the curve shifts to high temperature area. It may be due to slow diffusion of heat. These observations are in accord with reported literature [33].

Figure 4 shows KAS plots of $\ln(\beta/T^2)$ against $1/T$ at various degree of conversion for polypropylene. Straight lines observed for KAS show good regression coefficient at all fraction conversion. Using KAS plots, kinetic parameters were investigated and these are given in Table 2. It can be found out from the table that with increase in conversion fraction, an increase in *E*a can be observed. It starts from 79.81 kJ mol^{-1} at 0.1 and ends up at 107.25 kJ mol^{-1} at conversion of 0.7. Similarly, a linear relationship can also be observed in *A*-factor and fraction conversion. Average *E*a and *A* were determined and found to be 91.23 kJ mol^{-1} and 2.3×10^7 min^{-1}, respectively. These parameters are in accord with reported study. Rantuch et al. [34], determined the kinetic parameters of polypropylene using thermogravimetric analysis. Applying Kissinger–Akahira–Sunose model they determined activation energy values from 54.06 to 100.82 at fraction conversion from 0.1 to 0.9, which agree well with our results at high conversion. A comparative evaluation of *E*a calculated in this work using Arrhenius and KAS equations with reported work is shown in Table 3. The difference in activation energy may be due to two major reasons. Firstly, the selection of the kinetic model applied and

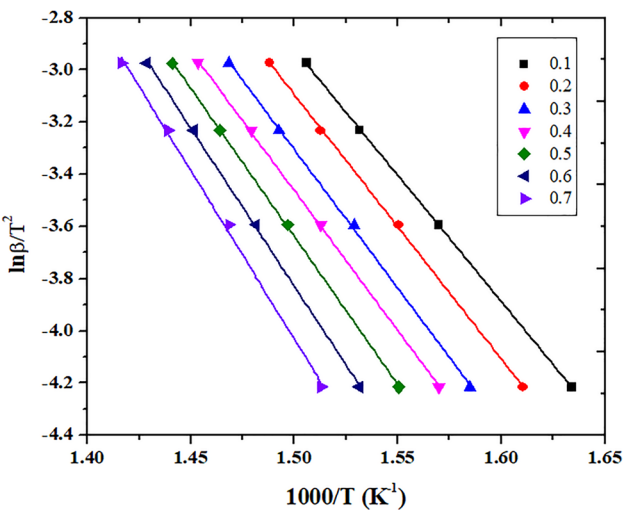

Figure 4: KAS plots obtained from pyrolysis of polypropylene at different percent conversion from 0.1 to 0.7.

Table 2: Kinetic parameters calculated from pyrolysis of polypropylene using KAS method.

A	*Ea* (kJ mol^{-1})	*A* (min^{-1})	R^2
0.1	79.81	1.0×10^6	0.999
0.2	83.14	1.6×10^6	0.999
0.3	88.12	3.1×10^6	0.999
0.4	88.95	6.9×10^6	0.999
0.5	91.45	1.8×10^7	0.999
0.6	99.76	5.5×10^7	0.999
0.7	107.25	7.9×10^7	0.999
Average	91.23	2.3×10^7	0.999

Table 3: Comparison of activation energy determined from pyrolysis of polypropylene in literature with present study.

Atmosphere	Temp. (°C)	*Ea* (kJ mol^{-1})	Method used	Reference
N2	25–600	114	Non-isothermal	[21]
N2	415–490	169	Isothermal	[32]
N2	415–490	153–265	Non-isothermal	[32]
N2	25–600	98–108	Non-isothermal	[33]
N2	25–600	105–150	Non-isothermal	[35]
N2	30–600	61–110	Non-isothermal	[37]
N2	25–600	57–102	Non-isothermal	[36]
Ar	404–421	94–100	Non-isothermal	[38]
N2	243–290	119	Isothermal	Present work
N2	25–600	91.23	Non-isothermal	Present work

secondly the inconsistency due to various experimental conditions used. However, the *E*a calculated in this work are almost in conformity with reported studies and this confirms the accuracy of both the methods used for calculation of kinetic parameters [33, 35–38].

4 Conclusions

Thermal decomposition of polypropylene using isothermal and non-isothermal methods was performed. In case of isothermal conditions, the best linear fits of different forms of $-\ln(1-\alpha)$ versus time showed that the pyrolysis of polypropylene follows a first order kinetics. *E*a and *A*-factor were investigated as 119.70 kJ mol^{-1} and 1.2×10^{10} min^{-1}, respectively. In case of non-isothermal kinetics, the average *E*a

and *A*-factor determined were found out as 91.23 kJ mol^{-1} and 2.3×10^7 min^{-1}, respectively. The results from both the methods showed some variation in *E*a and *A*-factor of the pyrolysis reaction which may be credited to the selection of the kinetic model applied and inconsistency due to various experimental conditions. Moreover, the kinetics results from non-isothermal experiments suggest that thermal decomposition of polypropylene is a complex reaction which is evident from increase in activation energy with conversion. The kinetics parameters determined will be useful in the utilization of polypropylene waste as energy source on commercial scale.

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