

Thermal degradation and kinetic study for different waste/rejected plastic materials

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Abstract—A kinetic analysis based on thermal decomposition of rejected polypropylene, plastic film and plastic pellets collected from different industrial outlet has been carried out. Non-isothermal experiments using different heating rates of 5, 10, 20, 30, 40 and 50 °C min⁻¹ have been performed from ambient to 700 °C in a thermo-balance with the objective of determining the kinetic parameters. The values of activation energy and frequency factor were found to be in the range of 107-322 kJ/mol, 85-331 kJ/mol, 140-375 kJ/mol and 3.49E+07-4.74E+22 min⁻¹, 3.52E+06-2.88E+22 min⁻¹, 7.28E+13-1.17E+25 min⁻¹ for rejected polypropylene, plastic film and plastic pellets, respectively, by Coats-Redfern and Ozawa methods including different models. Kissinger method, a model free analysis is also adopted to find the kinetic parameters. Activation energy and frequency factor were found to be 108 kJ/mol, 98 kJ/mol, 132 kJ/mol and 6.89E+03, 2.12E+02, 8.06E+05 min⁻¹ for rejected polypropylene, plastic film and plastic pellets, respectively, by using the Kissinger method.

Key words: Thermal Pyrolysis, Plastic Waste, TGA, DTG, Kinetic Parameters

INTRODUCTION

In the modern era, plastic contributes as a fundamental material to all fields such as the automobile industry, electricity and electronic industries, packing materials, agriculture, building materials etc. The central pollution control board of India (CPCB) reported [1] that the rates of production of plastics are about more than 200 MMT all over the world. As the production of plastic increases day by day it leads to generation of massive amounts of waste. The Ministry of the Environment and Forests of India estimated that the generation of plastic waste increased from about 3.4 MMT in 2000 to about 12.5 MMT in 2010 [2]. Generally, plastic waste has been mainly disposed of by landfill or incineration, though these methods face immense communal and economical resistance due to environmental issues such as air pollution, soil contamination and increase of space and disposal costs [3]. These processes are not fully acceptable under current policy due to which it is important to focus on recovery of energy and valuable products from the waste plastics. Pyrolysis is one of the promising routes for recovery of energy and valuable products from the waste plastics [4,5]. Pyrolysis apparently offers many advantages for contaminated plastic wastes and mixed plastics which cannot be easily recycled. One of these advantages is that the polymers present in the plastic waste can be thermally degraded back to basic hydrocarbons which can then be reprocessed in a refinery to produce petrochemicals. Moreover, pyrolysis of plastic waste based on the decomposition of polymers at different temperatures allows the treatment of polymers with simultaneous decomposition and separation [6,7]. As a result combustible gases, char and liquid are obtained. The reduction in land filling is

also an added advantage [8].

Thermo-gravimetric analysis (TGA) is a widely used thermal analysis technique to investigate plastic decomposition processes and to obtain their kinetics during pyrolysis of various plastic waste materials [9-16]. This technique provides information regarding measurement of the weight loss of the sample as a function of time and temperature. The behavior of different types of plastics during thermal decomposition as well as its kinetics plays a vital role in understanding the pyrolysis process as well as for the design of reactor and scaling up of industrially viable processes. The reaction mechanism of thermal decomposition of waste plastic is very complex, which includes chain fission, radical recombination, carbon-hydrogen bond fission, and hydrogen abstraction [17,18]. The plastics that have received much interest and attention are polyethylene and polypropylene, which are major contributors in the waste plastic scenario. Much research work on pyrolysis kinetics of polyethylene and polypropylene has appeared in literature; still, it requires resolving the burning issue of these waste plastics generated from many industrial outlets to generate liquid hydrocarbon, which can be further blended with conventional fossil fuels [19,20]. During this particular study, two important points were, first, the selection of kinetic models to understand the pyrolysis kinetics, and second, the magnitude of kinetic parameters that are reported differ significantly, as these parameters has to be controlled minutely to get best practice waste plastic pyrolysis for fuel generation. According to the literature, these changes might be due to different collected waste samples of polyethylene and poly propylene from industry outlets, experimental conditions employed, and methods followed for analysis and obtaining kinetic parameters [21]. In the literature, many models have been proposed and published [22,23]. An extensive literature survey and its review suggest that each material behaves differently with respect to its origin and hence requires detailed char-

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acteristics analysis with respect to the process employed for the energy recovery. Also, most of the previous studies of kinetics of plastic wastes are based on the assumption of first-order kinetics, which may not be appropriate since the pyrolysis of waste material is very complex.

Considering the above loophole, the objective of the present study was to understand the thermal behavior of rejected polypropylene, plastic film and plastic pellets obtained from various sources, by using a thermo-gravimetric analyzer. The thermal events taking place during pyrolysis of different materials would be identified. Kinetic study was carried out using Coats-Redfern and Ozawa methods with application of different models. Also, model free kinetic analysis was performed using the Kissinger method and the kinetic parameters obtained by different methods were compared. This kinetic analysis might be useful for the designing and operation of thermal conversion systems.

EXPERIMENTAL

1. Sample Collection and Preparation

The rejected polypropylene, plastic film and plastic pellets used in this work was collected from the nearby chemical industry, plastic packaging industry and MSW plant, respectively. Rejected polypropylene was used as received; whereas plastic film and plastic pellets were cut into 2-3 mm diameter particle size with cutter. Proximate, ultimate analyses [24] and higher heating value of the materials as reported in Table 1 were carried out as per ASTM D 5142-02A [25] and ASTM D 5865-03A [26], respectively.

2. Experimental Techniques

Rejected polypropylene, plastic film and plastic pellets were subjected to thermo-gravimetric analysis (TGA) in an inert atmosphere of nitrogen. Perkin Elmer (Model: Pyris 6 TGA) analyzer was used to measure and record the sample mass changing with respect to temperature over the course of pyrolysis reaction. Thermo-gravimetric analysis was carried out at six different heating rates (5, 10, 20, 30, 40, 50 °C min⁻¹) between 30 °C and 700 °C. Nitrogen gas was used as an inert carrier gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample. A flow rate of around 20 ml min⁻¹ was set during the experimental runs. All sample amounts used in this study averaged approximately 15 mg and experiments were duplicated.

RESULTS AND DISCUSSION

1. Thermal Degradation of Different Materials

TG curves at different heating rates for thermal degradation of rejected polypropylene, plastic film and plastic pellets are shown in Figs. 1-3 respectively.

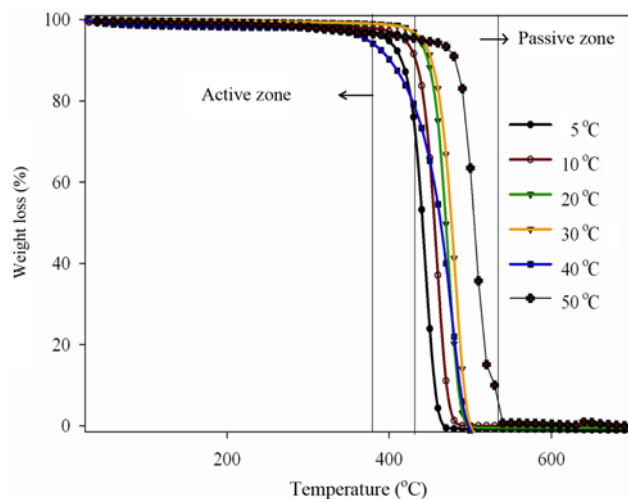


Fig. 1. TGA profile of rejected polypropylene at different heating rates.

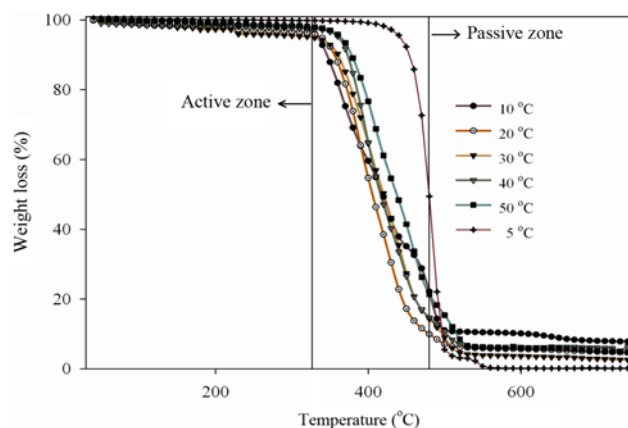


Fig. 2. TGA profile of plastic film at different heating rates.

The weight loss curves show that degradation of all three materials occurs almost in a two-step process. The thermal degradation starts in the range of 300-350 °C and it is almost completed at approximately 560-700 °C for all materials under study.

Results indicate that there are three separate zones occurring during the pyrolysis process. The first zone is from the ambient temperature to onset temperature of active pyrolysis. In this zone, there was no significant weight loss; the thermo-gram shows an almost horizontal line with slight loss of weight, which is followed by an onset degradation of the materials as evidenced by first visible weight loss after the horizontal line. This degradation might be due to evaporation of moisture and light volatile matter. The second zone repre-

Table 1. Proximate and ultimate Analysis and heating values of the different materials

Material	Proximate analysis, % wt (as received)				Ultimate analysis, % wt (dry basis)			HHV MJ/kg
	Moisture	VM	FC	Ash	C	H	O	
Rejected polypropylene	0.51	99.65	0.41	0	45.60	6.19	48.21	16.25
Plastic film	3.50	96.30	0.35	0.04	44.04	5.99	49.97	15.65
Plastic pellets	2.43	88.22	0.93	8.42	40.73	5.52	53.75	14.30

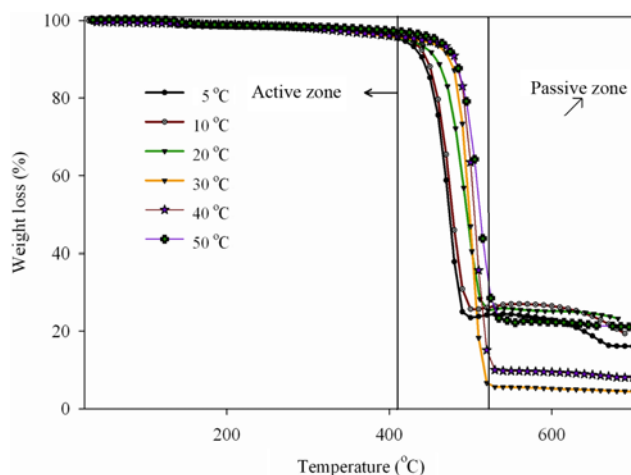


Fig. 3. TGA profile of Pellets at different heating rates.

sents the major decomposition of materials and is considered to occur between the initial temperature and final temperatures obtained by the intersection of the parts of TGA curve and are considered as the active pyrolysis zone. This step shows the intense loss of weight at rapid rates and release of different types of volatiles.

The major change in the slope of all TGA curves was observed at around 300-520 °C, including the initiation of third zone. This third zone represents temperature above the final temperature of active pyrolysis zone and also considered as passive pyrolysis zone. In this zone the amount and rate of mass loss is slower than the active pyrolysis zone. For rejected polypropylene, up to 300 °C, about 0.5-2% wt loss is taking place, which can be attributed to moisture in the materials. In active pyrolysis zone between 300-450 °C maximum amount of volatiles were released which is 60-80%. Similar kind of phenomenon for pyrolysis of polypropylene has been reported [20,27]. In case of plastic film and pellets, up to 300 °C, about 0.5-2% wt loss is taking place, which can be attributed to moisture in the materials. In active pyrolysis zone between temperatures range

450-650 °C, the maximum amount of volatile components is generated, which is 65-98%. Similar trends for pyrolysis of mixed plastic waste and municipal solid plastic wastes have been reported [16, 28,29].

In case of all materials, after 650 °C, about 0-2% wt loss is taking place, which is known as the passive pyrolysis zone. For the temperature range studied, the generation of total volatiles decreases with increasing heating rate. For given temperature of pyrolysis the corresponding conversion at higher heating rate is less than that at lower heating rate. The reason is that at lower heating rate the retention time will be more to reach a given temperature, which increases the conversion [30,31].

The effect of the heating rate, as observed in Fig. 1-3, is to horizontally spread the TGA curve such that maximum and final temperatures of active pyrolysis are shifted to higher temperature. Such type of lateral shift has been reported for different types of plastic waste materials, which might be due to combined effect of heat transfer at different heating rate and the kinetics of decomposition resulting in delayed decomposition [32]. Tables 2 and 3 show pyrolysis characteristics and amount of volatiles generated from different waste plastic materials covered during this study. As heating rate increased the maximum devolatilization temperature and maximum devolatilization rate increased. Increase in temperature is minor; however, the increase in devolatilization rate is much higher. When the rate of heating is increased the duration of retention is shorter and temperature required for material to decompose will also be higher [33].

The maximum rate of devolatilization is higher at 50 °C/min than 5 °C/min, which is consistent with literature where higher heating rates resulted in higher reactivity [16,20,34]. With a higher heating rate, a larger instantaneous thermal energy is provided in the system. This situation also results in a higher instantaneous rate as shown in Figs. 1-3. The proportional increase of thermal decomposition rate with increase in heating rate was more in the active pyrolysis zone than in the passive pyrolysis zone for all materials.

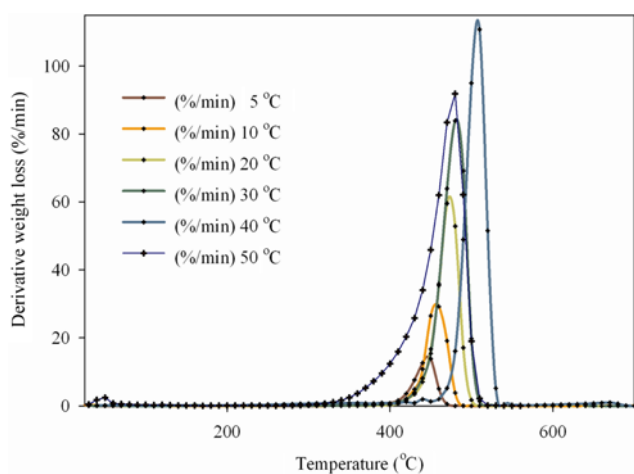
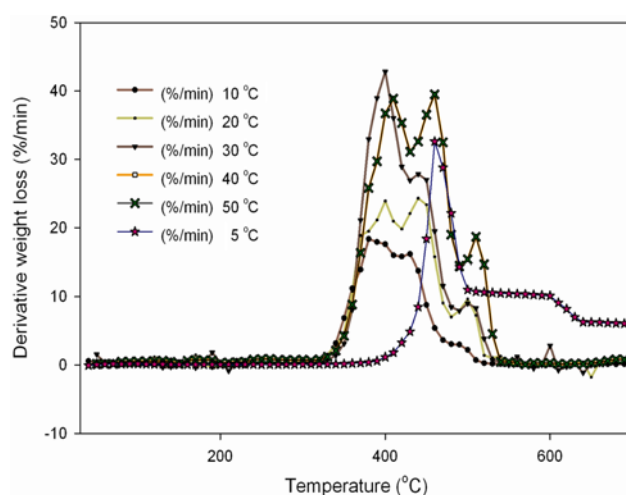
Weight loss, heat flow and derivative information curves of rejected polypropylene and plastic pellets degradation are presented

Table 2. Pyrolysis characteristics for rejected polypropylene, plastic film and plastic pellets

Heating rate (°C/min)	5	10	20	30	40	50
Active pyrolysis temperature range (300-500 °C)						
% Degradation for rejected polypropylene	92.5	96.3	97.0	98.9	98.2	99.1
% Degradation for plastic film	86.4	87.3	89.5	90.4	91.1	91.9
% Degradation for plastic pellets	71.1	72.2	72.1	71.8	74.9	74.6
Passive pyrolysis temperature range (500-750 °C)						
% Degradation for rejected polypropylene	4.3	1.3	2.2	1.2	0.9	0.6
% Degradation for plastic film	4.2	3.5	9.3	3.6	4.5	4.0
% Degradation for plastic pellets	8.9	3.9	4.3	6.8	6.9	7.1
Maximum temperature with rate of devolatilization (°C) Tmax						
For rejected polypropylene at Tmax (°C)	450	460	470	480	480	480
Max. rate of devolatilization (%wt/min) for rejected polypropylene at Tmax (°C)	13.89	29.18	59.56	83.94	85.2	91.89
For plastic film at Tmax (°C)	420	480	380	440	400	460
Max. rate of devolatilization (%wt/min) for plastic film at Tmax (°C)	9.0	8.0	18.3	24	42.8	39.5
For plastic pellets at Tmax (°C)	470	480	490	495	490	500
Max. rate of devolatilization (%wt/min) for plastic pellets at Tmax (°C)	8.63	18.7	40.3	40.5	37.4	44.2

Table 3. Amount of volatiles generated during different temperature range (for rejected polypropylene, plastic film and plastic pellets)

Temperature range (°C)	Ramp rate (°C)	<150	150-300	300-450	450-650	Total volatiles released (%)	Char (%)
For rejected polypropylene							
Amount of volatiles released (%)	5	2.4	1.8	66.4	28.4	92.4	7.6
	10	0.31	1.39	63.17	27.5	92.49	7.51
	20	1.76	1.55	79.49	14.2	95.52	4.48
	30	2.16	2.33	68.21	24.8	97.63	2.37
	40	1.58	0.62	71.25	21.1	94.11	5.89
	50	0.45	1.18	56.92	37.2	95.5	4.5
For plastic film							
Temperature range (°C)	Ramp rate (°C)	<150	100-250	250-450	450-650	Total volatiles released (%)	Char (%)
Amount of volatiles released (%)	5	0.36	0.44	0.74	94.13	95.67	4.33
	10	1.16	0.36	0.42	98.02	99.96	0.04
	20	0.15	0.36	0.38	95.92	96.81	3.19
	30	0.17	0.29	0.33	99.12	99.91	0.09
	40	0.2	0.31	0.37	98.5	98.1	1.9
	50	1.54	0.46	1.18	90.78	93.98	6.02
For plastic pellets							
Temperature range (°C)	Ramp rate (°C)	<150	150-300	300-450	450-650	Total volatiles released (%)	Char (%)
Amount of volatiles released (%)	5	1.44	0.64	12.67	66.49	83.93	16.07
	10	0.71	0.78	10.38	64.29	80.63	19.37
	20	0.99	1.14	6.04	67.3	76.72	23.28
	30	0.84	1.44	8.5	63.5	72.5	27.5
	40	1.22	1.7	9.2	65.4	74.4	25.6
	50	0.43	1.12	2.36	74.38	78.57	21.43

**Fig. 4. DTG curves for rejected polypropylene at different heating rates.****Fig. 5. DTG curves for plastic film at different heating rates.**

in Figs. 4-6. The nature of curves obtained at all heating rates was similar, except for a shift at T_{max} . Examination of this data clearly indicates that polypropylene degrades in a single-stage process. In case of plastic film two-three peaks corresponding to endothermic reactions are observed which might be due to its heterogeneous composition. Peak width increases with increase in heating rate may be due to the large heat transfer and at the same time diffusion effect characteristics of agglomerated system leading to peak broadening

[30,35].

2. Determination of Kinetic Parameters

Non-isothermal kinetics study of weight loss under pyrolysis of carbonaceous materials is an extremely complex task because of the presence of numerous complex components and their parallel and consecutive reactions.

The extent of conversion or the fraction of pyrolysis materials, x , is defined by the expression,

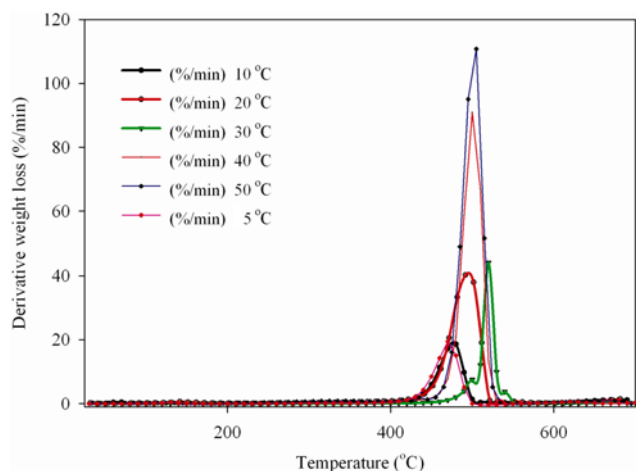


Fig. 6. DTG curves for pellets at different heating rates.

$$x = \frac{(w_0 - w)}{(w_0 - w_f)} \quad (1)$$

Where w is the weight of the sample at a given time t ; w_0 and w_f refer to values at the beginning and the end of the weight loss.

The rate of kinetic reaction can be described by Eq. (2):

$$\frac{dx}{dt} = K(T)f(x) \quad (2)$$

Where $K(T)$ is the temperature dependent rate constant and $f(x)$ is a dependent kinetic model function. There is an Arrhenius type dependency between $K(T)$ and temperature according to Eq. (3):

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

So,

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (4)$$

Where A is the pre-exponential factor (min^{-1}) of the pyrolytic process, E is the activation energy (kJ/mol) of the process, R is the universal gas constant ($\text{J/mol}\cdot\text{K}$), T is the absolute temperature (K), n is the order of reaction, t is the time (min) and x is the fraction of reactant decomposed at time t .

To determine the values of the kinetic parameters, the integral method is used to solve Eq. (4). The reaction rate depends on the conversion, which can be represented by a reaction model $f(x)$, which may take various mathematical forms, depending on the physical mechanism assumed in the mathematical derivation [36]. Different reaction models that are commonly used for the degradation of different types of plastic materials are listed in Table 4. From reaction models, models 1-3 are sigmoid models in which nucleation and growth are rate determining step; models 4-5 are geometric models in which the geometric nature of the growth of the reaction interface is important; models 6-9 are based on diffusion mechanism in which the diffusion is the rate controlling step; while models 10-12 are based on the order of the reaction [37].

These models can be adopted to find kinetic parameters and thereby understand the mechanism on which kinetics are dependent.

2-1. Coats-Redfern Method

For constant heating rate β ($\beta = dT/dt$), Eq. (4) can be expressed by the following equation:

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(x) \quad (5)$$

For the non-isothermal condition with a heating rate β , Eq. (5) can be rewritten as:

$$\frac{dx}{f(x)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

Integrating Eq. (6), the following expression can be obtained:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

Table 4. Commonly used reaction models for solid state thermal decomposition

No.	Model	$f(x)$	$g(x)$
Sigmoid rate equations			
1	Avrami-Erofe'ev	$2(1-x)[- \ln(1-x)]^{1/2}$	$[- \ln(1-x)]^{1/2}$
2	Avrami-Erofe'ev	$3(1-x)[- \ln(1-x)]^{2/3}$	$[- \ln(1-x)]^{1/3}$
3	Avrami-Erofe'ev	$4(1-x)[- \ln(1-x)]^{3/4}$	$[- \ln(1-x)]^{1/4}$
Geometric model			
4	Contracting area	$2(1-x)^{1/2}$	$1-(1-x)^{1/2}$
5	Contracting volume	$3(1-x)^{2/3}$	$1-(1-x)^{2/3}$
Diffusion mechanism			
6	One-dimensional	$1/2x$	x^2
7	Two-dimensional	$[- \ln(1-x)]^{-1}$	$(1-x)[\ln(1-x)] + x$
8	Three-dimensional	$3/2(1-x)^{2/3}[1-(1-x)^{1/3}]^{-1}$	$[1-(1-x)^{1/3}]^2$
9	Ginstiling-Brounshtein	$3/2[(1-x)^{-1/3} - 1]^{-1}$	$1 - [2x/3(1-x)^{2/3}]$
Order of reaction			
10	First order	$1-x$	$-\ln(1-x)$
11	Second order	$(1-x)^2$	$x/(1-x)$
12	Third order	$(1-x)^3$	$[1/(1-x)]^2$

Where, $g(x)$ is the integral form of the reaction model.

Plot of $\ln(g(x))/T^2$ will give a straight line of slope $-E/R$ and an intercept of $\ln[AR/\beta E]$ for proper form of $g(x)$. The criterion used for acceptable values of E and A is that the function of $f(x)$ should yield the best linear correlation coefficient.

2-2. Ozawa Method

The final form represented in Eq. (8) [38] is used to determine the activation energy for given values of conversion. The activation energy for different conversion values can be calculated from $\ln \beta$ versus $1/T_p$ plot.

$$\ln(\beta) = \ln \frac{AE}{Rg(x)} - 5.331 - 1.052 \frac{E}{RT_p} \quad (8)$$

Where T_p refers to the temperature corresponding to the maximum weight loss peaks for particular zone, and $g(x)$ in Eq. (8) is an integral function of the kinetics mechanism.

To solve these equations a program written in LINUX (using OCTAVE programming) was developed by using a numerical integration method. Using the data from the pyrolysis thermo-grams (Figs. 1-3) especially for active zone, the kinetic parameters under different heating rates were computed and listed in Tables 5 and 6. Best fit model was selected based on regression analysis for the materials under study. Best fit model obtained was model 7 for all materials, which is based on two -dimensional diffusion mechanism. By

Coats-Redfern method activation energies obtained were 107-322 kJ/mol, 85-168 kJ/mol and 209-243 kJ/mol for rejected PP, plastic film and plastic pellets, respectively.

It can be observed, the plastic waste presents different behavior: the activation energy varies with heating rate. On one hand, rejected polypropylene presents a decreasing trend of activation energy with increase in heating rate, whereas for plastic film and plastic pellets the activation energy is almost in the same range with increasing heating rate. Similar trend of variation of activation energy with heating rate, and also with the degree of conversion, has been observed and reported [39-41]. The reason for this behavior is a consequence of heat transfer limitation within the sample, which acquires major importance when the heating rate increases. In many cases, the values of activation energy obtained by non-isothermal methods are similar [29,42-44]. Kim et al. [34], in pyrolysis of PP by thermogravimetry, obtained an energy of 223 kJ/mol and pre-exponential factor of $1.5E+12 \text{ s}^{-1}$. Aboulkas et al. [45] and Ding et al. [46], in non-isothermal pyrolysis of mixed plastic, obtained an average activation energy of 222 kJ/mol. Results obtained by Ozawa method for the present study indicated that activation energies were 115.81 kJ/mol, 157.29 kJ/mol and 282.21 kJ/mol for rejected PP, plastic film and plastic pellets, respectively.

2-3. Kissinger Method

The final form given in Eq. (9) is used to determine kinetic param-

Table 5. Kinetic parameters for different material thermal decomposition Coates-Redfern method

Material	Temperature range (°C)	Heating rate °C/min	Activation energy E (kJ/mol)	Pre-exponential factor A, min ⁻¹	Correlation coefficient, R ²
Rejected polypropylene	346-466	5	163.595	1.19E+11	0.980
	413-483	10	291.130	3.03E+20	0.990
	421-496	20	322.620	4.74E+22	0.992
	423-500	30	280.089	3.90E+19	0.980
	350-490	50	107.330	3.49E+07	0.960
Plastic film	317-497	10	85.609	7.41E+05	0.986
	342-497	20	146.740	1.658E+10	0.999
	347-527	30	129.680	6.78E+08	0.991
	342-507	40	168.040	8.26E+11	0.988
	357-527	50	142.410	6.017E+09	0.989
Plastic pellets	400-500	5	243.970	4.76E+16	0.962
	425-500	10	209.000	7.28E+13	0.990
	440-515	25	222.404	1.54E+15	0.972
	450-530	50	228.840	3.69E+15	0.951

Table 6. Kinetic parameters for different material thermal decomposition by both Ozawa method and Kissinger method

Material	Activation energy E (kJ/mol)	Pre-exponential factor A, min ⁻¹	Correlation coefficient, R ²
By Ozawa method			
Rejected polypropylene	115.81	1.02E+10	0.984
Plastic film	157.29	1.33E+11	0.992
Plastic pellets	282.21	3.20E+17	0.998
By Kissinger method			
Rejected polypropylene	108.08	6.89E+03	0.98
Plastic film	98.68	2.12E+02	0.99
Plastic pellets	132.85	8.06E+05	0.99

eters, activation energy E and pre-exponential factor A from the linear plot of $\ln(\beta T_p^2)$ versus $1/T_p$ known as the Kissinger method [47], a model free kinetic analysis (Refer Eq. (9) which shows that it is independent of $g(x)$).

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left(\frac{AR}{E}\right) \quad (9)$$

Where, T_p refers to the temperature corresponding to the maximum weight loss peaks for particular zone.

Results obtained by Kissinger method, i.e., values of activation energies were found to be 108.08 kJ/mol, 98.68 kJ/mol and 132.85 kJ/mol for rejected PP, plastic film and plastic pellets, respectively, which are summarized in Table 6. The kinetic parameters obtained from Coats-Redfern, Ozawa and Kissinger methods show variations in the calculated kinetic parameters depending on the mathematical approach used for the kinetic analysis. These observations clearly indicate the problems in selecting and utilizing the different analytical methods to describe the thermal degradation of various materials. The Coats-Redfern method was applied and the best-fit values for each heating rate were obtained for the two-dimensional diffusion mechanism model. However, this approach gave activation energies that varied with respect to heating rate. The Ozawa method was applied and the best-fit values were obtained for the two-dimensional diffusion mechanism model. This method not only gives the activation energies upon conversion of all materials at anytime, but also it uses multiple heating rate experiments. However, the Ozawa [38] method is only applicable to the calculation of the activation energy. The Kissinger method uses multiple heating rate experiments; however, it uses only the point of maximum degradation rate as well as the assumption of a first-order reaction for thermal degradation of polymer [47].

Comparison between Coats-Redfern and Ozawa methods suggest that although the magnitude of activation energy varies but the best fit model obtained was the same, indicating the thermal degradation of plastic waste follows two-dimensional diffusion mechanism. Comparison of results obtained by Ozawa and Kissinger show the activation energy values that are nearly same. However, the best fit Ozawa method obtained is based on a three-dimensional diffusion mechanism, while Kissinger model is free and based on first-order reaction mechanism. Comparing the present study with other research groups like Kim et al. [33], Stuetz et al. [42], and Westerhout et al. [44] it was found that the activation energy for PP varies in between 220-244 kJ/mol, whereas Aboulkas et al. [20] and Wu et al. [43] found a little lower side for activation energy coming around 207 and 184 kJ/mol, respectively. The PP and the mixed plastic waste which are being used in the present study reflect the activation energy around 290 kJ/mol and 147-222, respectively. The finding for mixed plastic waste is in good agreement with Encinar and his group findings centered at 187-290 kJ/mol [29].

CONCLUSION

Thermal decomposition of rejected polypropylene, plastic film and plastic pellet was studied in inert nitrogen atmosphere. From the TGA and DTG results it was found that decomposition of different materials proceeds through three steps of mass loss. The first step, between 100 °C to 300 °C, corresponds to evaporation of mois-

ture and light volatiles. The major mass loss steps occurred between 300 °C to 500 °C. The next step occurred around 500 °C to 730 °C. The kinetic parameters of different plastic waste decomposition such as the activation energy and the pre-exponential factor were obtained by Coats-Redfern, Ozawa and Kissinger methods. The values of activation energy were 107-322 KJ/mol, 85-331 KJ/mol and 209-375 KJ/mol for rejected polypropylene, plastic film and plastic, respectively. Ozawa and Kissinger methods were also used to find the kinetic parameters and activation energy and found to be 108-115 KJ/mol, 98-106 KJ/mol and 132-140 KJ/mol and for rejected polypropylene, plastic film and plastic pellet, respectively. Variation in the activation energy was found with respect to the type of methods employed.

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