Pyrolysis Kinetics of Waste High-density Polyethylene using Thermogravimetric Analysis

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Abstract: Thermal behavior of plastic materials can be improved by knowing thermal degradation kinetics for the optimal design and operation of pyrolysis process. In the present study, thermogravimetric analysis has been used for the non-isothermal kinetic study of waste high-density polyethylene pyrolysis under nitrogen atmosphere at different heating rates 10, 20 and 40 °C/min. The kinetic parameters, activation energy and pre-exponential factor of waste HDPE pyrolysis were determined by the integral method. A first order degradation reaction was assumed, the activation energy values of waste HDPE have been calculated as 207.43, 268.22 and 473.05 kJ/mol at 10, 20 and 40 °C/min heating rates respectively. It was observed that when the heating rate increases, the activation energy and degradation temperature of the waste HDPE also increases.
Keywords: Thermogravimetric analysis, reaction kinetics, activation energy, pre-exponential factor, waste HDPE.

Introduction

Plastic materials have become very useful commodities in many aspects of human life due to their diversity, relatively low cost, easy processing and light properties. Therefore, the amount of waste plastics is increasing continuously and this situation causes serious environmental issues. Waste plastics are not suitable either for composting or landfilling, because they are essentially nonbiodegradable. The recycling of waste plastics has attracted much interest as an alternative method for their disposal and management over the last few decades. Waste plastic recycling is mainly divided into two routes: mechanical reprocessing of waste plastics, and thermal or catalytic degradation of waste plastics into gas and liquid products, which can subsequently be utilized as fuels and valuable chemicals. Pyrolysis is the most attractive technique of chemical feed stock recycling. Valuable products can be produced from waste plastics by using pyrolysis technology. However, there are many serious problems to be solved in the near future. The present issues are the necessary scale-up of the industry, minimization of production cost and optimization of higher-valued products for a wide range of plastic mixtures [1]. Especially, the lack of kinetic data hampers the optimal design of pyrolysis process and the

design of commercial pyrolysis reactors. Therefore, the kinetics of thermal degradation of waste plastics must be analyzed to provide the apparent kinetic parameters that are useful for the optimal design and operation of pyrolysis process. Thermal behavior of plastics can be improved by knowing thermal degradation kinetics. Thermogravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy. Many studies on pyrolysis kinetics of plastic wastes have been carried out, and also various reaction kinetic models are available to estimate plastic degradation, including integral method [2-4].

High-density polyethylene (HDPE) is the third-largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume [5]. The demand for HDPE has increased 4.4% a year to 31.3 million MT in 2009. The increased demand and production of waste HDPE has led to the accumulation of large amount of its waste in the final waste stream due to its low useful life [6]. Some researchers studied the pyrolysis kinetics of HDPE using different conditions, different methods and different heating rates [7-10]. In the present work, the kinetics of the thermal degradation of waste HDPE was studied using the thermo-gravimetric analysis (TGA) and integral method. The values of activation energy and the pre-exponential factor for waste HDPE have been obtained in non isothermal condition assuming first order reaction kinetic. Heating rates of 10, 20, and 40 °C/min were employed in TGA experiments.

Materials and Methods

A. Raw Material

Waste high-density polyethylene (used mobil oil containers) was collected from the nearby area of National Institute of Technology Rourkela, Orissa, India campus and used in this experiment. The plastic waste was cut into small pieces (approx. 1 mm^2) and used in the pyrolysis reaction.

B. Characterization of Raw Material

The waste high-density polyethylene was analyzed in order to observe the change in the properties of the solid material as a result of pyrolysis.

I. Ultimate Analysis

Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of these compositions is subtracted from 100, it gives oxygen percentage composition.

II. Calorific Value

Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. It was determined for waste HDPE using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

C. Thermo-Gravimetric Analysis

Pyrolysis is heating of a substance in absence of air at a particular temperature. Thermo-gravimetric analysis (TGA) of waste HDPE sample was done using a DTG60 instrument made by Shimadzu Scientific Instruments, North America. Around 10-15 milligrams of waste HDPE sample was taken and heated from room temperature to a final temperature of 600 °C and a residence time of 1 minute at 600 °C was allowed. TGA was performed in nitrogen atmosphere at the heating rates of 10 °C/min, 20 °C/min and 40 °C/min under the 45ml/min gas flow rate. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of waste HDPE takes place.

D. Non-isothermal kinetic study using TGA

Thermo gravimetric analysis (TGA) is one of the most commonly used methods to study the kinetics of thermal decomposition reactions. The kinetic parameters, activation energy and pre-exponential factor of waste HDPE

pyrolysis were determined by the integral method [2]. The approach adopted by many researchers in kinetic analysis of TGA data for solid fuel pyrolysis is to assume first order reaction for devolatalization [11-13]. So the first order reaction of waste HDPE pyrolysis with respect to the amount of undecomposed material states that,

A (Solids) → B (Solid) + C (Volatile)   (1)

For 1st order reaction, we have:

$$dx/dt = k(1 - \alpha)$$ (2)

$$k = k_0 * e^{(-Ea/RT)}$$ (3)

The extent of conversion or fraction of material pyrolysed, α was defined by expression

$$\alpha = (W_0 - W_t)/(W_0 - W_\infty)$$

Where W_0 is the initial weight (mg), W_t is the weight after "t" minutes (mg), and W_∞ is the final weight after pyrolysis (mg).

Where R = Universal gas constant, 8.314J K^{-1} mol^{-1}

k_0= Pre-exponential factor (min^{-1})

E_a= Activation energy (kJ/mol)

For a constant heating rate 'A' during pyrolysis,

$$A = dT/dt$$ (4)

Rearranging and Integrating Eq. (2) results in

$$\ln[-\ln(1 - \alpha)] = \ln\left[\left(\frac{k_0 RT^2}{AEa}\right)\left(1 - \frac{2RT}{Ea}\right)\right] - Ea/RT$$ (5)

Since it may be shown that for most values of E_a and for the temperature range of the pyrolysis, the expression $\ln[RT^2 k_0/AEa(1-2RT/E_a)]$ in Eq. (5) is essentially constant, if the left side of Eq. (5) is plotted versus *1/T*, a straight line may be obtained when the process is assumed as a first order reaction. From the slope, $-E_a/R$, the activation energy E_a can be determined, and by taking the temperature at which $W_t = (W_0 + W_f)/2$ in the place of T in the intercept term of Eq. (5), the pre-exponential factor k_0 can also be determined.

Results and Discussion

A. Characterization of waste HDPE sample

The ultimate or elemental analysis of waste HDPE is shown in Table 1. The oxygen is 5.19% in the ultimate analysis of waste HDPE. The oxygen in the waste HDPE sample may not be due to the fillers but rather to other ingredients that are added to the resin in the manufacturing of HDPE. Calorific value of waste HDPE was 45.78 MJ/kg. From the comparison of waste HDPE with mixed plastic waste [14] in Table 1, it was found that the carbon and hydrogen percentage and gross calorific value (GCV) are more in waste HDPE as compared to mixed plastic waste. Mixed plastic waste contained 1.13% of chlorine which was not found in case of waste HDPE.

B. Thermo-Gravimetric analysis and DTG analysis

The thermal stability of the polymeric materials plays a crucial role in determining the limit of their working temperature and the environmental conditions for uses, which are related to their thermal decomposition temperature and decomposition rate. TGA applied in determination of the study of thermal stability/degradation

of waste HDPE in various ranges of temperature. Figure 1 shows the TGA results of waste HDPE at the heating rates of 10 °C/min, 20 °C/min and 40 °C/min in nitrogen atmosphere. The initial temperature at which the degradation started and final temperature at which the degradation completed for waste HDPE was 385 °C and 490 °C, 400 °C and 505 °C, 410 °C and 510 °C at the heating rates of 10 °C/min, 20 °C/min and 40 °C/min respectively. As the heating rates increased, the initial and final degradation temperature for waste HDPE also increased due to the fact that polymer molecules does not have enough time to exhaust the heat with increasing heating rate, leading to slower decomposition rate and higher decomposition temperature due to slow diffusion of heat [15]. Similarly, when the heating rate increases, the decomposition temperature of the plastics samples also increases for raw and waste HDPE at 5, 10, 20 and 50 K/min heating rates [8]. Differential thermogravimetry (DTG) curve for waste HDPE at 10 °C/min, 20 °C/min and 40 °C/min heating rates contains only one peak, this indicates that there is only one degradation step in Figure 2 for different heating rates. The degradation temperatures for waste HDPE at which the maximum weight losses (T_{max}) take place were about 465 °C, 485 °C and 500 °C at the heating rates of 10, 20 and 40 °C/min respectively. DTG curves at different heating rates were shifted to higher temperature due to the heat transfer enlarging with increasing heating rate. Similar effect of various heating rates on DTG curves for HDPE pyrolysis has been obtained by A. Aboulkas [16].

Table 1. Ultimate or elemental analysis of waste HDPE

Sample	C (wt %)	H (wt %)	N (wt %)	S (wt %)	O (wt %)	Cl (wt %)	GCV (MJ/kg)
Waste HDPE	80.58	13.98	0.60	0.080	5.19	-	45.78
Mixed Plastics [14]	79.9	12.6	-	-	5.10	1.13	44.40

Figure 1. TGA plot of waste HDPE at different heating rates in N_2 atmosphere
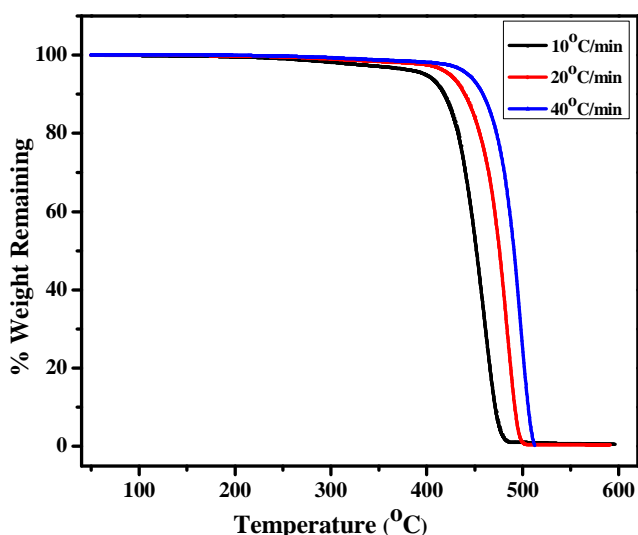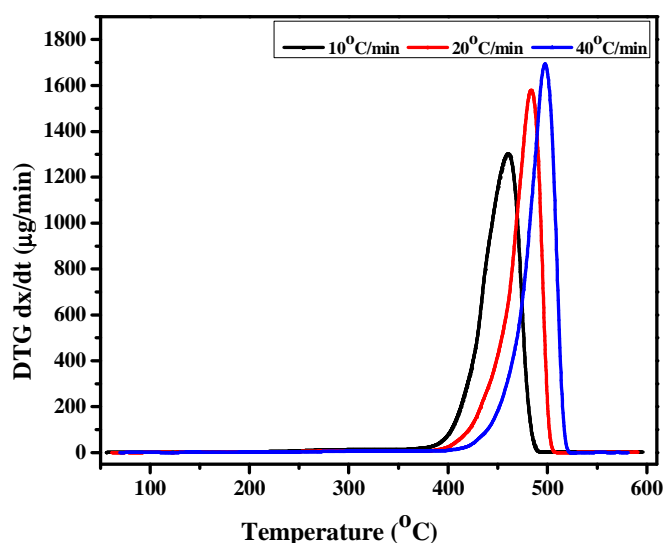
Figure 2. DTG plot of waste HDPE at different heating rates in N_2 atmosphere

C. Kinetic study using TGA under non-isothermal conditions

Pyrolysis kinetic analysis is valuable for the in-depth exploration of process mechanisms. On the basis of thermo gravimetric analysis of different kinds of polymeric materials, thermal kinetics analysis was performed to analyze the pyrolysis behavior of waste HDPE. With the apparent kinetic parameters derived, a kinetic model was proposed for the main reaction section of waste HDPE pyrolysis process. Figure 3 shows the plot of the integral method for waste HDPE under non-isothermal conditions. In this figure, as the entire range of ln(-ln(1-x)) as a function of 1/T , data could be represented by a single straight line (R^2=0.99) for all three heating rates. Reasonable fits of data to straight lines in this figure indicate that the assumption of first-order kinetics for thermal decomposition of waste HDPE is acceptable. The activation energy values of waste HDPE have been calculated as 207.43, 268.22 and 473.05 kJ/mol at 10, 20 and 40 °C/min heating rates (Table 2) under nitrogen atmosphere. Activation energy increased with increase in heating rate due to very low thermal conductivity of polymeric material and hence the temperature distribution in the waste HDPE sample will be significant at a high heating rate. Reported values in literature are 268 kJ/mol by Bockhorn et al. [17], 396-493 kJ/mol by Kayacan et al. [8], 146.5 kJ/mol by Khalturinskii et al. [18], 126-275kJ/mol by Sinfronio et al. [19], 243.8kJ/mol by Encinar et al. [20], 238.4 kJ/mol by Ballice et al. [21] and 233.2kJ/mol by Wu et al. [22]. The reason for the wide discrepancy in the measured values of activation energy (apart from the characteristics of the sample) could be attributed to a defective heat transfer and a complex mechanism of decomposition due to diverse operating conditions in the literature[9].

Table 2. Activation energy and pre-exponential factor determined by integral method for waste HDPE pyrolysis

Heating rate A, °C/min	Activation Energy (E_a) kJ/mol	Pre-exponential factor (k_0) min^{-1}
10	207.43	1.37×10^{11}
20	268.22	5.21×10^{13}
40	473.05	1.68×10^{30}

Figure 3. Kinetic study plot at different heating rates in N$_2$ atmosphere
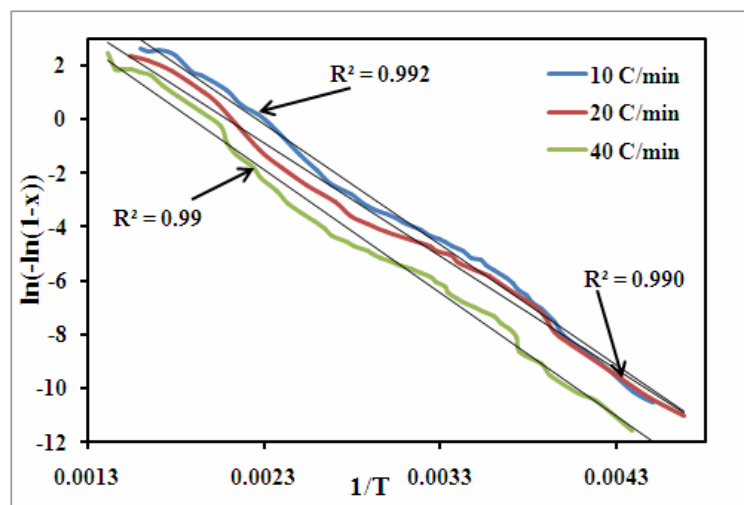
Conclusion

The kinetic parameters of waste HDPE pyrolysis under non isothermal conditions using TGA were determined. Determining the kinetic parameters also provides information to design more effective conversion systems and optimum pyrolysis regimes. The TGA experiment showed that the heating rate has an important role on the degradation reaction. When the heating rate increases, the activation energy and degradation temperature of the waste HDPE also increases. The degradation temperatures for waste HDPE at which the maximum weight losses (T_{max}) take place were about 465 °C, 485 °C and 500 °C at the heating rates of 10, 20 and 40 °C/min respectively. The activation energy values of waste HDPE have been calculated as 207.43, 268.22 and 473.05 kJ/mol at 10, 20 and 40 °C/min heating rates respectively. Reasonable fits of data to straight lines in kinetic study plot indicate that the assumption of first-order kinetics for thermal degradation of waste HDPE is acceptable.

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