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Thermal degradation kinetics of poly(ethylene terephthalate) from waste soft drinks bottles

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Abstract

To overcome certain demerits of recycling and incineration, researchers across the world have focused on development of value added products from waste plastics such as liquid and gaseous fuel, activated carbon and monomer recovery. Thermogravimetic analysis (TGA) is one of the widely used techniques to study the pyrolysis reaction kinetics. A kinetic model is necessary to predict the reactor behaviour as well as product range distribution. This paper investigates the thermal pyrolysis kinetics of poly(ethylene terephthalate) (PET) from different sources of soft drink bottles such as M/s Coca Cola and M/s Pepsi. Thermal degradation is carried out in dynamic condition at three different heating rates of 10, 15 and 25 K min^{-1} under nitrogen atmosphere. A simple *n*th order kinetic model is proposed to study the thermal degradation of waste plastics. Kinetic parameters are obtained from three dynamic TGA curves at three different heating rates using ASTM E698 and from one TGA curve at the heating rate of 10 K min^{-1} using *n*th order model techniques. PET pyrolysis exhibits 70–80% weight loss in the temperature range of 653–788 K. The *n*th order model technique better predicts the experimental data than ASTM E698 technique. Values of activation energy obtained by *n*th order model technique are 322.3 and 338.98 kJ/mole for Coca Cola and Pepsi samples, respectively.

Keywords: Pyrolysis; TGA; PET; Thermal degradation; Heating rate

1. Introduction

Packaging presents a major growth area where there has been an increasing demand for plastics and 52% of the plastics produced in India are utilized for packaging. Among the commodity plastics, polyethylene (PE) and polyethylene terephthalate (PET) are predominantly used in packaging. Low-density polyethylene (LDPE) is used in the manufacture of carry bags and PET is used in packaging beverages like soft drink and mineral water. PET in particular presents a major growth area in the years to come. Indian PET consumption has grown at an annual rate of 30% and the current PET consumption is estimated to be around 45,000 tonnes per annum [1]. India will probably see a rise in waste generation from less than 40,000 metric tonnes per year to over 125,000 metric tonnes by the year 2030 [2].

The most common ways to treatment of the solid waste are land filling, incineration and materials recycling. A life cycle assessment (LCA) tool is used to compare different alternative waste treatment strategies. The simulation model Orware (organic waste research) used for the material and energy flows in waste management based on life cycle assessment (LCA) was used in the quantification of emissions, energy use and financial costs. The results suggest the environmental preference of recycling over incineration over land filling [3]. The quality of recycled product remains questionable if poor state-of-the-art technologies are employed for recycling [1].

To overcome certain demerits of recycling and incineration, researchers across the world have focused on development of value added products from waste plastics such as activated carbon, liquid fuel and gaseous product and monomer recovery [4–8]. Again, extensive research is going on to look for alternative energy sources. The application of novel alternative process, pyrolysis or catalytic degradation as a means of reusing scrap tyres and waste plastic, have recently been the subject of renewed interest. In this process

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waste plastic and tyres break down to give oil, high calorific value gaseous product and a residual solid carbon. There are some valuable aromatic (limonene, indene, styrene, xylene and naphthalene) chemicals found in the oil that can be used in the petrochemical industry [4–7]. The residual carbon is being upgraded to produce a high-grade activated carbon [8]. These processes reduce the NO_x emission as well.

Thermogravimetic analysis (TGA) is widely used technique to study the pyrolysis reaction kinetics. Kinetic study of pyrolysis is essential to understand the degradation mechanism; to know the rate of reaction and reaction parameters; and to predict the products distribution. This information is very important for proper selection of the reactor; optimization of the reactor design and operation. Several studies on thermal and catalytic degradation of plastics such as polypropylene (PP), polyethylene (PE), low-density ployethelene (LDPE) and polystyrene (PS) are reported in literature [9–24]. Catalysts used are MCM-41, ZSM-5, Fe-K/Al_2O_3, DeLaZSM-5, USY and Ni-REY. Degradation of PET in supercritical methanol was investigated to develop a chemical recycling process for waste plastic, where PET decomposed to its monomer dimethyl terephthalate and ethylene glycol [25]. TGA is utilized to investigate pyrolysis of individual waste component including PET in order to calculate the composition of an unknown waste mixture [26]. The dynamic thermogravimetric kinetics of poly(trimethylene terephthalate) samples with various molecular weights and PET under argon, air and nitrogen are analyzed by Freeman-Carroll, Friedman and Chang method and kinetics parameters are reported [27]. Martin-Gullon et al. [28] investigated the kinetics of thermal degradation of PET under strict pyrolysis conditions and with different proportions of oxygen by TGA, which follows two independent reactions. Vyazovkin and Wight [9] reported model-free and model fitting kinetics of decomposition.

Acknowledging the increasing usage of PET day-by-day and understanding the underlying demerits associated with the commonly used incineration and recycling techniques, it has become necessary to study the usefulness of PET to produce value added products. Though a few literature references, discussed elsewhere, have dealt with the kinetic study of PET using either pure PET or PET from a mixture of solid waste, further study on the same is the need of the hour. In this present work we have studied the pyrolysis kinetics of PET. Thermal degradation kinetics of carbonated soft drinks PET bottles are studied using TGA. The results of kinetics investigation are presented in terms of an *n*th order kinetic model with values of kinetic parameters such as activation energy, frequency factor and order of the reaction.

2. Experiment

2.1. Equipment and procedure

The thermal degradation was carried out with individual waste PET soft drinks bottles (M/s Pepsi and Coca Cola). Experiments were carried out in a TGA instrument of METTLER TOLEDO with model No. TGA/SDTA 85 1^e under nitrogen atmosphere for a range of temperature 303–873 K. Nitrogen flow rate was maintained at 40–50 ml min^{-1} according to the specification of the equipment. PET bottles were shredded into very small pieces (mess size: $-40+60$) and directly fed to the TGA instrument. The total mass of sample taken was 7–10 mg for each run of the experiments. Alumina crucible (70 μm) is used as sample holder. The experiments were repeated for three times at heating rate of 10 K min^{-1} to confirm the repeatability of the experiments and authenticity of the generated data. Experiments were conducted in dynamic condition at different heating rates of 10, 15 and 25 K min^{-1}. Total mass of various PET samples with the corresponding heating rates are given in Table 1. Variation of rate of reaction (dα/dT) with temperature during pyrolysis of Coca Cola and Pepsi samples at different heating rates are reported, respectively, through Figs. 1 and 2.

Table 1
Experimental condition for TGA studies

Sample	Total mass (mg)	Heating rate (K min^{-1})
Coca Cola	8.25465	10
	9.45203	15
	9.60506	25
Pepsi	8.732	10
	8.0991	15
	7.5857	25

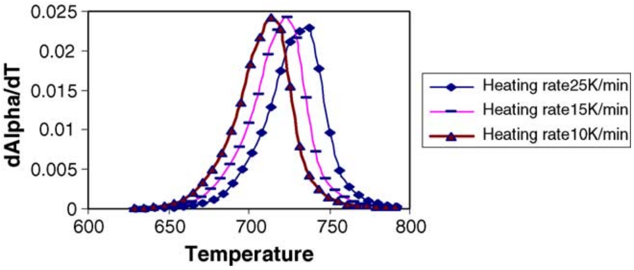

Fig. 1. Variation of rate of reaction with temperature during pyrolysis of Coca Cola sample.

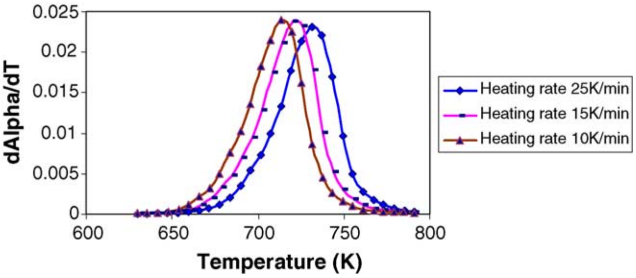

Fig. 2. Variation of rate of reaction with temperature during pyrolysis of Pepsi sample.

2.2. Kinetics model and methods

The *n*th order kinetic model equation combined with the Arrhenius approach of the temperature function of reaction rate constant is:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = k_0 \exp(-E/RT)(1-\alpha)^n \tag{1}$$

where, β is heating rate (K min^{-1}), $\frac{\mathrm{d}\alpha}{\mathrm{d}T}$, the rate of reaction (K^{-1}), k_0, the pre exponential factor, E, the activation energy (kJ mol^{-1}), R, the universal gas constant (kJ mol^{-1} K^{-1}), T, the sample temperature (K), α, the conversion of reaction $(W_0 - W)/(W_0 - W_\propto)$, W_0, the initial weight of the sample (mg), W, the sample weight at any temperature T (mg) and $W_\propto$ is final sample weight (mg).

Various techniques such as Freeman-Carroll, Friedman, Chang, *n*th order model and ASTM E698 technique can be applied to obtain kinetics parameters using the experimental data generated from the TGA experiments. In this article, we have used *n*th order and ASTM E698 techniques discussed below.

2.2.1. nth Order model technique

In this technique, the *n*th order kinetic model Eq. (1) is linearised as follows:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln k_0 - \frac{E}{RT} + n\ln(1-\alpha) \tag{2}$$

The above equation is used to fit the experimental data by linear regression analysis and to obtain the kinetics parameters directly.

2.2.2. ASTM E698 technique

ASTM E698 technique [9] occupies an intermediate position between the model fitting and model-free methods. It uses a model-free estimate for the activation energy, which is evaluated from Kissinger's plot of $\ln\left(\frac{\beta}{T_\mathrm{m}^2}\right)$ against $\frac{1}{T_\mathrm{m}}$ [9], where T_m, is the temperature corresponding to the maximum of $\mathrm{d}\alpha/\mathrm{d}T$. However, the pre-exponential factor is evaluated on assumption of a first-order reaction as follows [9]:

$$k = \frac{\beta E}{RT_\mathrm{m}^2}\exp\left(\frac{E}{RT}\right) \tag{3}$$

By definition of ASTM E698 method, the reaction order is set to unity while simulating to predict the experimental data obtained using three different heating rates [29].

3. Results and discussion

3.1. Thermal degradation

Martin-Gullon et al. [28] pointed out that the thermal decomposition of PET is divided into two major parts. The first part is finished at 750 K and the second part is finished at 1050 K. They observed no significant changes in the first part while the decomposition was conducted using N_2 and with air separately [28]. This in turn indicates no effect of environment on decomposition in the first part. Therefore, the present investigation considered thermal degradation of PET bottles in the first part only as it is the main pyrolysis step. The experiments were conducted with different heating rates under nitrogen environment. This pyrolysis step yielded 70–80% weight loss, starts at temperature around T_d and finishes at temperature around $T_{\mathrm{W}\propto}$. The temperatures at which initial weight of sample taken ($T_{\mathrm{W}0}$), degradation starts (T_d), maximum weight loss rate occurs (T_m) and the end of pyrolysis step ($T_{\mathrm{W}\propto}$) takes place are reported in Table 2 for each cases of experiments. The initial weight of PET sample is taken at temperature, $T_{\mathrm{W}0}$ to eliminate moisture and volatile compound content of PET. A quick thermal degradation of PET bottles is observed from the graphs in the range of T_d–$T_{\mathrm{W}\propto}$ and the highest decomposition rate is at around T_m, reported in Table 2. After this quick fall, the solid continues decomposing smoothly and slowly to the end of experiment. The experiments were repeated for three times at heating rate of 10 K min^{-1} to test the repeatability of the experiments, which showed the almost similar behaviours during pyrolysis. Variation of the reaction rate with temperature obtained from experiments for different heating rates are presented through Figs. 1 and 2 for Coca Cola and Pepsi samples, respectively. Single peak observed in both the figures imply a single step reaction taking place during pyrolysis of PET samples used for experiment.

3.2. Kinetics analysis

The authors used a one step *n*th order kinetic model to calculate kinetics parameters from one TGA curve for each sample using two different techniques as discussed earlier. As mentioned earlier in Section 2.2.2, in ASTM E698 method, the decomposition order is assumed to be one (by definition) [29]. It may be observed from Table 2 that the calculated values of kinetics parameters by *n*th order model technique gives higher values of E and ln(k) than ASTM E698 techniques

Table 2
Kinetics parameters derived from experiments

Sample	Method	E (kJ)	n	$\ln k_0$	$T_{\mathrm{w}0}/T_\mathrm{d}/T_\mathrm{m}/T_{\mathrm{w}\propto}$ (K)
Coca Cola	ASTM E698	162.15	1	26.37	625.51/655.43/715.05/786.64
	*n*th Order model	322.3	1.72	54.76	
Pepsi	ASTM E698	210.64	1	34.81	626.48/656.64/710.06/784.61
	*n*th Order model	338.98	1.82	57.73	

used. This can be attributed to fact that different calculating techniques, respectively, appropriate for the thermal degradation behaviours in different temperature ranges. As a matter of fact, kinetic parameters change more or less with temperature, even though we assume that they don't vary with temperature in every mathematical techniques [27]. In the present case the *n*th order model technique uses a wide temperature range starting from T_d to $T_{W\propto}$ and ASTM E698 method uses only T_m, which is much lower than $T_{W\propto}$. In case of *n*th order model technique, values of E, n and $\ln(k_0)$ are 322.3 kJ/mole, 1.72 and 54.76 respectively for Coca Cola and 338.98 kJ/mole, 1.82 and 57.73 respectively for Pepsi. Similarly, in case of ASTM E698 method, values of E, n and $\ln(k_0)$ are 162.15 kJ/mole, 1.0 and 26.37 respectively for Coca Cola and 210.64 kJ/mole, 1.0 and 34.81 respectively for Pepsi. The difference in kinetic parameters between Coca Cola and Pepsi samples may be due to difference in composition, which can be confirmed after ultimate analysis and pyrolysis product composition analysis. The *n*th order model technique while compared with ASTM E698 method is expected to be more suitable one to describe the pyrolysis behaviours of the samples studied since it doesn't assume on values of *n* like the later method. This expectation is supported by the study of numerical simulation of the model described in the following subsection.

3.3. Numerical simulation

The *n*th order kinetic model equation with initial condition $\alpha = 0$ at $T = 630$ K is solved numerically by Runge-Kutta 4th order method using the kinetics parameters obtained by ASTM E698 and *n*th order model techniques. It is observed that though the ASTM E698 techniques predicted fairly the experiment, *n*th order model better predicts the experimental data, which is evident from sample plots Figs. 3 and 4. It can be further observed that the simulation result from ASTM E698 method (except at point near T_m, where it intersects the experimental curve) poorly predicts all other points below and above T_m. This is further supported by the statistical analysis results reported in the form of standard deviations along with the figures captions. The standard deviation values are 0.0134 and 0.0.0643 using *n*th order model and ASTM E698 techniques, respectively, for Coca Cola sample and 0.031 and 0.021 using *n*th order model and ASTM E698 techniques, respectively, for Pepsi sample.

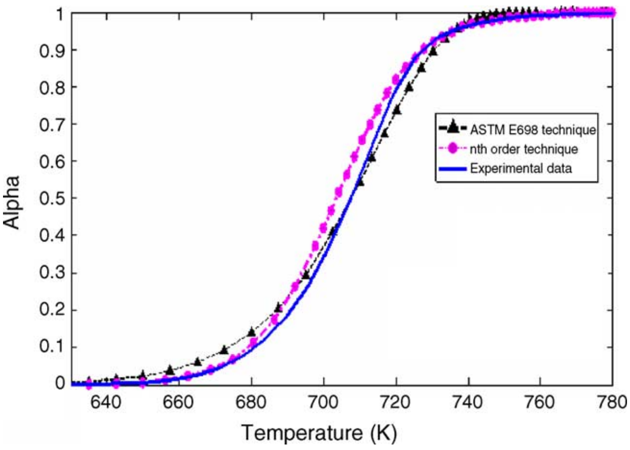

Fig. 3. Comparison between simulation and experimental data for Pepsi sample (standard deviations are 0.031 and 0.021 using *n*th order model and ASTM E698 techniques, respectively).

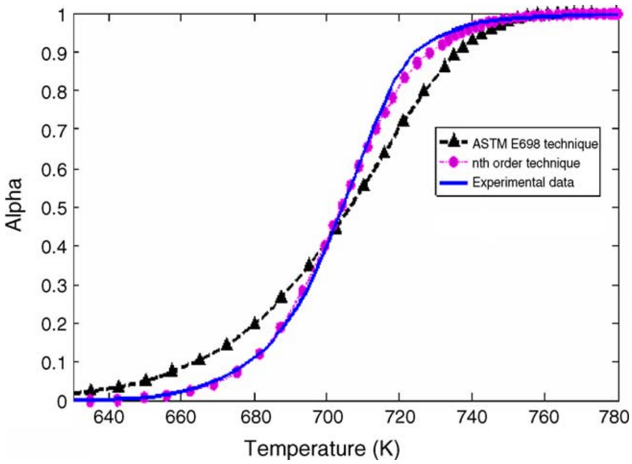

Fig. 4. Comparison between simulation and experimental data for Coca Cola sample (standard deviations are 0.0134 and 0.0.0643 using *n*th order model and ASTM E698 techniques, respectively).

4. Conclusion

Pyrolysis of waste PET bottles is investigated under dynamic condition. The kinetic parameters are determined for thermal degradation of waste PET bottles calculated using ASTM E698 and *n*th order model techniques. Temperature, sample weight and its loss rate, conversion, time and heating rates are the important variables in pyrolysis kinetics study. Based on these variables, a model is proposed to predict the conversion or weight or weight loss profiles of the samples. The single peak observed in the rate of reaction versus temperature curve indicated single step reaction during thermal decomposition of PET. The pyrolysis of PET from waste soft drink bottles exhibits weight loss (70–80%) occurring at temperature range of about 653–788 K. The *n*th order model technique is a suitable model that predicts the experimental data very well. It is well understood that many complex reactions are involved in the pyrolysis of waste PET. The authors envisage the establishment of kinetics mechanism in future correspondence.

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