Special issue on *Sustainable Environmental Processes and Technologies*

PYROLYSIS KINETICS OF KEYBOARD PLASTIC WASTE USING THERMOGRAVIMETRIC ANALYSER TO ASSESS ITS ENERGY POTENTIAL

Achyut Kumar PANDA[1], Satyanarayan PATNAIK[1], Sachin KUMAR[2*]

[1]*Department of Chemistry, Veer Surendra Sai University of Technology, 768018 Burla, Odisha, India*
[2]*Department of Energy Engineering and Centre of Excellence in Green & Efficient Energy Technology (CoE-GEET), Central University of Jharkhand, 835205 Ranchi, Jharkhand, India*

Highlights

▶ Thermal degradation behaviour of the keyboard plastic waste at different heating rates.
▶ Determination of kinetic parameters from keyboard plastic waste pyrolysis using different model free methods.
▶ An alternative approach to waste management by assessing the energy potential of keyboard plastic waste.

Abstract. In this paper, the kinetic parameters of discarded computer keyboard plastic waste are estimated using thermogravimetric analysis (TGA) with four different non-isothermal kinetic models at a wide range of heating rates 5, 10, 15, 20, 40, 60 and 100 °C/min. The gross calorific value of waste computer keyboard plastic is 38.96 MJ/Kg. FT-IR analysis confirms the presence of alcohol, phenol, ether, ester, carboxylic acid, aromatic, and alkene compounds in keyboard plastic waste. The average values of activation energy are calculated as 158.1668, 198.883, 193.612, and 197.765 kJmol^{-1} from Kissinger, Friedman, FWO, and Coats-Redfern methods, respectively. The kinetic data obtained in this work would be useful for accurate prediction of reaction behaviour and in the design of efficient commercial process for the conversion of such plastic wastes to energy.

Keywords: pyrolysis, keyboard plastic waste, thermogravimetric analysis, kinetic study, activation energy.

Introduction

Advances in information technology (IT) have improved all aspects of lifestyle by providing high end electronic gadgets with new functionalities. There are no sectors, where the applications of such technology can be excluded. Due to its virtual nature, the IT sector appears environmental friendly but in actual practice, it contributes in different types of pollutions. One of the major problems is generation of e-wastes that describes discarded electrical or electronic devices otherwise called waste from electrical and electronic equipment (WEEE). The Global annual generation of E-waste is 40 to 50 million tonnes (TCO Certified, 2015). Due to their negative effects, they pose grave concerns to public health and environment alike. A study reported during 2016 by the Associated Chambers of Commerce and Industry of India (ASSOCHAM) that, India ranked one of the top five countries in e-waste generation with an estimated 1.85 million tonnes generated

annually accounts for about 4 per cent of global figure. The United States ranked first in e-waste generation with 11.7 million tonnes of e-waste annually. It is followed by China ranked second with 6.1 million tonnes, Japan ranked third (2.2 million tonnes), and Germany ranked fourth (2 million tonnes). They also reported that, computer equipment accounts for almost 70% of e-waste material, followed by telecommunication equipment (12%), electrical equipment (8%) and medical equipment (7%). Other equipment, including household e-scrap account for the remaining 4% (Shenoy, 2018; Pandit, 2016; Wikipedia, 2017). The United States Environmental Protection Agency (USEPA) reported that about 0.423 million tons of waste computers, 0.067 million tons of waste keyboards and mice were generated in 2010 in the USA, out of which only 10 wt.% of keyboards and mice were recycled. The recycling process of waste computers recovers valuable materials that can be used to make new products. This process also inhibits the generation of hazardous waste,

including heavy metals and carcinogens that may contaminate the atmosphere, soil or waterways. As a result, recycling raw materials from waste desktop computers is the most effective solution to the growing e-waste problem. Further, recycling reduces the amount of greenhouse gas emissions caused by the manufacturing of new products (Al Razi, 2016).

The E- wastes mostly contain two types of compounds viz. metallic (49%) and plastic (33%) including hazardous constituents such as heavy metals (Cr, Cd, Hg, Pb and etc.), flame retardant (Chlorine, bromine, nitrogen or phosphorus), Poly Chloro Biphenyl and Polyvinyl Chloride. Thus, recycling of WEEE is significant not only from a waste treatment aspect but also from recovery of valuable ingredients. Effective separation of metals is the key for developing an effective recycling system (Ramesh et al., 2014).

Plastic materials constitute a most important share in the electrical and electronics accessories due to their distinct properties. Therefore, the amount of waste plastics from such sector is increasing continuously and this situation is creating serious environmental issues. As plastic wastes cannot be subjected to composting or land filling due to their non-biodegradable properties, the recycling of waste plastics by pyrolysis has attracted much interest as an alternative method for their disposal and management over the last few years.

Pyrolysis is considered as most useful method of plastic waste management, due to its lower emissions, reasonable cost and simple operation. Thermal or catalytic pyrolysis of waste plastics yields gas and liquid products that can subsequently be utilized as fuels and valuable chemicals. However, there are many difficulties to be resolved in these processes imminent. The 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 (Panda et al., 2010). The optimal design of the pyrolysis process and thus the reactor design require kinetics and thermodynamics data of the thermal degradation, and must be determined for better design and operation of the process. Thermogravimetric analysis technique is an excellent way to study the kinetics of thermal degradation (Kumar & Singh, 2014). It provides information on pre-exponential factor and activation energy (Coats & Redfern, 1964; Petrović & Zavargo, 1986). These kinetic data would help in the satisfactory design of the pyrolysis equipment. Literatures portray few works on the calculation of kinetic parameters using different waste plastics and are summarized as follows:

Thermal decomposition of natural polystyrene, recycled plastics, low density polyethylene, acrylonitrile butadiene styrene, polyenterophthalate of ethylene, and polypropylene was carried out at a temperature range of 415–490 °C and heating rate of 5–30 K·min^{-1} to calculate the activation energy for every plastic material. The values of activation energy are as: natural polystyrene: 136 and 168 to 286 kJ/mol. Recycled plastic: 250, and 150 to 290 kJ/mol, Low density polyethylene: 285, and 220 to 259 kJ/mol, Acrylonitrile butadiene styrene: 118, and 104 to 251 kJ/mol. Polyenterophthalate of ethylene: 161, and 117 to 255 kJ/mol, Polypropylene: 169, and 153 to 265 kJ/mol (Day et al., 1995).

The pyrolysis behavior of plastic waste-TV plastic shell-was investigated, based on thermogravimetric analysis and using a combination of model-fitting and model-free methods. The activation energy and linear correlation coefficient were determined at different conversion rates using four model-free methods. The values of activation energy (E_a) gradually decreased from 269.75 kJ/mol to 184.18 kJ/mol as the degree of conversion (α) increased from 0.1 to 0.8. Beyond this range, the E_α slightly increased to 211.31 kJ/mol (Yao et al., 2020).

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 were performed. Thermal degradation was carried out in dynamic condition at three different heating rates of 10, 15 and 25 K min^{-1} under nitrogen atmosphere. The activation energy for Coca Cola and Pepsi samples obtained by nth order model technique are 322.3 and 338.98 kJ/mol, respectively (Saha & Ghoshal, 2005).

The kinetics of pyrolysis of electronic packaging material are investigated under various heating rates (5, 10, 15, 20 °C/min) in an inert atmosphere using a TGA technique. The activation energy, Arrhenius constant and order of the reaction was calculated to be 251±10 kJ/mol, 7.78×10^{15} min^{-1} and unity, respectively (Liou, 2003).

Kinetics of thermal degradation of three different electronic wastes, namely keyboard, telephone wire, and printed circuit board were investigated using TGA under pyrolysis and combustion conditions at a heating rate of 10 °C/min up to 700 °C, using Arrhenius model. The activation energy for first step pyrolysis of keyboard, PCB waste and telephone line was 166.08, 149.28 and 96.76 kJ/mol, respectively. Thus the order of thermal stability of the three studied samples was found as: keyboard > printed circuit board > telephone line (Quan et al., 2013).

The kinetic study of Scrap printed circuit boards (PCBs) under various heating rates and different particle sizes was carried out by thermogravimetric analysis. The average activation energy value obtained was 72.55 kJ/mol for the conversion, X = 0.2 to 0.8. The activation energy obtained was considered relatively low and no large amount of energy was required in initiating the reaction (Ali et al., 2014).

Jing Sun et al. carried out kinetic study of the decomposition of waste printed circuit boards was under conventional and microwave-induced pyrolysis conditions. The activation energy decreased from 267 to 168 kJ/mol with increased heating rates from 20 to 50 °C/min in conventional condition in the temperature range of 300 to 600 °C. The activation energy decreased to 49 kJ/mol in the microwave-induced pyrolysis of the material using a microwave power of 700 W at a similar heating rate (Jing et al., 2012).

Although, the kinetic study of computer keyboard materials is already reported in literature (Quan et al., 2013), but the detail kinetic study at a wide range of heating rates with different kinetic models is missing in that work. Therefore, to the best of our knowledge, this is the first study to report detail kinetic study of used computer keyboard plastics waste. The present work focus on the study of kinetic parameters for the thermal degradation of computer keyboard plastics waste through thermogravimetric analysis. The values of activation energy and the pre-exponential factor for the sample are obtained in non-isothermal condition by four model free methods including Kissinger method, Friedman method, Coats-Redfern (modified) method and Flynn–Wall–Ozawa (FWO) method.

1. Experimentals

1.1. Materials

Used computer keyboard plastics waste (Figure 1), used in this work were collected from dumping yards of VS-SUT, Burla, Odisha, India. Keyboard plastic wastes were first crushed into smaller sized particles and the metallic part was removed using magnetic separator. Then these are grinded into small size of 1–3 mm and subjected to pyrolysis process.

Figure 1. Discarded keyboard plastic waste used in the determination of kinetic parameters

1.2. Methods

Proximate analysis of the above samples such as the moisture, volatile matter, fixed carbon and ash content was carried out using prescribed standard methods ASTM D 4442, ASTM D 3172, ASTM D 3177 and ASTM D 3175, respectively. Ultimate analysis of the sample was carried out using a CHNS elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition.

The FTIR spectrum of the raw material is recorded in a Bruker Alpha FTIR spectrophotometer with spectral range 500–4000 cm^{-1}, resolution 2 cm^{-1}, DLA TGA detector, Universal ZnSe ATR, gold coated mirrors, ZnSe beam splitter and window and OPUS software for analysis of the sample to know the functional group composition of the sample. The powered solid samples are analyzed directly on the Universal ZnSe ATR plate.

Pyrolysis experiments were performed using a SHIMADZU DTG60 instrument at different heating rates 5, 10, 15, 20, 40, 60 and 100 °C/min, by taking a definite weight of waste plastic sample in a silica crucible operating in a stream of N_2 atmosphere with a flow rate of 40 ml/min from 35 °C to 900 °C temperature. The parameters of thermal-decomposition, statistical parameters (R^2) and kinetic analysis were carried out using Microsoft Office Excel 2016 (version 16.0.12325.20344), R version 3.6.2 (2019-12-12), RStudio (version 1.2.5033), and Origin 2020 (Learning Edition) softwares.

1.3. Study of kinetic by model-free method

Kinetic study helps in determining the pre exponential factor and activation energy. The general representation of thermal degradation may be as follows:

A (solid) → B (liquid) +
C (gas/volatile components) + D (solid/char).
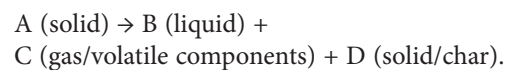
Although this reaction involves decomposition of solid reactants, the isothermal homogeneous gas or liquid phase kinetic formulations can be applied to it. Thermal degradation of plastics is a very complex process and identification of a single kinetic model that explains the complete mechanism of such reaction is difficult. However, a partial or relative kinetic description may be obtained using different established equations. So, four different model-free methods such as Kissinger method, Friedman method, Coats-Redfern (modified) method and Flynn–Wall–Ozawa (FWO) method are used for obtaining kinetic parameters of thermal decomposition. Among the above methods, Kissinger method is not an isoconversional method as the peak temperature at different heating rates and the extent of the conversion at that temperature is used to find the activation energy. However, this equation cannot identify complexities of the reaction (Vlaev et al., 2008; Turmanova et al., 2008).

The simplified form of Kissinger equation (Equation (1)) used in this work is

$$\ln\left(\frac{\beta}{T_m{}^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m}, \qquad (1)$$

where, β = heating rate, T_m = maximum decomposition temperature, A = pre exponential factor, R = gas constant, E_a = activation energy.

The plot between $\ln\left(\frac{\beta}{T_m{}^2}\right)$ and $\frac{1}{T_m}$ is a straight line with slope equal to $-\frac{E_a}{R}$. So, the activation energy can be calculated from the graph.

Friedman method is the first and the more general isoconversional method for kinetic analysis using the differential Equation (2):

$$\ln\left(\frac{dX}{dt}\right) = -\frac{E_a}{RT} + \ln\left(Af(X)^n\right). \qquad (2)$$

X = conversion $\left(= \frac{W_0 - W_t}{W_0 - W_\infty}\right)$, W_0, W_t and W_∞

indicate the initial weight, weight of the sample left after time t, and weight after pyrolysis of the plastic sample, n = order of reaction, T = temperature.

A plot of $\ln\left(\dfrac{dX}{dt}\right)$ versus $1/T$ gives the slope equal to $-E_a/R$ and an intercept of $\ln\left(Af\left(X\right)^n\right)$.

Coats and Redfern method is a common integral kinetic method used to describe the reaction process during pyrolysis. The equation obtained in the method is:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{-AR\left(1 - \dfrac{2RT}{E_a}\right)}{E_a \ln(X)}\right] - \frac{E_a}{RT}. \tag{3}$$

At different heating rates, $\ln\left(\dfrac{\beta}{T^2}\right)$ is plotted against $1/T$ giving a series of straight lines with slope E_a/R, and E_a can be calculated from the slope. The value of frequency factor may be calculated from the intercept by taking the help of E_a.

FWO method calculates the activation energy without prior knowledge of the reaction mechanism and is based on the Doyle approximation for heterogeneous chemical reactions:

$$\ln\beta = \frac{AE_a}{Rf\left(X\right)} - 5.331 - 1.052\left(\frac{E_a}{RT}\right). \tag{4}$$

Activation energy can be determined from the slope of the linear equation by plotting $\ln\beta$ against $1/T$ at progressing values of the conversion (Vlaev et al., 2008; Turmanova et al., 2008; Boonchom & Puttawong, 2010; Boonchom & Thongkam, 2010).

Table 1. Proximate and ultimate analysis of keyboard plastic waste sample alongwith available literature on the air-dried basis (adb)

Proximate Analysis (Wt %)	Present work	Quan et al. (2013)
Moisture	0.17%	0.35
Volatile Matter	97.7%	96.18
Ash content	1.01%	2.93
Fixed Carbon	1.12%	0.53
Ultimate Analysis (Wt %)		
C	82.89	83.73
H	8.686	7.68
N	00	5.82
S	00	00
O	8.424	2.77
Empirical formula	$C_{14}H_{17}O$	Not Calculated
Gross calorific value (MJ/Kg)	38.96	Not Calculated

2. Results and discussion

2.1. Proximate and ultimate analysis

Table 1 reports the proximate and ultimate analysis results of the sample. The percentage of volatile matter was found to be very high 97.7% and the percentages of moisture, ash content and fixed carbon was found very low in proximate analysis. From the ultimate analysis data, it was found that the sample has very high carbon content (82.89%) with low hydrogen (8.686%) and oxygen (8.424%) content. Nitrogen and sulphur was absent in the sample. Empirical formula of keyboard plastics waste was calculated to be $C_{14}H_{17}O$. The calculated gross calorific value based on the ultimate analysis is also found high which is 38.96 MJ/Kg. Similarly, high percentage of volatile matter (96.18%) and carbon content (83.73%) was also determined for keyboard plastics waste (Quan et al., 2013).

2.2. FTIR analysis of keyboard plastic waste sample

FTIR spectra of keyboard plastic waste is represented in Figure 2 and several peaks with their intensities of various bond types is shown in Table 2. The main characteristics were ascribed to the presence of alkanes, alkenes or aromatic and alcohol in the sample. The lowest transmittance was observed at 3404 cm^{-1}. This indicates the hydrogen bonded stretching bands of OH group. The peak observed at 2918 cm^{-1} confirms the presence of C–H stretching of alkanes. The C=C stretching between at 1593 cm^{-1} confirms the presence of aromatics compounds. The C–O vibrations observed at frequency 1016 and 1188 cm^{-1} show the presence of alcohol, ether, ester, carboxylic acid. Aromatic out of plane band was obtained with C–C vibrations at a frequency of 693 cm^{-1}.
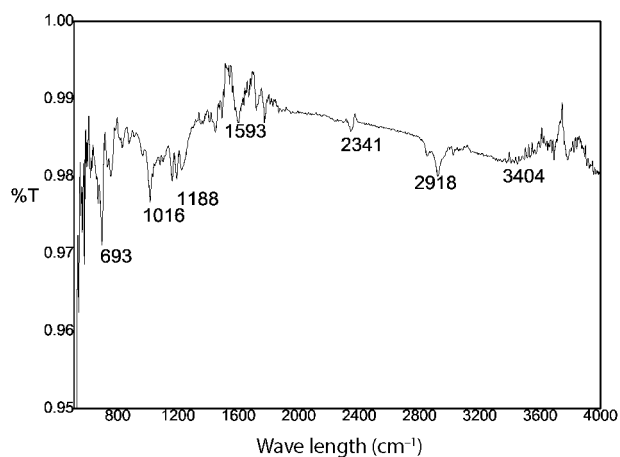

Figure 2. Fourier Transform Infrared Spectroscopy analysis spectra of keyboard plastic waste sample

The computer keyboards are generally made up from ABS (Acrylonitrile-Butadiene-Styrene), PBT (Polybutylene terephthalate), POM (Polyoxymethylene) and PC (Polycarbonate) (Ramesh et al., 2014). ABS has property of yellowing on prolonged exposure to UV light. Keyboard

plastics waste didn't turn into yellow on exposure to UV light due to the absence of ABS. Hence, the keyboard plastics may be composed either from PBT, POM or PC plastics. FT-IR analysis of keyboard waste plastic sample confirms the presence of semicrystalline thermoplastic polyesters.

2.3. Thermogravimetric analysis

The TG and DTG plots of the sample at different heating rates of 5, 10, 15, 20, 40, 60 and 100 °Cmin^{-1} are represented in the Figures 3 and 4. From the thermographs of the sample, it was observed that the thermal degradation occurred primarily into three stages. First stage is the dehydration stage which occurred in the temperature range from 50 °C to 300 °C. The weight loss in the sample was due to removal of moisture content in this first stage. Second stage is devolatilization stage in which the maximum weight loss of about 75–80% takes place at the temperature range of about 400–500 °C for different
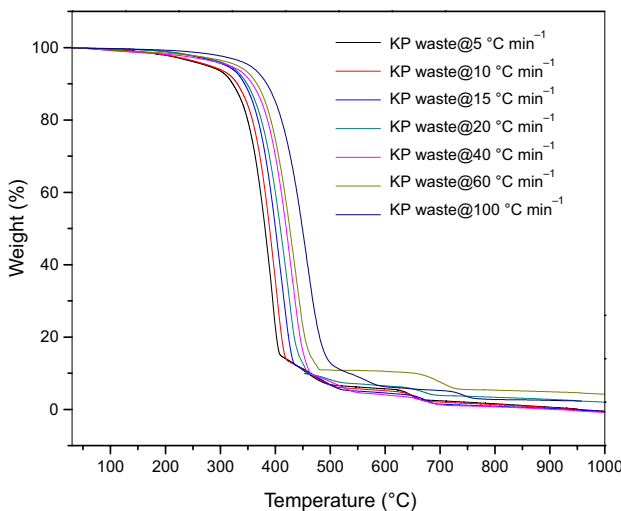
Figure 3. Thermogravimetric analysis plot (weight loss vs. temperature) of keyboard plastic waste at 5, 10, 15, 20, 40, 60 and 100 °C/min heating rates
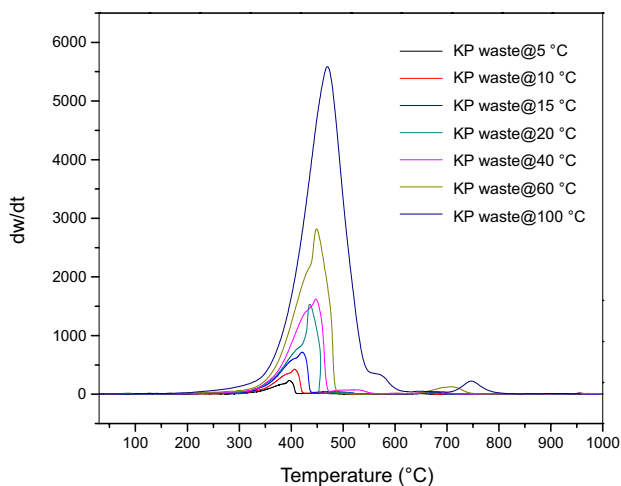
Figure 4. Derivative thermogravimetry plot (derivative weight vs. temperature) of keyboard plastic waste at 5, 10, 15, 20, 40, 60 and 100 °C/min heating rates

heating rates. The volatile content of the waste sample was removed in this stage. Third stage is char formation stage in which the degradation curves have appeared to have a long flat tail at the temperature from 500 °C to 900 °C. The shape of TGA curves has no change with the variation of heating rate. Differential thermogravimetry (DTG) curve for keyboard plastic waste at different heating rates also contains only one major peak which indicates that there is only one major degradation step. As the heating rate increased, the initial and final degradation temperature for keyboard plastic waste was 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 (Boonchom & Puttawong, 2010). Similarly, when the heating rate increases, the decomposition temperature of the keyboard plastic waste also increases. DTG curves at different heating rates were shifted to higher temperature with increasing heating rate due to the heat transfer enlarging with increasing heating rate (Kayacan & Doğan, 2008). With increase in heating rate, the single stage temperature range increased from 396 to 470 °C as the curve shifted towards right. The reason for shifting the temperature range to the higher temperature is the change in mechanism cause by increasing the heating rate (Das & Tiwari, 2017).

2.4. Kinetic study

The non-isothermal thermogravimetric analysis experimental results of keyboard plastic waste pyrolysis obtained under nitrogen atmosphere were used for kinetic modeling. The activation energy of keyboard plastic waste pyrolysis process was determined by isoconversional model free methods. In the present study, different model free methods such as Kissinger, Friedman, FWO, and Coats-Redfern methods were investigated at different heating rates 5, 10, 15, 20, 40, 60 and 100 °Cmin^{-1}.

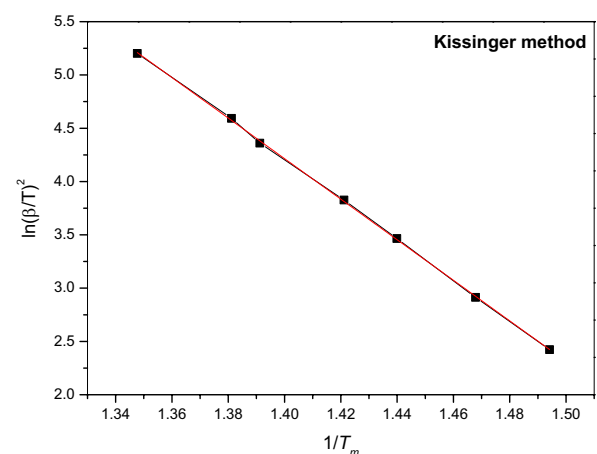Figure 5 shows the estimation of activation energy for keyboard plastic waste at seven different heating rates

Figure 5. Kinetic study plot [$\ln(\beta/T_m^2)$ vs. $1/T_m$] of keyboard plastic waste using Kissinger method at a single heating rat

using Kissinger method. In this method, the degree of conversion (α) at the peak temperature (T_m) was constant under different heating rates. The slope and intercept were found by plotting linear regression line between

$$\ln\left(\frac{\beta}{T_m^2}\right) \text{ and } \frac{1}{T_m} \text{ (K)}$$

and further, activation energy (E_a) and pre-exponential factor (A) of 158.166 kJmol^{-1} and 4.91×10^{17} min^{-1} were determined respectively from the calculated slope and intercept values.
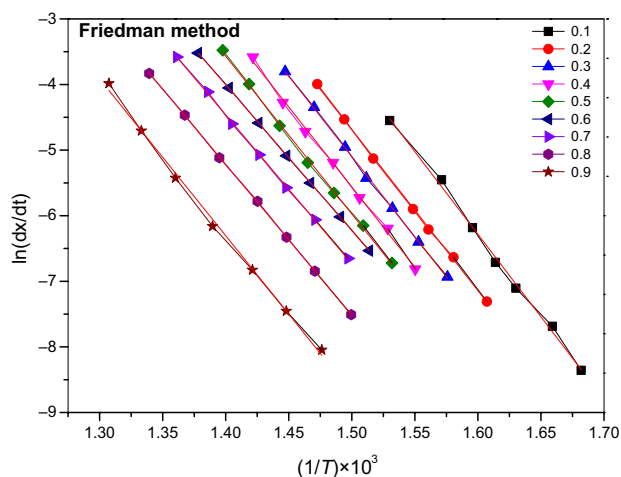

Figure 6. Kinetic study plot [$\ln\left(\frac{dX}{dt}\right)$ vs. $(1/T)\times10^3$] of keyboard plastic waste using Friedman method at different conversion rate
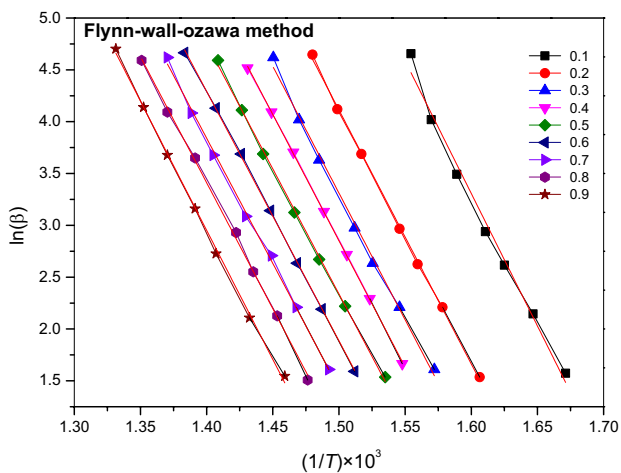

Figure 7. Kinetic study plot [$\ln\beta$ vs. $(1/T)\times10^3$] of keyboard plastic waste using Flynn-Wall-Ozawa method at different conversion rates
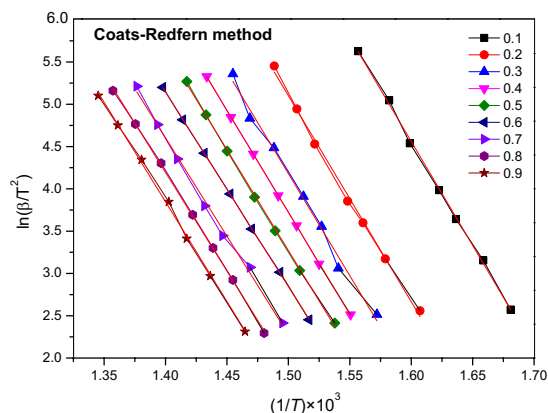

Figure 8. Kinetic study plot [$\ln(\beta/T^2)$ vs. $(1/T)\times10^3$] of keyboard plastic waste using Coats-Redfern method at different conversion rates

Similarly kinetic parameters were also calculated from the different isoconversional plots Figures 6, 7 and 8 using Friedman, FWO, and Coats-Redfern method, respectively at different fractional conversion ranging from 0.1 to 0.9. Based on linear regression fit equations the correlation coefficient (R^2), activation energy (E_a) and pre-exponential factor (A) from the slope and intercept respectively are summarized in Tables 3 and 4. The activation energy is found to be a function of fractional conversion, because most of the plastics pyrolysis reactions are not one step mechanism and it follows a complete multistep reaction. Figures 6, 7 and 8 show how the activation energy varies with the function of fractional conversion (α). The low correlation coefficient (R^2) of conversion (α) values less than 0.1 and greater than 0.9 are not considered. The values of activation energies obtained at different conversion are not same might be due to of complex nature of thermal degradation reactions of waste plastics. From the table it is observed that, the values of activation energy is high at the beginning, decreased gradually up to 70% conversion and further increased at higher conversions. The higher activation energy value at the beginning was due to cleavage of some strong bonds leading to elimination of volatile components (Heydari et al., 2015). With the progress of pyrolysis process, the value of activation energy decreased owing to weakening of bonds. During the decomposition process at high temperature with high conversion when most of the stable bonds are broken, less stable molecules which are easier to break are present, so less energy barrier is required for decomposition at this step and the value of activation energy decreases with progress of conversion

Table 2. Important assignments from Fourier Transform Infrared Spectroscopy analysis of keyboard plastic waste

Frequency (cm^{-1})	Type of vibrations	Assignments
3404	O–H stretching	Alcohol/phenol, H-bonded
2918	C–H stretching	Alkanes
1593	C=C stretching	Alkenes or aromatic
1188	C–O	Alcohol, ether, ester, carboxylic acid
1016	C–O	Alcohol, ether, ester, carboxylic acid
693	C–C	Aromatic out of plane blend

Table 3. Average values of activation energy (E_a) and pre-exponential factor (A) using Friedman, FWO and Coats-Redfern methods at different conversion rates

Conv-erion (x)	Friedman method				FWO method				Coats-Redfern method			
	Fitted equation	R^2	E_a (kJ/mol)	A	Fitted equation	R^2	E_a (kJ/mol)	A	Fitted equation	R^2	E_a (kJ/mol)	A
0.1	$y = -25.1788x + 34.00273$	0.99663	209.3362	6.501E+14	$y = -25.5675x + 44.21519$	0.98843	212.5683	1.159E+23	$y = -24.5722x + 43.87557$	0.99884	204.2935202	1.277E+19
0.2	$y = -24.5479x + 32.13377$	0.99946	204.0913	1.128E+14	$y = -24.5053x + 40.87087$	0.99914	203.7368	3.794E+21	$y = -24.3636x + 41.64725$	0.99657	202.5590535	9.013E+17
0.3	$y = -24.4811x + 31.62418$	0.99947	203.5362	7.747E+13	$y = -24.4504x + 39.987$	0.9962	203.2802	1.375E+21	$y = -24.1369x + 40.38511$	0.99114	200.6739372	1.83E+17
0.4	$y = -24.4209x + 31.06821$	0.99762	203.0351	5.184E+13	$y = -24.3681x + 39.40369$	0.99978	202.596	6.597E+20	$y = -24.0828x + 39.84769$	0.99995	200.2239835	7.999E+16
0.5	$y = -24.0435x + 30.09182$	0.99877	199.8977	2.343E+13	$y = -24.1472x + 38.55843$	0.9989	200.7594	2.383E+20	$y = -23.8112x + 38.98782$	0.99916	197.9662337	2.474E+16
0.6	$y = -22.2342x + 27.12465$	0.99995	184.8553	1.507E+12	$y = -24.0733x + 37.99513$	0.99968	200.1455	1.088E+20	$y = -23.0009x + 37.34659$	0.99994	191.2295657	3.253E+15
0.7	$y = -22.6949x + 27.30989$	0.99961	188.6851	2.418E+12	$y = -24.1561x + 37.65945$	0.99798	200.8334	5.816E+19	$y = -23.2564x + 37.16174$	0.99578	193.353377	1.901E+15
0.8	$y = -22.9693x + 26.93847$	0.99993	190.967	2.501E+12	$y = -24.3049x + 37.4384$	0.99861	202.0712	3.089E+19	$y = -23.3076x + 36.82438$	0.99947	193.7789707	8.442E+14
0.9	$y = -23.9216x + 27.1851$	0.99677	198.8839	6.403E+12	$y = -24.9138x + 37.83191$	0.99843	207.1333	2.233E+19	$y = -23.5523x + 36.81987$	0.9984	195.8139053	4.004E+14
Average			198.8839				203.6804				197.7658385	

Table 4. Value of activation energy (E_a) and pre-exponential factor (A) using Kissinger method at a single heating rate

Fitted equation	R^2	E_a (kJ/mol)	A (min^{-1})
y = −19.0242x + 30.84886	0.99973	158.1668	4.91×10^{17}

(Heydari et al., 2015). The increased activation energy at higher conversion may be explained due to the formation of carbonaceous char which would act as a physical barrier and slows heat transfer, thus decreasing the reaction activity, and makes degradation more difficult. More energy is needed to activate the system. Consequently, the activation energy increases (Quan et al., 2013).

The arithmetic means of the activation energy calculated by Friedman method, FWO method and Coats-Redfern methods are 198.883, 193.612, and 197.765 kJmol^{-1}, respectively, which are close to each other and in good agreement. However, the activation energy calculated from Kissinger method is not matching with the values obtained from other three methods. The discrepancy in the values may be attributed to selection of only peak temperature in the plot in Kissinger method. The kinetic data obtained for pyrolysis of keyboard plastic waste are found to agree closely with some of the available literature (Yao et al., 2020).

Conclusions

The kinetics parameters of keyboard plastic waste pyrolysis were determined using thermogravimetric analysis. The TGA experiment showed that the heating rate has an important role on the thermal degradation reaction. The degradation temperatures for keyboard plastic waste at which the maximum weight losses (75–80%) take place ranges from 400–500 °C at different heating rates ranging from 5 to 100 °C/min. Kinetic study was carried out using four different isoconversional methods. Reasonable fits of data to straight lines in kinetic study plot indicated that the proposed models are suitable for understanding the kinetics of keyboard plastic waste pyrolysis. The activation energy obtained by three methods viz. Friedman method, FWO method and Coats-Redfern method is in the range of 190–200 kJmol^{-1} while activation energy obtained by Kissinger method is 158.166 kJmol^{-1}. This study would definitely provide information to predict optimum pyrolysis regimes and design more effective conversion systems for the thermal degradation of keyboard plastic waste to liquid/gaseous fuel.

References

Al Razi, K. H. (2016). Resourceful recycling process of waste desktop computers: A review study. *Resources, Conservation and Recycling, 110*, 30–47. https://doi.org/10.1016/j.resconrec.2016.03.017

Ali, S., Ng, C. H., & Hashim, H. (2014). Catalytic pyrolysis and a pyrolysis kinetic study of shredded printed circuit board for fuel recovery. *Bulletin of Chemical Reaction Engineering and Catalysis, 9*, 224–240.

https://doi.org/10.9767/bcrec.9.3.7148.224-240

Boonchom, B., & Puttawong, S. (2010). Thermodynamics and kinetics of the dehydration reaction of FePO$_4$ 2H$_2$O. *Physica B: Condensed Matter, 405*(9), 2350–2355. https://doi.org/10.1016/j.physb.2010.02.046

Boonchom, B., & Thongkam, M. (2010). Kinetics and thermodynamics of the formation of MnFeP$_4$O$_{12}$. *Journal of Chemical and Engineering Data, 55*, 211–216. https://doi.org/10.1021/je900310m

Coats, A. W., & Redfern, J. P. (1964). Kinetic parameters from thermogravimetric data. *Nature, 201*, 68–69. https://doi.org/10.1038/201068a0

Das, P., & Tiwari, P. (2017). Thermal degradation kinetics of plastics and model selection. *Thermochimica Acta, 654*, 191–202. https://doi.org/10.1016/j.tca.2017.06.001

Day, M., Coone, J. D., & MacKinnon, M. (1995). Degradation of contaminated plastics: a kinetic study. *Polymer Degradation and Stability, 48*, 341–349. https://doi.org/10.1016/0141-3910(95)00088-4

Heydari, M., Rahman, M., & Gupta, R. (2015). Kinetic study and thermal decomposition behavior of lignite coal. *International Journal of Chemical Engineering, 2015*, 481739. https://doi.org/10.1155/2015/481739

Jing, S., Wenlong, W., Zhen, L., Qingluan, M., Chao, Z., & Chunyuan, M. (2012). Kinetic study of the pyrolysis of waste printed circuit boards subject to conventional and microwave heating. *Energies, 5*, 3295–3306. https://doi.org/10.3390/en5093295

Kayacan, I., & Doğan, Ö. M. (2008). Pyrolysis of low and high density polyethylene. Part I: Non-isothermal pyrolysis kinetics. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(5), 385–391. https://doi.org/10.1080/15567030701457079

Kumar, S., & Singh, R. K. (2014). Pyrolysis kinetics of waste high-density polyethylene using thermogravimetric analysis. *International Journal of ChemTech Research, 6*, 131–137.

Liou, T. H. (2003). Pyrolysis kinetics of electronic packaging material in a nitrogen atmosphere. *Journal of Hazardous Materials, 103*, 107–123. https://doi.org/10.1016/S0304-3894(03)00244-9

Panda, A. K., Singh, R. K., & Mishra, D. K. (2010). Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products – A world prospective. *Renewable and Sustainable Energy Reviews, 14*(1), 233–248. https://doi.org/10.1016/j.rser.2009.07.005

Pandit, V. (2016). India's e-waste growing at 30% annually. *The Hindu Business Line.* https://www.thehindubusinessline.com/info-tech/indias-ewaste-growing-at-30-annually/article8686442.ece

Petrović, Z. S., & Zavargo, Z. Z. (1986). Reliability of methods for determination of kinetic parameters from thermogravimetric and DSC measurements. *Journal of Applied Polymer Science, 32*, 4353–4367. https://doi.org/10.1002/app.1986.070320406

Quan, C., Li, A., & Gao, N. (2013). Combustion and pyrolysis of electronic waste: Thermogravimetric analysis and kinetic model. *Procedia Environmental Sciences, 18*, 776–782. https://doi.org/10.1016/j.proenv.2013.04.104

Ramesh, V., Biswal, M., Mohanty, S., & Nayak, S. K. (2014). Recycling of engineering plastics from waste electrical and electronic equipments: Influence of virgin polycarbonate and impact modifier on the final performance of blends. *Waste Management & Research*, *32*(5), 379–388. https://doi.org/10.1177/0734242X14528404

Saha, B., & Ghoshal, A. K. (2005). Thermal degradation kinetics of poly (ethylene terephthalate) from waste soft drinks bottles. *Chemical Engineering Journal*, *111*(1), 39–43. https://doi.org/10.1016/j.cej.2005.04.018

Shenoy, J. (2018, June 4). India among the top five countries in e-waste generation: ASSOCHAM-NEC study. *The Times of India*. https://timesofindia.indiatimes.com/india/india-among-the-top-five-countries-in-e-waste-generation-assocham-nec-study/articleshow/64448208.cms

TCO Certified. (2015, May 25). *Global E-waste reaches record high, says new UN Report.* https://tcocertified.com/news/global-e-waste-reaches-record-high-says-new-un-report

Turmanova, S. C., Genieva, S. D., Dimitrova, A. S., & Vlaev, L. T. (2008). Non-isothernal degradation kinetics of filled with rice husk ash polypropene composites. *eXPRESS Polymer Letters*, *2*, 133–146. https://doi.org/10.3144/expresspolymlett.2008.18

Vlaev, L., Nedelchev, N., Gyurova, K., & Zagorcheva, M. (2008). A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate. *Journal of Analytical and Applied Pyrolysis*, *81*, 253–262. https://doi.org/10.1016/j.jaap.2007.12.003

Wikipedia. (2017, April 25). *Electronic waste in India.* https://en.wikipedia.org/wiki/Electronic_waste_in_India

Yao, Z., Yu, S., Su, W., Wu, W., Tang, J., & Qi, W. (2020). Kinetic studies on the pyrolysis of plastic waste using a combination of model-fitting and model-free methods. *Waste Management and Research*, *38*(1), 77–85. https://doi.org/10.1177/0734242X19897814