



Kinetics of Granulated Waste Tyre Pyrolysis via Thermogravimetry and Model-Free Methods

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Abstract

There has been an increase in global consumption of waste tyres over the years. However only a portion of the total amount of waste tyres can be recycled or reused for other applications. Land-filling has been considered an alternative to address the problem of continued waste tyres accumulation, but huge space is needed for this and the reusable resources are wasted. This therefore has led to environmental and economic problem of disposal of the large mass of waste tyres. Waste tyre pyrolysis, which is the thermal decomposition in absence of oxygen, can be used to recover both energy and material. Thermogravimetric analysis (TGA) is the technique commonly used to evaluate the weight loss kinetics associated with the vaporisation of materials during pyrolysis. The purpose of this study was to establish the kinetics of thermal degradation of waste tyres by TGA and to compare the activation energies (E) obtained using two model-free methods. The experiments were carried out in a nitrogen environment and a temperature range of 20°C to 600°C at three heating rates. Results show that the pyrolysis process of the tyre crumb occurs in three stages as the various components of the tyre undergo decomposition. A mean activation energy of approximately 232 kJmol⁻¹ was obtained using the two models.

Key words

Waste tyre, activation energy, thermal degradation, model-free.

1. INTRODUCTION

The amount of waste tyres dumped all over the world is roughly 1.5 billion [1], but only 15-20 % is reused whereas the remaining percentage is simply dumped into the earth [2]. The valorisation of waste plastics and tyres plays a big role in the reduction in fossil fuel consumption and helps to address the issue of climate change [3]. Due to the high calorific value of waste tyres (33-35 MJkg⁻¹), recovery of energy is considered an alternative to recycle them [4]. Pyrolysis, which is the process of thermal degradation in absence of oxygen, can be potentially involved to recover energy from waste tyres. During pyrolysis, the organic volatile matter in the tyres is transformed into low-molecular weight products, whereas the inorganic constituents, are retained as solid residue [5].

Tyres are made up of more than 100 different substances such as rubber, steel, silica gel, carbon black etc. During tyre production, the rubbers commonly used are natural rubber (NR), butadiene rubber (BR,) and styrene-butadiene rubber (SBR).The degradation of these components occurs at different temperature ranges. The thermal degradation behaviour of waste tyres depends on the type of rubber as well as its contents [6, 7].

The study of kinetics of waste tyre pyrolysis has recently been an area of interest since understanding of kinetics of this process is important in the design and optimisation of industrial scale waste tyre recycling units. Model-free and model-fitting methods are commonly used to determine the kinetic parameters during solids decomposition [8-10].

The following expression is commonly used for thermal degradation of solids:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

where α is the degree of conversion, $k(T)$ the reaction rate constant, and $\frac{d\alpha}{dt}$ the conversion rate over time. The conversion degree, α is determined as:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \quad (2)$$

where w_0 is the initial weight of the sample, w_t the weight of the sample at a given temperature, and w_f the final mass of the sample. $k(T)$ is expressed according to Arrhenius law as :

$$k(T) = A \cdot \exp^{-\frac{E}{RT}} \quad (3)$$

where E is the activation energy, R the gas constant, and A the pre-exponential factor. Combining equations (1) and (3) yields:

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E_a}{RT}} \cdot f(\alpha) \quad (4)$$

Equation (5) is the underlying equation used in determination of kinetic parameters in non-isothermal degradation of solid materials.

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \int_{T_0}^T \cdot e^{-\frac{E}{RT}} dT \quad (5)$$

where $g(\alpha)$ is the conversion integral function.

The Friedman (FR) method [11] is one of the iso-conversional methods used to calculate the activation energy. The expression for FR equation is:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[\beta\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln(A_\alpha) + \ln[f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (6)$$

where E_α and A_α represent the activation energy and pre-exponential factor at a specific conversion degree respectively. The slope in the plot of $\ln\left[\beta\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right]$ against $\frac{1}{T_i}$ yields the activation energy. The Kissinger-Akahira-Sunose (KAS) method [12, 13] is expressed as follows:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - \frac{E_\alpha}{RT} \quad (7)$$

where the plot of $\ln\left(\frac{\beta}{T^2}\right)$ versus $\frac{1}{T}$ gives a straight line. The slope from this plot is then used to determine the E

The aim of this study was to establish the non-isothermal kinetics of pyrolysis of waste tyres by applying two model-free methods to the TG/DTG data in order to determine the activation energies. The models used were KAS and FR.

2. MATERIALS AND METHODS

Tyre crumb from Mathe group, South Africa was used during this study. The elemental analysis of the tyre crumb was done using vario EL cube elemental analyser, while the thermogravimetric analysis was carried out in a Differential Scanning Calorimeter – Thermo Gravimetric Analyser SDT Q600. The tyre crumb samples were heated from 20°C to 600°C at three different heating rates in nitrogen (100 mLmin⁻¹) environment to prevent oxidation of the samples. Three heating rates of 2°C, 5°C, and 10°C min⁻¹ were used to establish the behaviour of thermal degradation of the tyre crumb, while the TA Instruments software was used to extract the data that aided to plot the TG and DTG curves.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis

The elemental analysis results showed that the carbon content in the tyre crumb was 83.54 wt. % while the hydrogen content was 7.55 wt.%. The contents of nitrogen and sulphur were 0.35 wt.% and 1.84 wt.% respectively whereas the oxygen content (calculated by difference) was 6.73 wt.%.

3.2. Thermal Degradation of the Tyre Crumb

The TG/DTG thermograms of the tyre crumb thermal degradation for the heating rates of 2, 5 °C , and 10 °C min⁻¹ are shown in Figures 1,2, and 3 respectively.

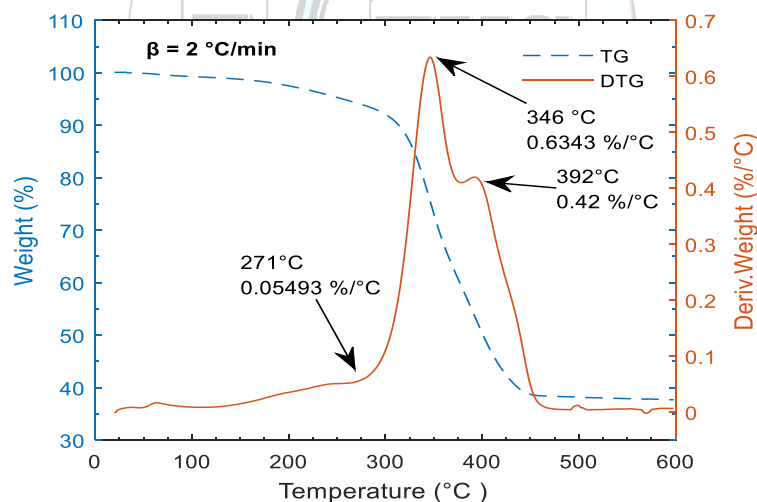


Figure 1. TG/DTG thermogram at 2 °C/min

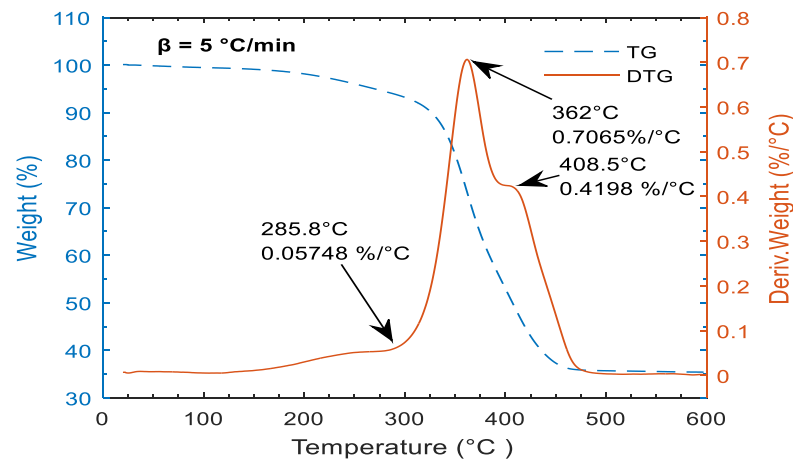


Figure 2. TG/DTG thermogram at 5 °C/min

The thermal decomposition started at about 270 °C and 285 °C and was complete at about 460 °C and 480 °C for the heating rates of 2 and 5 °C min⁻¹ respectively. At the heating rate of 10 °C min⁻¹, the decomposition started at about 290 °C and was complete at about 495 °C. There was no further weight loss above the temperature of 500 °C for the three heating rates. Three stages of decomposition are notable from the peaks seen in the DTG curves i.e. removal of lubricants and oil in the waste tyre with a mean temperature peak value of about $T_m = 285$ °C, breakdown of NR with $T_m = 367$ °C and breakdown of BR and SBR with $T_m = 411.0$ °C. The TG/DTG thermograms indicate that the temperature peaks increase as the heating rates increase during the three-stage thermal degradation process.

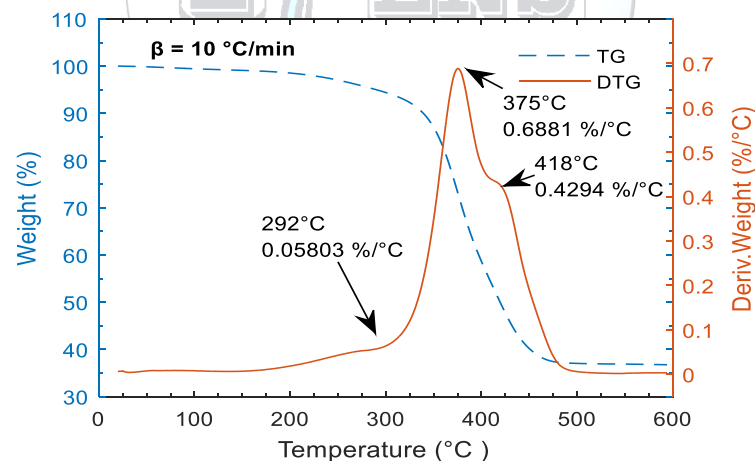


Figure 3. TG/DTG thermogram at 10 °C/min

3.3. Non-isothermal Kinetics of Tyre Degradation

The KAS and FR models were used to determine the activation energies. The two models aided to establish the relationship between the conversion degree and the activation energies. Using KAS model, the plot of $\ln\left(\frac{\beta}{T^2}\right)$ against $\frac{1}{T}$ gave a slope of $-\frac{E}{R}$, from which the activation energy was determined while the plot of $\ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$ was used to determine the activation energies by the FR model. The kinetic plots of tyre crumb thermal degradation using the two models are shown in Figures 4 and 5.

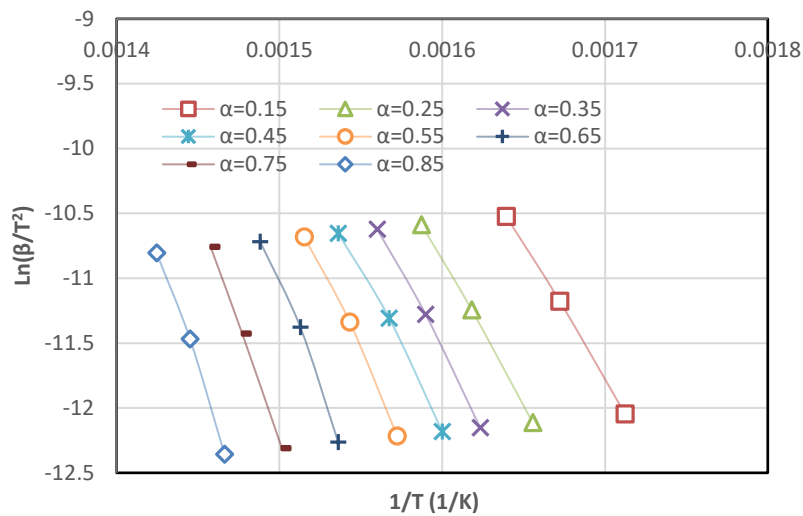


Figure 4. KAS plot at various conversion degrees

The degrees of conversion considered using the KAS and FR models ranged between 0.15 - 0.85. Figure 6 shows the variation of activation energy with conversion degree for the two models. The relationship between the activation energies obtained from KAS and FR models at same conversion degrees is shown in Figure 7. In both models, the activation energy increases with conversion degree up to $\alpha = 0.45$ where the activation energy drops (Figure 6). The trend of increasing activation energy with conversion degree then continues without any further fluctuation. The mean activation energies obtained using KAS and FR models were $231.76 \text{ kJmol}^{-1}$ and $231.92 \text{ kJmol}^{-1}$ respectively. This clearly shows that the values obtained from the two models are similar and it indicates that the models used can accurately predict the non-isothermal thermal degradation of the tyre crumb. The similarity in E values from KAS and FR models is further justified by the linear relationship (Figure 7) between the E values from the two methods. The regression coefficient values obtained from the plots using the two models were high. The lowest R^2 values using the KAS and FR methods were 0.9895 and 0.9903 respectively while the highest values were 0.9998 and 0.9999. This indicates the thermogravimetric data fit well into the models used.

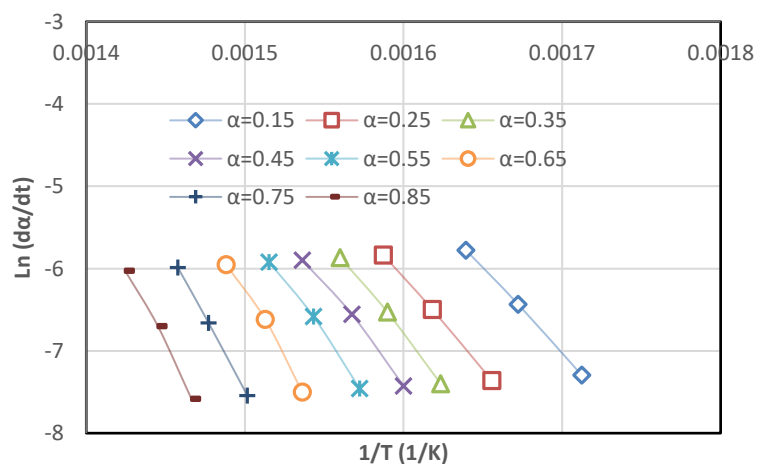


Figure 5. FR plot at various conversion degrees

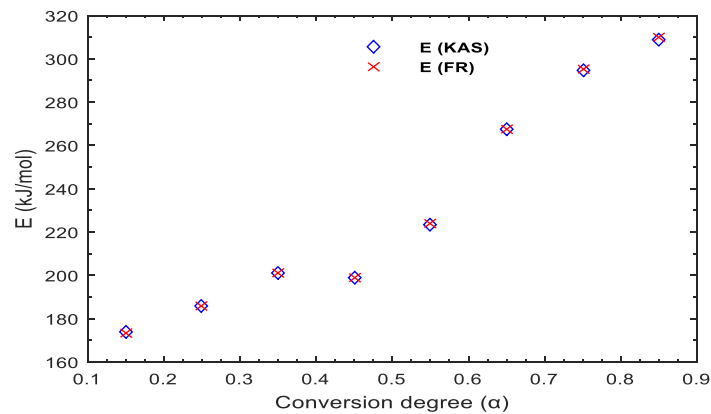


Figure 6. Activation energy versus conversion degree

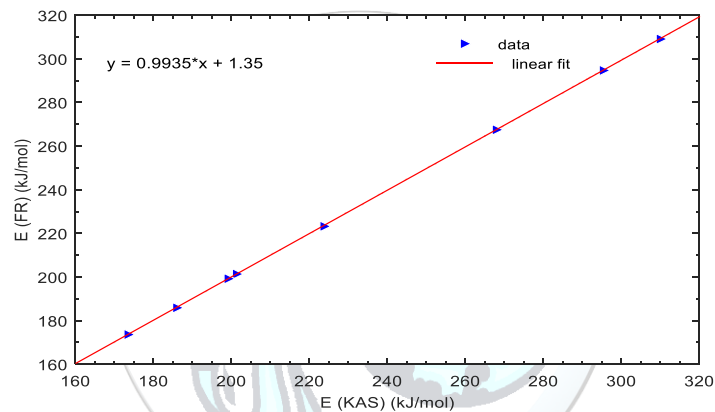


Figure 7. E_{FR} versus E_{KAS}

4. CONCLUSION

This study aimed to establish the thermal degradation process of the tyre crumb by applying two model-free methods to the thermogravimetric analysis data. The thermogravimetric analysis was carried out at heating rates of 2°C, 5°C, and 10°C min⁻¹ in presence of nitrogen. Results show that the pyrolysis process of the tyre crumb takes place in three stages as the various components of the tyre undergo decomposition. The activation energy generally increases with increasing conversion degree in the early stages of thermal degradation. There is, however, a slight drop in activation energy at $\alpha = 0.45$, after which the trend of increasing activation energy with conversion degree continues. A mean activation energy of approximately 232 kJmol⁻¹ was obtained using the KAS and FR models, an indication that the values from the two models are similar. The data obtained from this kinetic study could play a big role in the optimisation of the design of industrial scale waste tyre pyrolysis units.

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