Kinetic modeling and analysis of pyrolysis of polymethyl methacrylate using isoconversional methods

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Abstract. Pyrolysis the waste plastic into fuel is a promising way to protect the environment. In this study, we study the thermal decomposition processes of polymer Poly (methyl methacrylate) PMMA. This work used the microscale combustion calorimeter (MCC) as a tool to study the degradation. MCC is an applicable method to calculate the material combustion parameters by using milligram samples. The experiments were carried out at four heating rates 0.25, 0.5, 0.75, and 1 K/s. The temperature range in which the pyrolysis reaction occurs is ≈ 300-470 °C. We applied several isoconversional methods such as Friedman, Ozawa, Flynn-Wall-Ozawa (FWO), and Kissinger-Akahira-Sunose (KAS) to estimate the apparent activation energy of thermal degradation of Poly(methyl methacrylate). Determine the activation energy from each method evaluated against the experimental data. With investigation, the FWO method shown much higher values for activation energy for PMMA polymer more than the other two methods, and the average value much higher than the Friedman and KAS methods. On the other hand, as a differential method, Friedman showed more accurate results $E_a = 216.65 \text{kJ/mol}$, and KAS method 228.61 kJ/mol. Our investigation may give a few experiences to how to more readily portray trial results with hypothetical expectations and essential data for calculating the activation energy of potential pyrolysis reactors.

1. Introduction

The simulation of degradation polymers is essential and exciting from viewpoints. It helps understand the degradation process of polymers, which is complex in typical cases. It assists design the reactors during the pyrolysis or the incineration or recovery of chemicals from recycling processes. One of the requirements to simulate degradation polymers is activation energy affected by the method used to determine the activation energy. Those methods are divided into main groups, model fitting, and model-free methods. Specific parameters characterize every method to determine the activation energy, and then we find the model-free need to proceeding the pyrolysis at different heating rates to perform the analysis[1,2].

Poly (methyl methacrylate) (PMMA) is considered an inexpensive and economical thermo-plastic. PMMA is widely used, as it has good thermal stability. PMMA is characterized as a combustible polymer with a low oxygen index [3,4].

The analyzing thermal degradation of the original sample can proceed as a single-step or multi-step reaction. For analyzing non-isothermal solid-state kinetic data, any method tries to analyze and determine the kinetic triplet. These methods can be divided into two types model-fitting and model-free (isoconversional) methods[5–7].

The model-free methods can be differential iso-conversional methods or integral iso-conversional methods. one of the differential iso-conversional methods is Friedman which is characterized as an accurate method, but it rarely used in determine the activation energy, this due to it relatively complicated computations and the sensitivity to measurements can because more errors. On another hand there are
integral isoconversional methods like Kissinger–Akahira–Sunose (KAS) and Ozawa–Flynn–Wall (FWO). Using the FWO method is widely used even it less accurate method but this refers to the simplicity of using it [8].

Micro combustion calorimetry (MCC) measured the heat release rate and the other important parameter of the pyrolysis and combustion process by using a milligrams sample and measuring the consumed oxygen. MCC as an instrument divided into two parts, first pyrolyzer where the sample rapidly heated in an inert (nitrogen) atmosphere, this allows the sample to release the gas continues, then it followed by a combustor where the oxidation pyrolyzed gas in high temperature in excess oxygen [9,10] MCC method has been established as a standard ASTM test method (ASTM 7309) [11].

In this study employ and analyze the isoconversional methods as the estimated values of the activation energy using more than one isoconversional method can give an area for values for every value, where can predict true values of Ea. For that we will use the three-model free method to predicate the activation energy cause it important parameter in modeling degradation for the PMMA (Friedman, FWO, and KAS), with considering the limitation of every method. The results are evaluated and reliability against the experimental data out using MCC.

2. Materials and methods

In this work, the methodology is described in [1], PMMA as a flammable material with molecular weight 35 kg/mol, it supplied by Scientific Polymer Products Inc. The mass of the sample varied from 2-3 mg was placed into a ceramic crucible, which was put into a pyrolysis chamber. The specimen was subjected to a controlled heating (at a constant heating rate) in the nitrogen flow. Run the MCC at choosing heat rate $\beta=0.25$, 0.5, 0.75, and 1 K/s with temperature of combustor 900°C and maximum temperature pyrolyzer is 750°C. The measurements were preceded in accordance with in ASTM D7309-07a [11], and every experiment repeat the measurement to performed 3 to 6 times to ensure the repeatability of heat release tests, then it averaging the results data and calculate the standard deviation as shown by vertical bars in Fig. 1.

Kinetic Model

Determine the heat release rate of the oxidation of volatiles by measure the oxygen consumption by using the following equation

$$\dot{q} = -\Delta q_{0T} \sigma_{0T} \left( \frac{m_{0T}}{m_0} \right) - \Delta q \left( \frac{\dot{m}}{m_0} \right)$$

where $m_{0T}$ is the initial sample mass, $\sigma_{0T}$ is the stoichiometric oxygen to fuel mass ratio, $\dot{m}$ is the sample mass loss rate, and $\Delta q_{0T}$ is the heat of combustion per unit mass of volatiles.

Due to complete volatile oxidation and synchronization of oxygen consumption rate with the sample temperature, the dependence measured in MCC characterizes the rate of sample decomposition, similar to the mass loss rate $\dot{m}(T)$ measured in TGA. Both dependencies provide the same information about the pyrolysis rate if the heat of combustion, $\Delta q_{0T}$ does not change [12].

Heat release based global conversion

$$\Delta q = \int_0^\infty \Delta q' \, dt$$

(2) where heat rate $\beta = \frac{dT}{dt}$

Heat release based global conversion

$$\alpha = \frac{1}{\Delta q} \int_0^\infty \dot{q}(T) \, dt \int_0^\infty \Delta q' \, dt$$

(3) With integration reaction rate $RR = \frac{d\alpha}{dt} = -\frac{3}{\Delta q}$ 

The rate of pyrolysis from solid to volatile is described by Arrhenius equation.

$$\frac{d\alpha}{dt} = A f(\alpha) \exp \left( -\frac{E_a(\alpha)}{RT} \right) \quad RR$$

(4)

where $E_a$ is the activation energy. A pre-exponential factor and R is the gas constant 8.314 J/K. mol.

2.1 Isoconversional method

For the calculation of the activation energies all heating rates have been used and they were estimated using the Friedman, Kissinger–Akahira–Sunose and Flynn–Wall–Ozawa methods for comparison reasons all mathematical equations for three methods are describe in Table 1.

Table 1. Mathematical equations of Friedman, FWO and KAS methods.
3. Results and discussion

The Figure demonstrates an increase in the heat release rate with an increase in the heating rate for PMMA samples. This follows from the fact that increasing the heating rate decreases the residence time to reach the peak temperature. The temperature range, in which the pyrolysis reaction occurs, for the samples of the investigated materials: ≈ 300–470 °C.

![Figure 1. MCC measurements Heat release rate for PMMA (solid lines with vertical bars), b) Heat release rate for polymer blends (solid lines with vertical bars).](image)

The calculated activation energy for PMMA samples is employed at four heating rates 0.25, 0.5, 0.75, and 1 K/s, during the conversion range 0.1 to 0.9 by using the model-free methods (Friedman, FWO, and KAS). As mention above every method determines the Ea by the assumption and the slope of its linear plots, this shown in Figures 2, 3, and 4. As shown in every figure the plots of Friedman (ln RR), FWO (ln β), and KAS (ln (β/T²) versus 1/T at selected conversion. KSA and FWO plots, it shows a parallel for every conversion against the others, and this gives a reason to consider and assume the reaction order is the first-order reaction.

![Figure 2. Friedman linear plots for a PMMA at α 0.1-0.9](image)
Ea via $\alpha$ is important because it shows how the reaction going on, and the order of the reaction. As the Ea higher variate this refers to its complex kinetic process and can’t apply the single-step reaction equation. So, shown Fig. 5 the FWO shows a higher activation energy than KAS, as mention in ICTAC FWO is widely used but it has very low accuracy and limited to linear heating rate conditions method [20]. On another hand, Friedman method is more accurate, because its a differential method and there is not any assumption, it supposed to show more accuracy and more sensitivity to measurement. According to ICTAC the chosen average Ea should be less than 20% difference between lower and higher Ea. Ea average activation energy using Friedman method (differential method) about 216.56 kJ/mol, and KAS 228.61 kJ/mol., the difference between them is about 7%, but FWO average Ea equal 260.2 kJ/mol. And the difference between FWO and Friedman is about 9.5%.

Figure 3. KSA linear plots for a PMMA at $\alpha$ 0.1-0.9

Figure 4. FWO linear plots for a PMMA at $\alpha$ 0.1-0.9

Figure 5. Estimated activation energy $E_a$ for PMMA using Friedman, FWO and KAS methods on the conversion ($\alpha$)
4. Conclusions
In this study, the kinetic analysis of PMMA pyrolysis using microscale combustion calorimeter (MCC) carried out at four heating rates 0.25, 0.5, 0.75, and 1 K/s. The MCC is confirmed to be a tool for determining the kinetic parameters for the polymer. For that, we able the modal-free method by using the measurements MCC for PMMA to determine activation energy. The activation energy was calculated by the iso-conversional methods (Friedman, Kissinger– Akahira–Sunose, Flynn–Wall–Ozawa). Finally, the degradation of PMMA is a single-step reaction according to the dependency of activation energy and conversional. The calculated activation energy by Friedman shows more accurate than KAS and FWO.

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