Kinetic Modeling of Pyrolysis and Combustion of High-Density Polyethylene-Based Polymer Mixtures

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Abstract. In this study, the pyrolysis and combustion of a binary mixture of most waste polymers (HDPE and PC) were investigated using MCC measurements at different heating rates of 0.25, 0.5, 1, 1.5 K/s. The non-isothermal kinetic analysis of mixture was conducted for equally mass fraction ratio of 50% HDPE and 50% PC, as well as for individual polymers. The activation energy was calculated by the isoconversional methods (Friedman, Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa). The estimated activation energy on the conversion equals to 0.1-0.95. The Friedman method being more sensitive, as is shown by the variation of decomposition of PC and the first stage for a blend of HDPE/PC. As the equations used in FWO and KAS methods are derived assuming constant activation energy, which produces systematic errors in the estimation of Ea, so they have the same profile but FWO always is higher than KAS.

1. Introduction

Over the past decades, considerable experience has been gained in experimental research and mathematical modeling of the pyrolysis and combustion of a wide range of polymer materials. The need to predict the power of heat generation during the processing and incineration of shredded household waste, as well as gasification and combustion of the fire load, raises the use of measurement results obtained for individual substances.

The additivity of heat generation during the combustion of volatile components formed during the independent pyrolysis of individual components of the fuel mixture is a natural assumption used in engineering calculations. This assumption is valid in the absence of chemical interaction between different polymers, which, however, is possible both in the condensed phase of decomposing solid material and in the gas phase during the oxidation of volatile materials. In fact, it is known there can be both a decrease and an increase in the thermochemical stability of the mixture compared to the expected one in accordance with the additivity rule [1–3].

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 there is any method that tries to analyze and determine the kinetic triplet. These methods can be divided into two types: model-fitting and model-free (isoconversional) methods [4–6].
The model-fitting method can give statistical fit as the model from which the kinetic parameters are calculated. On the other hand, model-free requires several kinetic curves at a different heating rate to perform the analysis. So, to calculate the activation energy for each conversion, it is necessary to calculate kinetic curves from several curves at different heating rates performed at the same value of the conversion [5].

In this study, the pyrolysis and combustion of a binary mixture of most waste polymers (HDPE and PC) were investigated using MCC measurements [1]. By means of MCC data, the non-isothermal kinetic analysis was performed using different kinetic methods to describe the mixture pyrolysis by a single global reaction with activation energy, \( E_a \), depending on conversion.

2. Materials and methods

In this work, we considered two flammable materials, namely, HDPE and PC. These polymers were supplied by Scientific Polymer Products Inc. At first, we studied each material individually. The second part of our measurements was conducted after mixing polymers. The mixture of HDPE and PC was prepared in a laboratory in equal proportions: 50% HDPE and 50% PC. Also, to ensure repeatability of heat release tests, each measurement was performed 3 to 6 times as described in ASTM D7309-07a [7]. After that, the average value and standard deviation were assessed as shown by vertical bars in figure 1.

The measured curves were pre-processed by selecting the material and samples with a mass of about 10 mg for all tests. The MCC measurements were carried out at heat rates \( \beta = 0.25, 0.5, 1, 1.5 \) K/s, the combustor temperature of 900°C, and maximum temperature of pyrolizer equal to 750°C.

| Designation | Name                        | Molecular weight, kg/mol | Appearance | Density, kg/m³ | Melting/softening point, °C |
|-------------|------------------------------|--------------------------|------------|----------------|-----------------------------|
| HDPE        | High-density polyethylene    | 125                      | Pellets    | 950            | 121                         |
| PC          | Polycarbonate                | 45                       | Pellets    | 1200           | 151                         |

3. Kinetic Model

According to the measured oxygen consumption, the heat release rate, which occurs during the oxidation of volatiles, can be written as:

\[
\dot{q} = -\Delta q_{O_2} \sigma_{O_2} \frac{m_{O_2}}{m_0} = -\Delta q \frac{\dot{m}}{m_0} \tag{1}
\]

where \( m_0 \) is the initial sample mass, \( \sigma_{O_2} \) is the stoichiometric oxygen to fuel mass ratio, \( \dot{m} \) is the sample mass loss rate, and \( \Delta q_{O_2} \sigma_{O_2} = \Delta q \) is the combustion heat per unit mass of volatiles. Due to complete volatile oxidation and synchronization of oxygen consumption rate with the sample temperature, the dependence \( \dot{q}(T) \) 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, \( \Delta q \), does not change [8].

\[
\Delta q = \int_0^\infty \Delta q \, dt \tag{2}
\]

Heat release based on global conversion

\[
\alpha = \frac{1}{\Delta q} \int_0^1 \dot{q}(t) \, dt \int_0^\infty \Delta q' \, dt \tag{3}
\]

With integration reaction rate \( RR = \frac{\dot{a}}{\Delta q} = \frac{\dot{q}}{\Delta q} \),

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

\[
\frac{d\alpha}{dt} = A f(\alpha) \exp \left( -\frac{E_a(\alpha)}{RT} \right) = RR \tag{4}
\]

where \( E_a \) is the activation energy, \( A \) is the pre-exponential factor, and \( R \) is the gas constant 8.314 J/K.mol.
3.1. 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 described in Table 2.

| Method  | Expression | Plot | Slope equal |
|---------|------------|------|-------------|
| Friedman | \( \ln RR = -\frac{E_a}{RT} + \ln Af(\alpha) \) | \( \ln RR \) against \( \frac{1}{T} \) | \( -\frac{E_a}{R} \) |
| FWO     | \( \ln \beta = -1.0516\frac{E_a}{RT} + \text{constant} \) | \( \ln \beta \) against \( \frac{1}{T} \) | \( -1.5016\frac{E_a}{R} \) |
| KAS     | \( \ln \frac{\beta}{T_a^2} = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT} \) | \( \ln \frac{\beta}{T_a^2} \) against \( \frac{1}{T} \) | \( -\frac{E_a}{R} \) |

4. Results and discussion

Figure 1-a shows MCC measurements for individual polymers obtained at \( \beta = 0.25, 0.5, 1, 1.5 \)°C/s. As shown, HDPE is faster in reaction; according to the temperature 10%-90% rules, observed that the maximum heating release rate occurs within the temperature range of 493-530°C earlier than that in PC within the range of 520-570°C. As noticed, there is one peak in the heat release rate which mean one step reaction. The MCC measurements in a mixture of HDPE/PC for mass fraction ratio \( Y_i = 0.5 \) shown in figure 1-b, were carried out at four different heating rates (0.25, 0.5, 1, and 1.5 K/s). Therefore, HDPE, as expected, decomposes at a much lower temperature than PC. Accordingly, the maximum decomposition temperatures (\( T_p \)) observed for PC and HDPE at 1.5 K/s are 477 and 565 °C, respectively. Comparing curves for a blend with those for individual components, we see that the reaction progress in a multi-step reaction is referred to as the pyrolysis peaks emerging in distinct temperature ranges [16].

![Figure 1](image)

**Figure 1.** The MCC measurements: a) Heat release rate for individual polymers blends (solid lines with vertical bars), b) Heat release rate for polymer blends (solid lines with vertical bars).

The kinetic analysis helping in investigated degradation mechanisms as well as in predicting and the thermal stability of polymers, and simulate the degradation process with establishing mathematical relationships between reaction rate, the extent of conversion, and the temperature [17,18]. This can be achieved in several ways. For that, choosing the accurate method for determining the activation energy (Ea). The estimated activation energy on the conversion is shown in figures 2-4 for \( \alpha = 0.1-0.95 \) to HDPE, PC, and a blend of HDPE/PC based on three isoconversional methods, respectively.
The apparent activation energy values for HDPE by the FWO method are higher than the values of apparent activation energies obtained by Friedman and KAS methods. The KAS and Friedman methods are very identical especially within the range of 0.1-0.6. However Friedman method gradually decreases as shown in figure 2.

It is also noticeable that FWO and KAS have the trend but FWO’s trend is higher. This refers to both FWO and KAS methods. The equations used are derived assuming constant activation energy, which produces systematic errors in the estimation of \( E_a \). Figure 3 shows the Friedman method being more sensitive as is shown by the variation of PC decomposition.

For a blend of HDPE/PC, as shown in figure 1, the decomposition occurs between two stages, first stage 0.1-0.7 conversion and the remain will be the second stage this is referred to the effect of PC in the blend and his late decompression. This, in turn, has impacted the activation energy, the sensitivity of the Friedman method, appeared in the first stage give lower values. Thus, the activation energies as a function of the conversion degree obtained from the Friedman method are more reliable than those obtained from the FWO and KAS methods. But the second stage is very steady and identical to KAS. On the other hand, KAS and FWO methods are steady with respect to the first stage.

**Figure 2.** Estimated activation energy \( E_a \) of HDPE using Friedman, FWO, and KAS conversion (\( \alpha \)).

**Figure 3.** Estimated activation energy \( E_a \) for PC using Friedman, FWO, and KAS conversion (\( \alpha \)).

**Figure 4.** Estimated activation energy \( E_a \) for a blend of HDPE and PC using Friedman, FWO, and KAS conversion (\( \alpha \)).

5. **Conclusions**

In this study, the pyrolysis and combustion of a binary blend of most waste polymers (HDPE and PC) were investigated using MCC measurements at different heating rates of 0.25, 0.5, 1, 1.5 K/s. The non-isothermal kinetic analysis of blend was conducted both for equal mass fraction ratio (50% HDPE and 50% PC) and for individual polymers. The activation energy was calculated by the isoconversional methods (Friedman, Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa). The estimated activation energy for the conversion is 0.1–0.95.

The Friedman method being more sensitive, as is shown by the variation of decomposition of PC and the first stage for a blend of HDPE/PC. As the equations used in FWO and KAS methods are
derived assuming constant activation energy, which produces systematic errors in the estimation of $E_a$, so they have the same profile but FWO always is higher than KAS.

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