Identification of Reaction Model of Pyrolysis Reaction of HDPE

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This paper demonstrates how to derive Arrhenius parameters as well as reaction model of pyrolysis reaction of high density polyethylene (HDPE) from isothermal kinetic data. We introduced a state-of-the-art thermobalance that enables to record a weight decrease with time under pure static condition. As a result of comparing experimental reduced time plots (RTPs) with theoretical ones, the pyrolysis reaction of HDPE accommodates "contracting cylinder" model, allowing its model to be $2(1-\alpha)^{1/2}$. The reaction model derive here was used to evaluate each Arrhenius parameters from isothermal and non-isothermal data. A couple of evidences strongly support the properness of the reaction model derived from RTP and the corresponding Arrhenius parameters.

A variety of kinetic studies on the HDPE has been introduced to elucidate its pyrolysis kinetics.[1–7] Many previous studies assumed that reaction order function with a reaction order of one would represent reaction model of the HDPE without confirmation.[1,3] Fixation of reaction model could allow a force-fitting of Arrhenius parameters.[8,9] Hence, it is essential to estimate the correct form of reaction model. It was demonstrated that RTP using isothermal decomposition data was useful to determine the reaction model.[8–10] The objective of this research was to derive a reaction model of HDPE pyrolysis reaction from RTP and then to determine Arrhenius parameters.

Powdered HDPE with an average molecular weight of 182000 was used in this study and supplied by Samsung Chemical Co. (B230A Powder). The samples were dried in a desiccator before analyses.

Thermobalance (TB) was designed and manufactured for isothermal kinetic experiments (Figure 1). The TB consisted of a laboratory scale pyrolysis reactor and a weight detection unit. A high stainless steel tube (5.5-cm i.d. × 1.0 m) was used as a pyrolysis reactor. The reactor was heated to a reaction temperature under a stream of nitrogen with a linear velocity of 8.3 cm/s, forming a laminar flow region. HDPE sample of 10 ± 0.1 mg was loaded and suspended in a 100 mesh stainless steel wire basket. The sample basket was connected to an electric balance (Satorius BP61) by a 0.3-mm diameter nichrome wire. The balance was lowered down quickly by a winch to insert sample to a reaction zone after a target temperature was stabilized. Weight loss of a sample was recorded continuously over time by an on-line personal computer. We performed four isothermal kinetic experiments at operating temperatures of 718, 723, 728, and 733 K.

Generally, the kinetic equation for solid state decomposition is based on a single step kinetic with Arrhenius relationship for temperature dependency as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp(-E/RT)f(\alpha) \qquad (1)$$

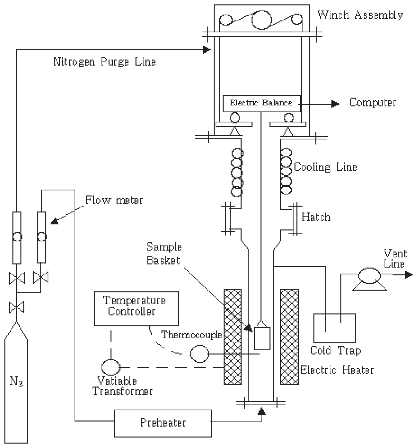

Figure 1. Schematic diagram of thermobalance operable under isothermal conditions.

Table 1. Reaction models of solid state reaction

	Reaction Model	$f(\alpha)$
1	Power law	$4\alpha^{3/4}$
2	Power law	$3\alpha^{2/3}$
3	Power law	$2\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$
6	Mample (first-order)	$1-\alpha$
7	Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
8	Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
9	Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$
11	Contracting sphere	$3(1-\alpha)^{2/3}$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$
13	Second-order	$(1-\alpha)^2$

The reaction model may take various forms, some of which are shown in Table 1.

The RTP was constructed by plotting α as a function of a reduced time, t/t_α, where t_α is the time needed to attain a specific conversion ($\alpha = 0.9$) at an isothermal operating temperature, T_i. In order to determine the reaction model of HDPE pyrolysis reaction, we compare theoretical RTPs corresponding to reaction models in Table 1 with experimental ones at the isothermal operating temperatures of 718, 723, 728, and 733 K (Figure 2). Four isothermal experimental data demonstrate similar RTPs one another and a best fit to model 12, implying that the reaction model of HDPE pyrolysis reaction would be accounted for by "contracting cylinder" model. The reaction model deduced here offers an insight that the pyrolytic decomposition of HDPE might be carried out by the isotropic shrinkage of a cylindrical

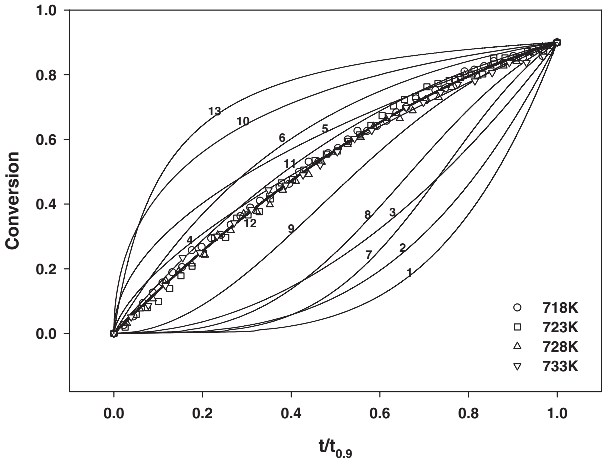

Figure 2. Reduced time plots of theoretical reaction models and four isothermal experiments of HDPE at 718, 723, 728, and 733 K.

reactant particle with a constant rate of interface advancement.

Integrating equation (1) leads to:

$$g(\alpha) = \int_0^{\alpha} [f(\alpha)]^{-1} d\alpha = k(T_i)t \qquad (2)$$

If one would substitute the identified reaction model into Eq 2, the rate constant at a temperature could be determined from the slope of a plot of $g(\alpha)$ vs t.

The reaction constants, $k(T_i)$, are evaluated to be 0.0481, 0.0593, 0.0694, and 0.0912 min^{-1} at the isothermal operating temperatures of 718, 723, 728, and 733 K, respectively. Arrhenius parameters can be estimated from the Arrhenius plot of $\ln k(T_i)$ vs $1/T_i$ as follows:

$$\ln k(T_i) = \ln A - \left(\frac{E}{R}\right)\frac{1}{T_i} \qquad (3)$$

Consequently, the Arrhenius plot assigns the E and $\ln A$ to be 191.80 kJ·mol^{-1} and 29.03 (A: min^{-1}), respectively. High linearity ($r^2 = 0.984$) of the Arrhenius plot upholds the appropriateness of the Arrhenius relationship as well as the reaction model.

In order to verify the E value, model-free method was introduced and its final equation under isothermal conditions can be expressed by:

$$\ln t_{\alpha,i} = -\ln\left(\frac{A_\alpha}{g(\alpha)}\right) + \left(\frac{E_\alpha}{R}\right)\frac{1}{T_i} \qquad (4)$$

Model-free method allows the functional relationship of E value with α. The average E value within the α range from 0.1 to 0.9 is 190.49 ± 10.83 kJ·mol^{-1} within a confidence interval of 95%. The relative standard deviation of E values is estimate to be 7.4% that is low enough to reflect that the E value is relatively constant with respect to α. The E values obtained from model-fitting and model-free method are so similar that the reaction model of HDPE derived here would be appropriate.

Assuming that the reaction model would be denoted by $2(1-\alpha)^{1/2}$, one of the integral methods, Coats–Redfern method,[11] was introduced to check whether or not the Arrhenius parameters derived here would be similar to those from the integral method analyzing non-isothermal kinetic data. The integral method exhibits the E and $\ln A$ to be 186.02 kJ·mol^{-1} and 28.10 (A: min^{-1}), respectively. Despite using different data set and applying different analysis methods, the similarity of E and A value derived from both methods may support the reliability of the estimated Arrhenius parameters.

The reaction model for pyrolysis reaction of HDPE is basically equal to reaction order function with a reaction order of 0.5. Additionally, several recent studies reported that the reaction model of HDPE would be accounted for by the reaction order function with a reaction order of ≈0.55.[5–7] It is expected that the first-order kinetics would be inappropriate to represent the pyrolysis reaction of HDPE. A couple of evidences strongly support the properness of the reaction model derived from RTP and the corresponding Arrhenius parameters.

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12 A pre-exponential factor (min^{-1})
13 E activation energy (kJ·mol^{-1})
14 $f(\alpha)$ reaction model
15 $g(\alpha)$ $\int_0^{\alpha}[f(\alpha)]^{-1}d\alpha$
16 k rate constant
17 R gas constant (kJ·mol^{-1}·K^{-1})
18 t time (min)
19 T absolute temperature (K)
20 α weight conversion at an absolute temperature
21 i certain isothermal operating temperature