

Kinetics of the thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics

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Abstract—We did a kinetic analysis of the thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics using the nonisothermal weight loss technique with heating rates of 10, 20, 30 and 40 °C/min. The weight loss data according to degradation temperature were analyzed by using the integral method based on Arrhenius form to obtain the kinetic parameters. To verify the effectiveness of the proposed kinetic analysis method, the experimental values were compared with those of the numerical integration results using kinetic parameters obtained in this work. It was found that the proposed kinetic analysis method gave reliable kinetic parameters of the thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics.

Key words: Kinetic Analysis, Thermal Degradation, Wax Materials, Mixed Waste Plastics

INTRODUCTION

The amount of waste plastics is continuously increasing and causes serious pollution problems. Because waste plastics are essentially nonbiodegradable, they are not suitable either for composting or landfilling [1]. Accordingly, the thermal treatment by pyrolysis, which converts waste plastics to fuel or useful hydrocarbon, has been recognized as a useful approach. A proper thermal treatment system not only resolves the disposal problems, but also recovers energy from these wastes. In the last few years, many efforts have been devoted to the development of a pyrolysis process for waste plastics [2-7]. But pyrolysis processes of waste plastics were never commercialized due to the lack of sufficient economic, environmental and political incentives as well as operation problems such as excessively long degradation time and the coking of reactants [8,9]. Recently, a pyrolysis reactor of kiln type has been studied to recover fuel oil from mixed waste plastics [10]. Rotary kilns have been evaluated for a variety of organic wastes such as wood, used tires, plastic wastes, etc. [11]. Therefore, pyrolysis process with a rotary kiln has been recognized as an effective method to recover fuel oil from mixed wastes including plastics, rubber, glass, sand and dirt of all kinds. However, wax materials are formed when mixed waste plastics are thermally cracked, and the pyrolytic oil containing these wax materials is not good to use as alternative fuel oil. Therefore, the re-treatment of wax materials is required by thermal or catalytic cracking.

It is well known that a kinetic investigation is very important to get information for rationally designing a reactor for thermal degradation. Thermogravimetric analysis (TG) cannot be used to elucidate a clear mechanism of thermal degradation. Nevertheless, much effort has been recently devoted to developing a new mathematical method for kinetic analysis using TG because it gives reliable information of the pre-exponential factor, the activation energy, and the

overall reaction order [12-14]. Our aim was to propose the kinetic analysis method using TG, and the proposed method was applied to the kinetic analysis of thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics. There is no intention in this work to describe the fundamental chemical mechanisms of thermal degradation or to analyze product yield. Rather, we focus on the measurement of apparent kinetic parameters useful for the engineering design of chemical processes. To verify the effectiveness of the kinetic analysis method proposed herein, the experimental values were compared with those of the numerical integration results using kinetic parameters obtained in this work. Also the kinetic results were compared with those of various analytical methods in the literature [10].

EXPERIMENTAL

The samples of wax materials used in kinetic analysis of this work were obtained from mixed waste plastics by field pyrolysis process using a rotary kiln. The mixed waste plastics pyrolyzed in rotary

Table 1. Proximate and elemental analysis of wax material used in this work

Analysis	Item	Weight fraction (%)
Proximate analysis	Initial moisture	1.80
	Volatile matter	98.16
	Fixed carbon	0.00
	Ash	0.04
Elemental analysis	Carbon	51.22
	Hydrogen	9.09
	Nitrogen	0.06
	Oxygen	39.42
	Sulfur	0.02
	Chlorine	0.19

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kiln reactor are EPR (extended producer responsibility) waste plastics and no special pretreatment procedure is adopted. And the yield of wax materials obtained from this pyrolysis process is about 12%. Proximate and elemental analysis of the sample used in this work is shown in Table 1. From proximate analysis, it can be seen that the volatile material is the major component and the amount is 98 wt%. Also, we can see that the carbon and oxygen are major components from elemental analysis. For kinetic analysis, a thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. It consists of an electrically heated reaction tube (18 mm i.d. and 165 mm in length). The sample was placed in a quartz cell of 6 mm in diameter. The cell was then put on a platinum crucible connected to a thermobalance. Carrier gas was supplied from a gas bottle and regulated by a mass flow meter. The gas passed through the reaction tube from top to bottom. The experiments were performed in a nitrogen atmosphere with a flow rate of 50 ml/min and a purge time of 20 min. The samples were studied at various heating rates between 10 and 40 °C/min. The initial mass of the sample was 8.87–11.07 mg.

KINETIC MODEL

All kinetic studies utilize the basic rate equation of conversion α for thermal degradation in a nitrogen atmosphere as

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp(-E/RT) \quad (1)$$

where A , E , T and R are the pre-exponential factor (1/min), the activation energy (J/mol), the temperature of reaction (K) and the gas constant (8.314 J/mol·K), respectively, and n denotes the overall reaction order. However, the pre-exponential factor, A is not strictly constant but depends on the reaction temperature [15]. And if the heating rate $\beta = dT/dt$ (K/min) is employed, it can be shown that

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} T^m (1-\alpha)^n \exp(-E/RT) \quad (2)$$

where m is the order on the degradation temperature. From Eq. (2), it can be shown that

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A_0}{\beta} T^m \exp(-E/RT) dT \quad (3)$$

where on integrating and introducing the initial condition of $\alpha=0$ at $T=T_0$ the following expression is obtained:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A_0}{\beta} \int_{T_0}^T T^m \exp(-E/RT) dT \quad (4)$$

The integral approximation [16] is to consider Eq. (4) when it can be shown that

$$\begin{aligned} \frac{A_0}{\beta} \int_{T_0}^T T^m \exp(-E/RT) dT \\ = \frac{A_0 R}{\beta E} T^{m+2} \left(1 - (m+2) \frac{RT}{E} \right) \exp(-E/RT) \end{aligned} \quad (5)$$

And

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{1-(1-\alpha)^{1-n}}{1-n} \quad \text{for } n \neq 1 \quad (6)$$

$$= -\ln(1-\alpha) \quad \text{for } n=1 \quad (7)$$

From the logarithm of Eqs. (5), (6) and (7), the following results are obtained:

$$\ln\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right) = F - \frac{E}{RT} \quad \text{for } n \neq 1 \quad (8)$$

$$\ln(-\ln(1-\alpha)) = F - \frac{E}{RT} \quad \text{for } n=1 \quad (9)$$

where

$$F = \ln\left[\frac{A_0 R}{\beta E} T^{m+2} \left(1 - (m+2) \frac{RT}{E} \right)\right] \quad (10)$$

The plot of $\ln[(1-(1-\alpha)^{1-n})/(1-n)]$ or $\ln(-\ln(1-\alpha))$ versus $1/T$ should give a straight line with the slope determining the activation energy E . Also, A_0 and m can be calculated from the activation energy E and the intercept F on the Y axis by using least square method.

RESULTS AND DISCUSSION

Fig. 1 shows the variations of the TG and DTG curves with respect to temperature for various heating rates in pure nitrogen. The TG curves show that the weight loss curves of wax materials are displaced to higher temperatures due to the heat transfer lag with increased heating rate. When the degradation temperature is 100 °C,

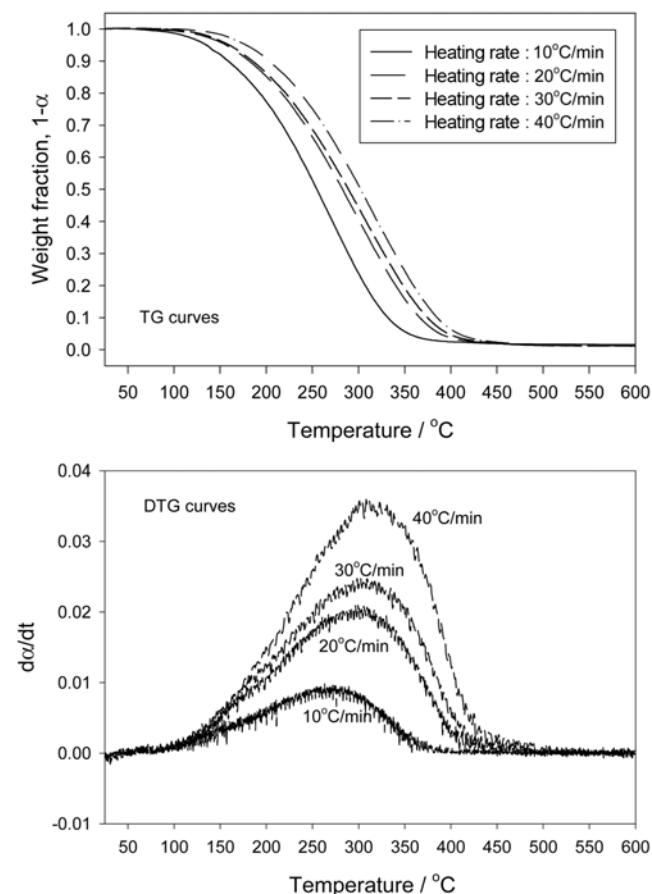


Fig. 1. TG and DTG curves of wax materials in nitrogen atmosphere.

a small conversion is obtained. A rapid increase in the conversion is seen above 150 °C. And when the degradation temperature reached 400 °C, about 99% of conversion was obtained. From DTG curves, we can see that the maximum degradation rates occur at different reaction temperatures for various heating rates. A higher heating rate shifts the rate curve to the higher temperature range, and also results in a higher peak rate. It is also noted that there is one peak rate from 100 to 400 °C.

Figs. 2-5 show the application of the kinetic analysis method pro-

posed in this work at heating rates of 10, 20, 30 and 40 °C/min, respectively. This method was applied to our data and the best fit values for each heating rate were determined by employing reaction order values n of 0.0-2.0 with interval of 0.25. The best overall fit values were obtained using a value for $n=1.25$ in all cases. And the kinetic method proposed in this work gave apparent activation energies of 43.1, 46.5, 46.6 and 50.9 kJ/mol for heating rates of 10, 20, 30 and 40 °C/min, respectively. The kinetic parameters obtained from this work are summarized in Table 2.

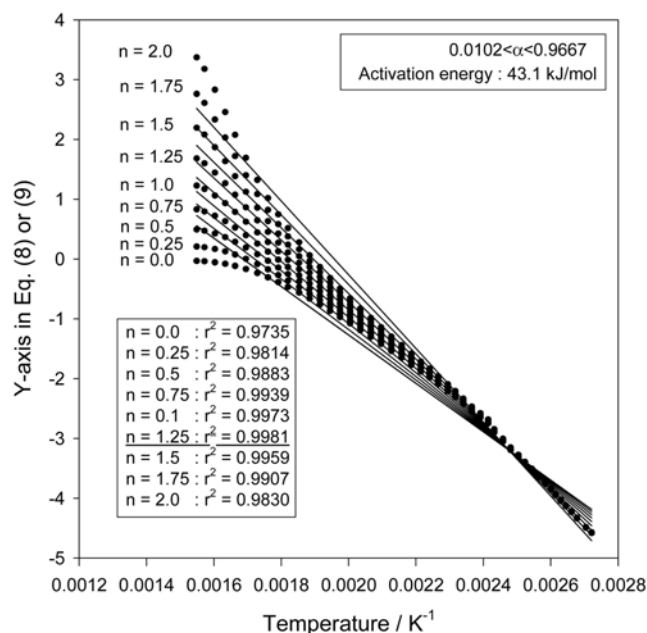


Fig. 2. Application of the kinetic analysis method at heating rate of 10 °C/min.

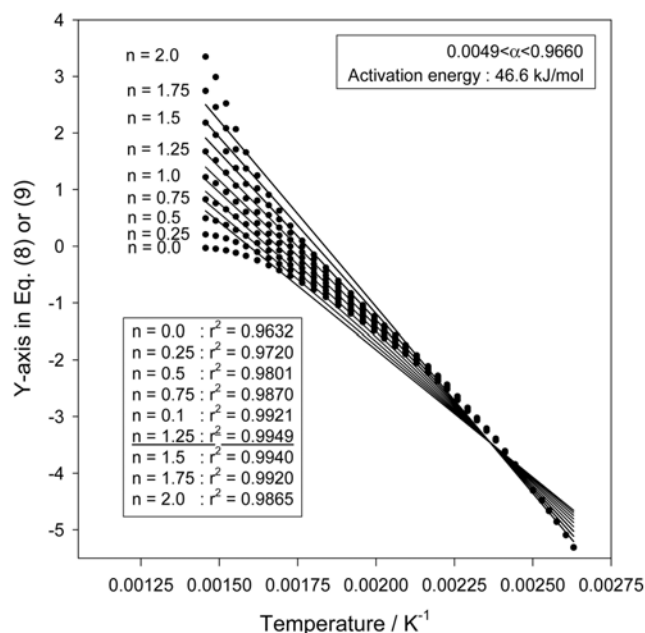


Fig. 4. Application of the kinetic analysis method at heating rate of 30 °C/min.

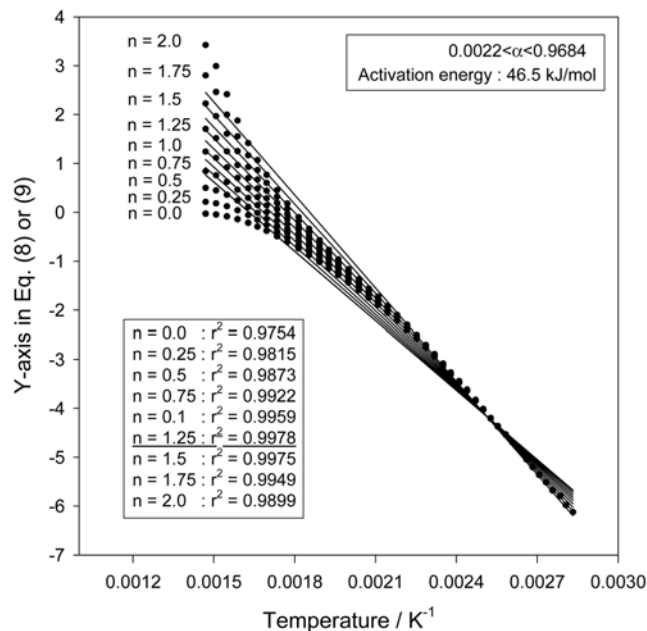


Fig. 3. Application of the kinetic analysis method at heating rate of 20 °C/min.

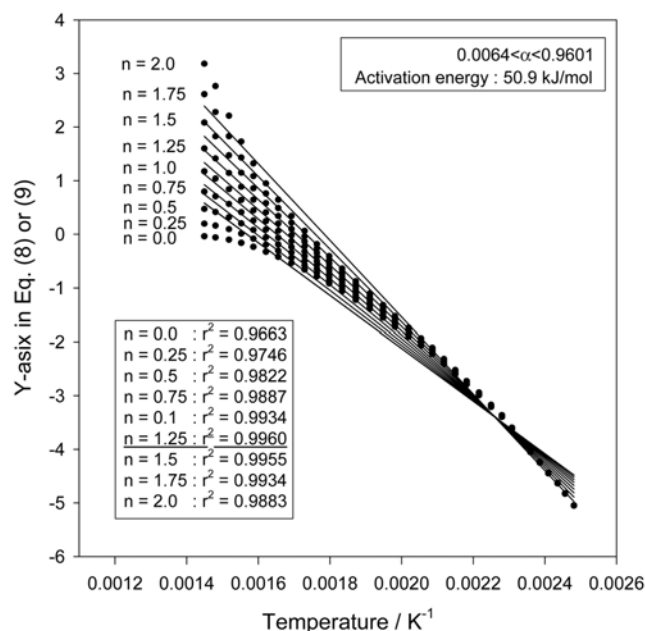


Fig. 5. Application of the kinetic analysis method at heating rate of 40 °C/min.

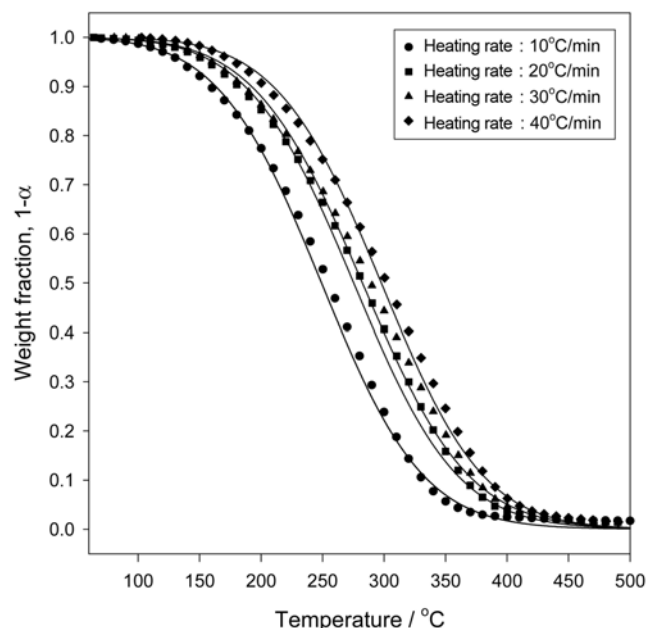
Table 2. The kinetic parameters obtained from this work

Heating rates, β (°C/min)	Reaction order, n	Activation energy, E (kJ/mol)	Factor, A_0 (min ⁻¹ K ^{-1/2})	Order, m
10	1.25	43.1	6.9684×10^8	-1.98
20	1.25	46.5	2.1470×10^9	-1.99
30	1.25	46.6	2.5552×10^9	-1.97
40	1.25	50.9	6.9395×10^9	-1.97

When polymers are subject to heating condition, complicated processes occur, such as random-chain scission, end-chain scission, chain stripping, cross-linking and coke formation. In this work there is no intention to describe fundamental chemical mechanisms for

Table 3. The kinetic parameters by various analytical methods in the literature [8]

Method	Heating rates, β (°C/min)	Reaction order, n	Activation energy, E (kJ/mol)
Freeman-Carroll	10	0.83	28.7
	20	0.81	28.3
	30	0.79	28.2
	40	0.79	31.5
Flynn-Wall	10	1.67	58.9
	20	2.86	102.0
	30	2.57	90.8
	40	2.94	109.6
Coats-Redfern	10	1.00	30.3
	20	1.00	31.5
	30	1.00	31.1
	40	1.00	35.0
Friedman	10-40	-	75.4
Ozawa	10-40	-	75.6

**Fig. 6. Comparison of TG data (symbol) and calculated values (line) for the thermal degradation of wax materials.**

the thermal degradation of wax materials. We focused on the apparent kinetic parameters useful for chemical engineering design. As a matter of fact, the actual values of kinetic parameters obtained by using a conventional thermogravimetric technique are dependent not only on such factors as atmosphere, sample mass, sample shape, flow rate, heating rate, etc., but also upon the mathematical treatment used to evaluate the data. Therefore, the kinetic results were compared with those of various analytical methods in the literature [10]. Table 3 shows the kinetic parameters by various analytical methods. From Table 3, it is seen that the kinetic parameters varied with respect to the analytical methods. These observations clearly indicate the problems of describing the thermal degradation of wax materials.

To verify the performance of the kinetic analysis method used in this work, Fig. 6 shows the experimental values and the computed values by the kinetic parameters obtained from this work and the numerical integration of Eq. (3). The computed values agree very well with the experimental values, and the kinetic analysis method proposed in this work gives a reliable value of kinetic parameters for the thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics.

CONCLUSIONS

The kinetic analysis of the thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics was studied. The weight loss data according to degradation temperature was analyzed using the integral method based on Arrhenius form to obtain kinetic parameters such as apparent activation energies and overall reaction orders. From this work, it was found that the overall reaction order was 1.25 and the apparent activation energies were 43.1, 46.5, 46.6 and 50.9 kJ/mol for heating rates of 10, 20, 30 and 40 °C/min, respectively. Also, from the comparison of the experimental values and the computed values by the kinetic parameters obtained from this work, the computed values agree very well with the experimental values, and the kinetic analysis method proposed in this work gives a reliable value of kinetic parameters for the thermal degradation of wax materials obtained from pyrolysis of mixed waste plastics.

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