Studies on the thermal degradation of synthetic polymers: 16. Estimation of the product yield on the basis of intensity function for thermal gasification of polyethylene

Takashi Sawaguchi, Sadayuki Niikuni, Takeshi Kuroki and Tadashi Ikemura
Department of Industrial Chemistry, College of Science and Technology, Nihon University, Kandasurugadai, Chiyoda-ku, Tokyo 101, *Japan*

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The kinetic equation for the pyrolysis gasification reaction of four kinds of polyethylene, differing from one another in average molecular weight, has been established. Differences in the molecular weight of the samples have no effect on the kinetic parameters when the molecular weight is 10^4 or above. The intensity function, $I_F = T\theta^a$ (K s^a), describing the severity of the decomposition conditions, has experimentally turned out to be a temperature throughout the residence time, θ, for reactions constrained by Arrhenius parameters A and E. The value of the exponent, a, may be found approximately from the kinetic parameters in this experiment. The values of the product yield calculated from the Arrhenius equation, $k = A\exp(-E/RI_F)$, for a particular I_F, agree with the experimental values.

INTRODUCTION

Attention has recently been directed towards plastic waste matter and the recovery resources by pyrolysis. The most suitable control for recovery by pyrolysis requires the development of a method for estimating the product yield corresponding to the decomposition conditions. The prediction of product yield should be made on a kinetic basis: i.e., by the analysis of material balances equations in the elementary reactions which occur by free-radical mechanisms. However, this analysis, even in the thermal decomposition of petroleum hydrocarbons[1], becomes difficult with increasing numbers of carbon atoms in the sample, and it is impossible to analyse the elementary reactions in the case of polymers. We have thus studied the kinetic parameter which represents the severity of the decomposition conditions, i.e. the intensity function ($I_F = T\theta^a$), which correlates well with the product yield From experience, 0.06[2] is used as the value for the exponent a, and this value is also applied for the pyrolysis of crude petroleum[3]. The authors[4-7] introduced the concept of I_F for polymers and, in cases where property values differ completely from naphtha, crude petroleum etc., an experimental induction method for finding a was established. I_F exhibits good correlation with product yield. Moreover, the authors[4] found previously that the value of a for polymers differs from that for petroleum hydrocarbons, and they suggested its value depends on the molecular structure of the sample and correlates with the kinetic parameter (activation energy). I_F is useful as a means of estimating product yield, and it is clear that a depends considerably on the pyrolysis reaction, according to the type of material used. To use the concept of I_F for pyrolysis of a wide range of hydrocarbons, further theoretical study of a must be undertaken.

Davis and Farrell[2] recently defined I_F (which corresponds to the temperature required to obtain an optional conversion ratio x in a residence time of 1 s) and established a standard kinetic equation involving I_F, using $a = 0.062$. It is noteworthy that, as a first attempt, elucidation of the relation between I_F and kinetics was made from the definition of I_F.

We have recently established a kinetic equation for the pyrolysis gasification reaction of polyethylene low polymers, and have clarified theoretical definition of I_F from a kinetic standpoint, and have studied the dependence of kinetic parameters on the value of the exponent a in the expression for I_F[8]. Moreover, we developed a useful means of estimating the product yield from I_F on the basis of the kinetic parameters, which quantitatively reflect the pyrolysis reactions.

Here, I_F is shown to be applicable to the thermal gasification of polyethylene.

THEORY

Calculation of product yield

Kinetics related to I_F. The relation between a in the expression for I_F and kinetic parameters has been

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Table 1 Average molecular weights of samples used

Sample	$\bar{M}_n$	$\bar{M}_w$
A[a]	370	1000
B	8900	36 000
C	20 000	150 000
D	200 000[b]	

[a] From ref 8;
[b] Manufacturer's data

described[8]. The intensity function equation, first-order reaction velocity equation, and Arrhenius equation are as follows:

$$I_F = T\theta^a \tag{1}$$

$$\frac{\mathrm{d}x}{\mathrm{d}\theta} = k(1-x) \tag{2}$$

or

$$k = [\ln(1-x)^{-1}]/\theta$$

$$k = A\exp(-E/RT) \tag{3}$$

where I_F = intensity function (Ks^a); T = reaction temperature (K); θ = residence time (s); a = constant; x = conversion ratio (gasification ratio); k = reaction velocity constant (s^{-1}); A = frequency factor (s^{-1}); E = activation energy (cal/mol); and R = gas constant (cal mol^{-1} K^{-1}). From this definition[2], I_F is equal to T for $\theta = 1$ in equation (1). Thus equations (4) and (5) are obtained when $\theta = 1$ and $I_F = T$ are substituted in equations (2) and (3):

$$k_{I_F} = \ln(1-x)^{-1} \tag{4}$$

$$k_{I_F} = A_{I_F}\exp(-E_{I_F}/RI_F) \tag{5}$$

with $k_{I_F} = I_F$ standard reaction velocity constant (s^{-1}); $A_{I_F} = I_F$ standard frequency factor (s^{-1}); and $E_{I_F} = I_F$ standard activation energy (cal mol^{-1}). Comparing equations (3) and (5); $k = k_{I_F}$, *i.e.* $A = A_{I_F}$ and $E = E_{I_F}$ for $\theta = 1$. Accordingly, a can be expressed by:

$$a = \frac{-\ln[1-\ln\theta(RT/E)]}{\ln\theta} \tag{6}$$

If $A = A_{I_F}$ and $E = E_{I_F}$ hold in the range of $\theta \neq 1$, I_F also turns out to be a temperature in this range and equation (6) becomes a general formula.

Comparison of equations (7) and (8) permits evaluation of the value of a from kinetics:

$$\theta_2 = \theta_1(T_1/T_2)^{1/a} \tag{7}$$

$$\theta_2 = \theta_1\exp[(1/T_2 - 1/T_1)E/R] \tag{8}$$

Product yield can thus be found from the following equation:

$$x = 1 - \frac{1}{\exp[A\exp(-E/RI_F)]} \tag{9}$$

EXPERIMENTAL

Sample

Polyethylene in this experiment was a commercial grade, used without further purification. The molecular weight is given in *Table 1*.

Apparatus and procedure

The apparatus used and the procedure for this experiment have been described in previous report[8]. The samples were melted at 80°C (sample A)[8], 200°C (sample B) or 250°C (samples C and D) by constant electric heating.

Analysis

The gaseous product was analysed by a Shimadzu 4B-PT gas chromatograph. the analytical procedure for each sample has already been reported[5]. Average molecular weight was determined by gel permeation chromatography using a Toyo Soda HLC-811 high speed liquid chromatograph. The calibration curve was produced using a standard polystyrene, and Q was taken as 11.0[9].

Definitions

Definitions of residence time, effective reactor volume, gasification ratio etc. have been described previously[8].

RESULTS AND DISCUSSION

Effect of reaction conditions on gasification

The i.r. spectra of liquid products obtained from sample C with different gasification ratios are shown in *Figure 1*. Up to a gasification ratio of ~0.5, the main constituent of the liquid products comprised aliphatic olefins such as terminal vinyl (990, 910 cm^{-1}) and *trans*-vinylene (965 cm^{-1}) types. When the gasification ratio was 0.5 or more, aromatics (1600, 1500 cm^{-1}) were observed, and their absorption became stronger with increasing gasification ratio. *Figure 2* (sample C) shows the composition of gaseous products corresponding to the gasification ratio. Near 0.7, the product gas composition was constant. With a gasification ratio of 0.5 or more, secondary reactions such as the further decomposition of olefins may occur

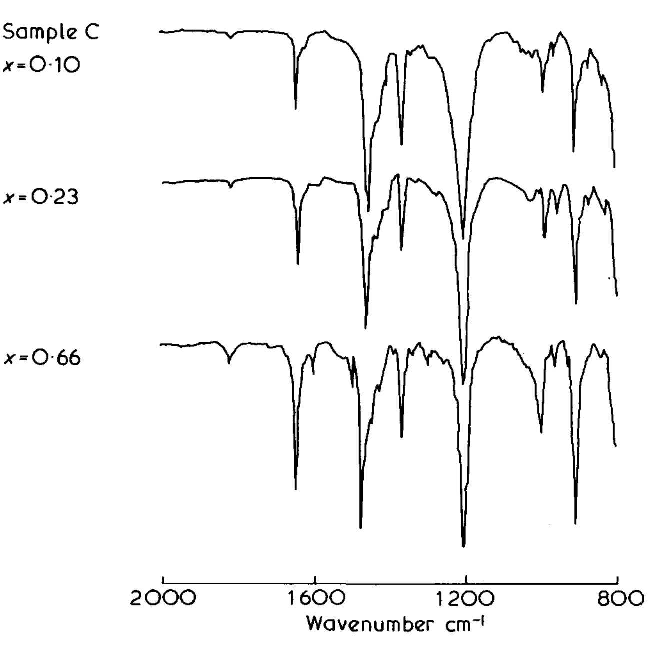

Figure 1 I.r. spectra of pyrolysis products from polyethylene:

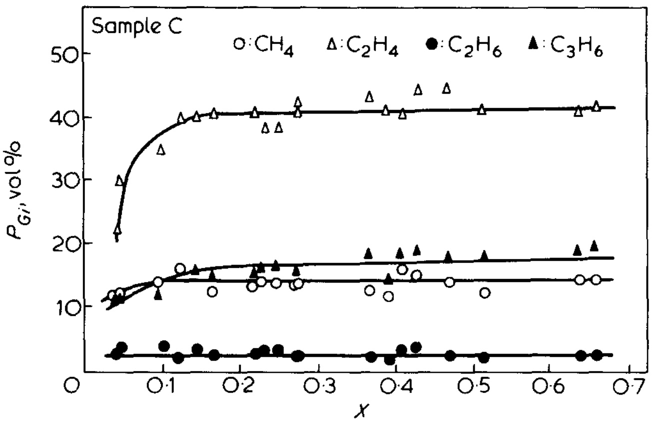

Figure 2 Composition of gaseous products corresponding to the gasification ratio

Table 2 Coefficients for each component in equation (10)

		Sample			
Component	Coefficient[a]	A[b]	B	C	D
CH_4	a	0.18	0.16	0.16	0.16
C_2H_4	b	0.44	0.44	0.45	0.46
C_2H_6	c	0.04	0.03	0.03	0.03
C_3H_6	d	0.17	0.18	0.18	0.17
C_3H_8	e	0.01	0.01	0.01	0.01
C_4H_8	f	0.05	0.05	0.05	0.05
H_2	g	0.12	0.13	0.12	0.12

[a] Mole fraction of gaseous products;
[b] From ref 8

and these initial olefins form aromatics by condensation, etc. The change in composition occurring at a gasification ration of 0.1 or less is thought to be caused by the initial degradation of polymers. The i.r. spectra and composition for samples B and D were similar to those for sample C.

Two groups of reactions were observed in the gasification of polyethylenes and low polyethylenes (sample A)[8]. The first stage reaction occurs at a gasification ratio of up to 0.5, where the products are not subject to secondary reactions; the second stage occurs at 0.5 or above where secondary reactions can occur. For the first stage, the following quantitative chemical equation is obtained:

$$[\text{Polymer}]\rightarrow[\text{Depolymerized polymer}]\rightarrow$$
$$a\,CH_4+b\,C_2H_4+c\,C_2H_6+d\,C_3H_6+e\,C_3H_8+f\,C_4H_8+g\,H_2 \qquad (10)$$

The coefficients of each component are expressed as mole fractions of gaseous porducts, given in *Table 2*.

Kinetics of gasification and I_F

As shown in equation (10) and *Table 2*, the reactions of the polyethylenes, and also those of polyethylene low polymers (sample A)[8], are first-order with respect to the depolymerized polymer weight fraction for the first stage of the gasification reaction. Gasification velocity is analysed in equation (2).

A linear relation is established by plotting $-\ln(1-x)$ vs. θ for short residence times. For long residence times, secondary reactions occur and linearity is lost. The various reaction velocity constants for the first stage are obtained from the slopes of the straight line. Their temperature dependences are shown in *Figure 3* (samples C and D). Kinetic parameters for each sample are given in *Table 3*. Differences in average molecular weight of the sample does not affect the kinetic parameters significantly at molecular weights of 10^4 or above (*Tables 2* and *3*).

The value of a in equation (1) is obtained by induction[4]. Based on the methane yield, the value of a is about 0.3 for each sample in the first stage. The following experimental equation is thus obtained:

$$I_F=T\theta^{0.03} \qquad (11)$$

k_{I_F} and I_F under various conditions are obtained from equations (4) and (11). Plots of $-\ln k_{I_F}$ vs. I_F for each

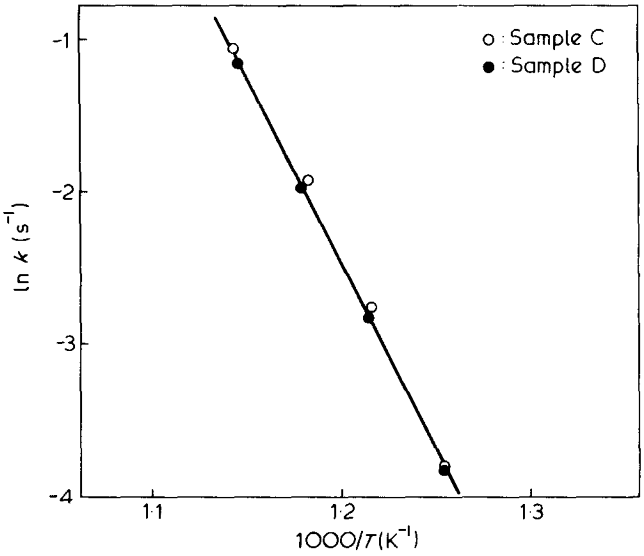

Figure 3 Arrhenius plot for *k*

Table 3 Kinetic parameters and I_F standard kinetic parameters for each sample

Sample	A (s^{-1})	$E\times10^{-3}$ (cal mol^{-1})	A_{I_F} (s^{-1})	$E_{I_F}\times10^{-3}$ (cal mol^{-1})
A[a]	9.9×10^{12}	53.7	9.7×10^{12}	53.6
B	6.4×10^{11}	49.1	9.0×10^{11}	49.3
C	2.1×10^{12}	51.0	2.2×10^{12}	50.9
D	8.4×10^{11}	49.7	1.1×10^{12}	49.8

[a] From ref. 8
(1 cal = 4.1868 J)

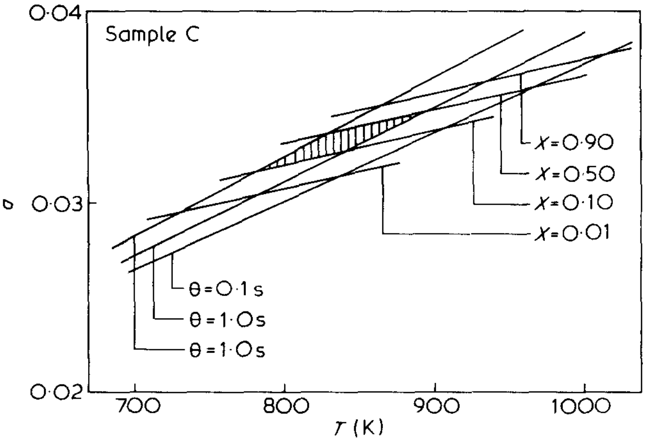

Figure 4 Change range for the value of *a* in equation (6)

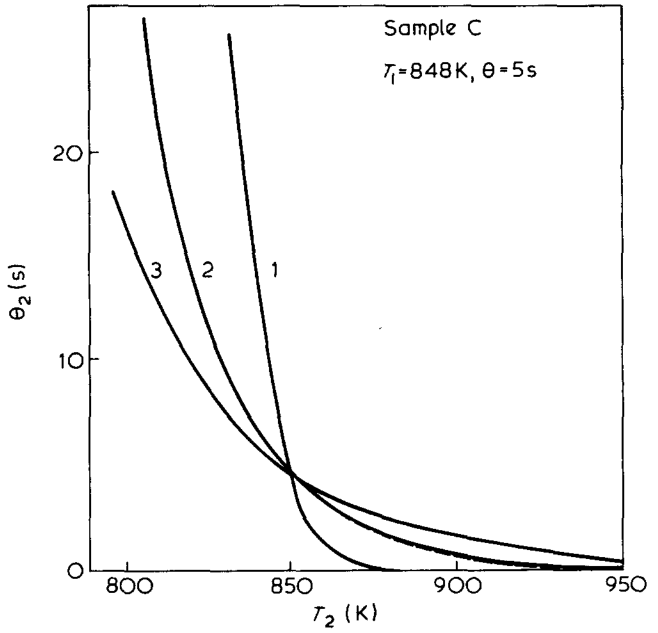

Figure 5 Comparison of equation (7) with (8). (——), equation (7); (— — — —), equation (8). 1: a = 0.010; 2: a = 0.033; 3: a = 0.050

sample show good linearity, and A_{I_F} and E_{I_F} obtained from the straight lines are given in *Table 3*. Good agreement between A and A_{I_F} as well as E and E_{I_F} is observed. Thus, a can be calculated from kinetic parameters, [equation (6)].

Figure 4 (sample C) shows the change in a with experimental conditions. This is determined by residence time, reaction temperature, activation energy, frequency factor and conversion ratio (gasification ratio). An approximate value can be obtained for experimental conditions wherein kinetic parameters are defined. Since a obtained from the kinetic parameters in this experiment changes in the shaded part of the figure, the following approximations are used here: 0.032 (sample A)[8]; 0.034 (sample B); 0.033 (sample C); and 0.032 (sample D).

Evaluation of a from kinetic parameters is by comparison of equations (7) and (8). *Figure 5* (sample C) shows the change in T_2 and θ_2 for given values of T_1 and θ_1. Putting $a = 0.033$ in equation (7) and $E = 49.1 \times 10^3$ cal mol^{-1} in equation (8), gives good agreement with experiment. Considerable dependence of a on the activation energy is also seen.

Figure 6 (samples C and D) compares experimental values with calculated values for various product yields (equation (9)). Results are in good agreement up to a gasification ratio near 0.5 (first stage reaction range).

The product yield theory is applicable to both thermal gasification of polyethylenes and low polymeric polyethylene[8].

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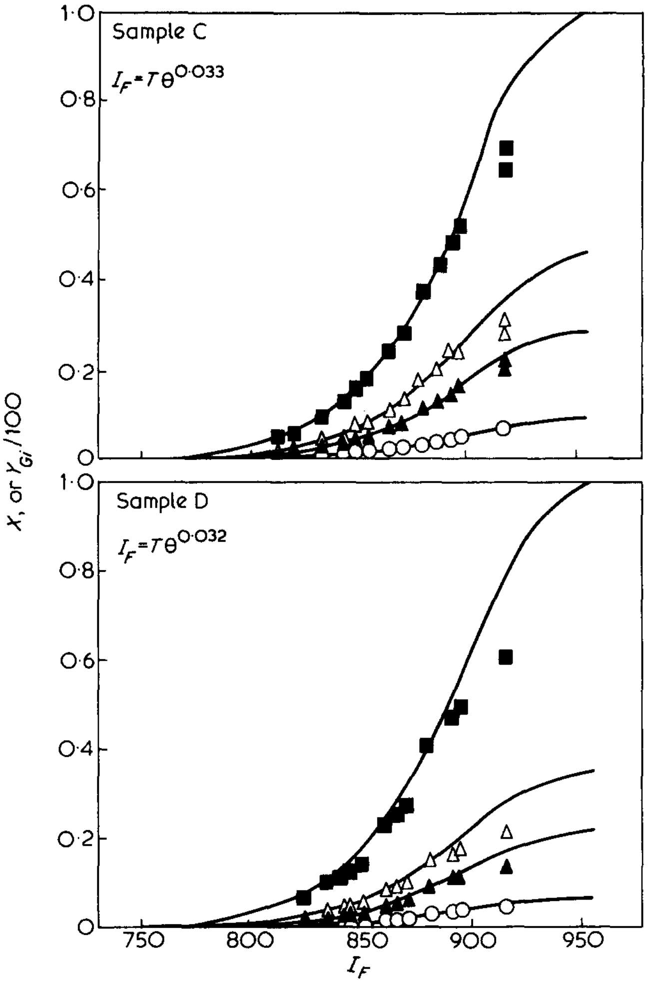

Figure 6 Comparison of the experimental values with the calculated values for the various product yields, dependence on I_F; ■, X; ○, CH_4; △, C_2H_4; ▲, C_3H_6. (——), equation 9

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