



# Effect of pressure on thermal degradation of polyethylene

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## Abstract

A thermal degradation of polyethylene was carried out in a stirred tank reactor by continuous flow operation under elevated pressures ranging from 0.1 to 0.8 MPa, in order to investigate the effect of reaction pressure on thermal degradation behavior of polymers.

Rate of volatilization, rate of double bond formation and the distribution of degradation products were studied at various temperatures and pressures under a steady state. It was found that the reaction pressure had a significant effect on both rates and the distribution of degradation products during thermal degradation of polyethylene. Since there exists a one to one correspondence between the double bond formation and the scission of C–C links in polymers, it can be concluded that the reaction pressure takes part directly in the scission of C–C links during thermal degradation of polymers. With the higher pressure, the carbon number distribution of gaseous and liquid products, and the molecular weight distribution of reactor contents shifted to the lower molecular weight side.

Thermal degradation by continuous flow operation is a suitable technique for converting waste plastics into liquid hydrocarbons, which could be used as feedstock materials. The elevation of pressure during thermal degradation provides a potential alternative to control the distribution of products.

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## 1. Introduction

In a thermal degradation process for disposal of waste plastics, it is desirable to operate the apparatus under an elevated pressure, e.g. ranging from 0.1 to 1.0 MPa, to prevent the

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oxygen leak into reactor and to suppress the foaming phenomena of reactor contents. In order to develop an industrial scale waste plastics treatment plant which processes a large amount of polymer in a continuous flow reactor, comprehensive data are necessary on the rate of thermal degradation of polymers and the product distribution obtained at various temperatures and pressures.

A lot of researchers have contributed to thermal degradation of polymers since polyethylene was synthesized in 1933, e.g. works on polyethylene [1–3], polypropylene [4–6], polystyrene [7–9] and polyisobutylene [10–12]. But none of them have taken notice of an effect of pressure on thermal degradation of polymers.

The thermal degradation of polymers has been tacitly understood to occur in a liquid phase, where the elevation of pressure in reactor could not have an appreciable effect on reaction itself. Most of the previous works on thermal degradation of polymers were carried out by using a batch reactor system to investigate the stability and/or the degradation mechanism of synthesized polymers. In a batch reactor, it would be difficult to distinguish an effect of pressure on the scission rate of C–C links in polymers due to suppression of the product vaporization caused by elevation of reaction pressure.

In the preceding paper [13], we have reported that two sorts of scission simultaneously occur during thermal degradation of polymers in reactor. One is a random scission of C–C links which causes a molecular weight reduction of raw polymer, and the other is a chain-end scission of C–C links which causes a generation of volatile products. The latter one, the chain-end scission takes place at a gas–liquid interface in working reactor. Consequently, the volatilization of products during thermal degradation of polymers is a heterogeneous reaction in which the reactant is in a liquid phase and the product is in a gas phase.

The macroscopic mechanism proposed by the authors is shown in Fig. 1 for the above-mentioned chain-end scission to produce volatile products at a gas–liquid interface in working reactor for thermal degradation of polymers. Provided that the thermal degradation of

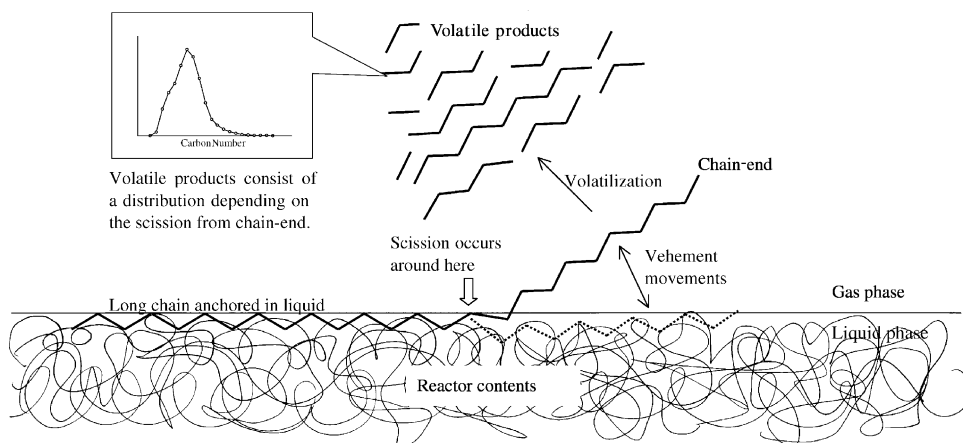


Fig. 1. Proposed macroscopic mechanism of the chain-end scission of polymers to produce volatile products at gas–liquid interface.

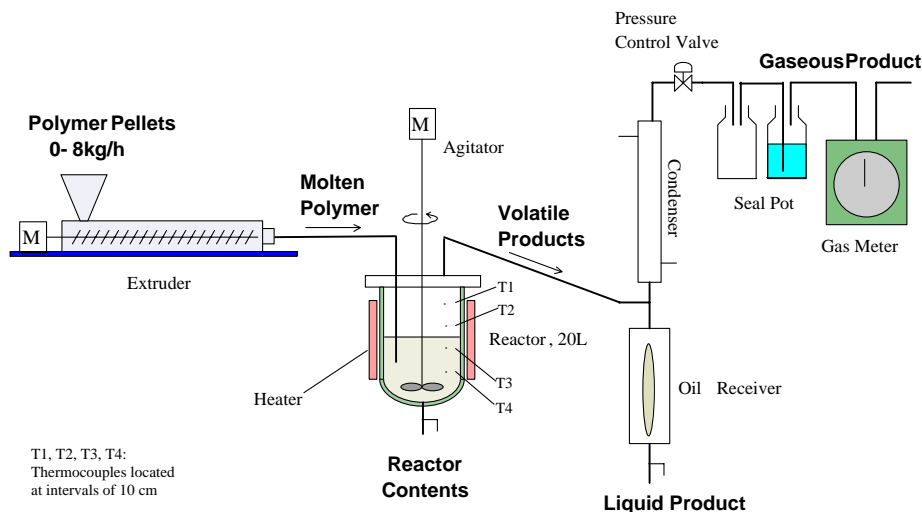


Fig. 2. Continuous flow stirred tank reactor for thermal degradation of polymers.

polymers proceeds along this mechanism, not only the liquid phase condition but also the gas phase condition in reactor, exactly the reaction pressure, must have an effect on the thermal degradation behavior of polymers.

When a thermal degradation of polymers is carried out in a continuous flow operation, the experimental data can be obtained at a steady state, i.e. a constant temperature, pressure and a constant amount of reactor contents. Therefore, a continuous flow reactor is superior to a batch one to investigate the effect of pressure on thermal degradation of polymers.

In the preceding paper [13], we have also explained about “degradation and volatilization reactor (DVR)”, a continuous flow reactor system shown in Fig. 2. The DVR is a continuous flow stirred tank reactor in which thermal degradation of polymers and volatilization of products simultaneously occur under steady state. In the DVR system, the fluid leaving reactor does not have the same composition as that of reactor contents.

In DVR, the input polymer is continuously melted into a viscous liquid and mixed with reactor contents. At degradation temperature, reactor contents are liquid thermally decomposing into small molecules which are convertible to hydrocarbon vapor and leave the reactor. As shown in Fig. 2, all volatile products vaporize in the reactor before coming out as the output product of DVR. Thus, there coexist gas (volatile products) and liquid (reactor contents) in the reactor, that is, there is a gas–liquid interface in DVR.

In the present work, the authors carried out a thermal degradation of polyethylene in the DVR system under elevated pressures ranging from 0.1 to 0.8 MPa to investigate the reaction pressure affects on the reaction rate and the product distribution in thermal degradation of polymers. Based on the observed information, the characteristics of the continuous flow reactor for thermal degradation of polymers, the effect of reaction pressure on degradation products and the macroscopic mechanism of thermal degradation of polymers were discussed.

Table 1  
Properties of original polyethylene

Density ( $\text{g cm}^{-3}$ )	0.968
Ash (wt.%)	0.03
Conradson carbon (wt.%)	0.10
Higher calorific value ( $\text{J g}^{-1}$ )	48950
Average molecular weight ( $M_w$ )	1.12E+05
Polydispersity	8.4

## 2. Experimental

### 2.1. Material

The original polyethylene (high density polyethylene) was obtained from Mitsui Chemicals Inc., Japan. Its physicochemical properties are shown in Table 1.

### 2.2. Experimental procedure

Fig. 2 shows a schematic diagram of the experimental apparatus used for thermal degradation of polyethylene under elevated pressure by continuous flow operation in the present study.

The principal part of the apparatus consists of an extruder with variable feed rates of  $0\text{--}8 \text{ kg h}^{-1}$ , a stainless steel vessel reactor having a volume of 20 l installed with a rotating agitator and a heater, a water-cooled reflux condenser, a liquid product receiver having a glass level gauge, a seal pot, and gas meter.

The input raw polymer (polyethylene pellets) was heated and melted at a temperature of  $200\text{--}220^\circ\text{C}$  in the extruder. The molten polymer was pressurized and continuously sent into the reactor by the extruder. Firstly,  $4\text{--}5 \text{ kg}$  of polymer was fed into the reactor. Then, the reactor was heated up to a reaction temperature at which the raw polymer thermally decomposed. It took  $30\text{--}60 \text{ min}$  for a liquid product to appear in the oil receiver, after reaching the degradation temperature of  $410\text{--}440^\circ\text{C}$  for polyethylene.

Meanwhile, the pressure in the reactor was kept at a fixed value by the pressure control valve. The elevation of pressure in the reactor was attained by the vapor pressure of the degradation product itself derived from polyethylene.

Volatile products from the reactor enter into the condenser, where they are cooled and separated into a gaseous product (not condensable with cooling water temperature) and a liquid product (condensate).

When volatile products began to be observed, an aliquot amount of raw material corresponding to the output was continuously fed into the reactor by the extruder. The rate of feed input was gradually adjusted to that of product output in order to keep an amount of reactor contents constant as shown in Fig. 3. Eventually, not only the amount of reactor contents became constant under a fixed temperature and a pressure, but also the concentration of C–C double bonds in reactor contents attained a steady state [14].

As the original polyethylene contains only a small amount of ash and Conradson carbon as shown in Table 1, this reactor system can attain a steady state without any appreciable accu-

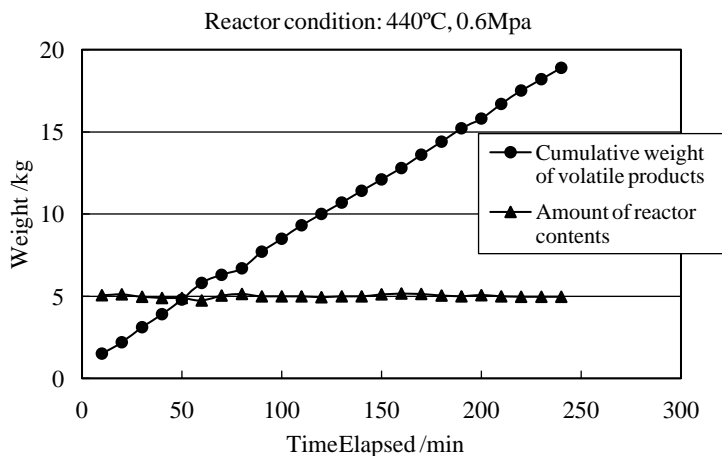


Fig. 3. Cumulative weight of volatile products and amount of reactor contents.

mulation of residues [13–17]. All of the observed results in this investigation were obtained under the conditions where negligible accumulation of residues in the reactor was found.

In this paper, “volatile products” represents “gaseous product” plus “liquid product”, and “degradation products” refers to “volatile products” and “reactor contents”.

The gaseous product consisted of low molecular weight hydrocarbons which were not condensable with cooling water temperature; the liquid product was a condensate which consisted of a series of hydrocarbons; and the reactor contents were in the form of liquid under the degradation condition. They are degradation products of the original polymer, but the molecular weight was not small enough to leave the reactor during volatilization. They could be intermediates which established a dynamic equilibrium in the system. The reactor contents also consisted of a lot of hydrocarbon compounds, such as oligomers and polymers, even though their molecular weights were lower than that of the original polymer. They remain in the reactor for as long as the thermal degradation is in progress.

The continuous flow operation was carried out until the cumulative weight of volatile product exceeded three times the amount of reactor contents. A sample of gaseous product was collected in a Teflon bag before passing through the seal pot. After finishing the operation, the reactor was cooled down and the reactor contents were withdrawn from the reactor bottom. The observed amount of reactor contents agreed with the theoretical value within a range of  $\pm 1.0\%$  throughout the experimental run.

It is necessary to know the specific gravity of the liquid product and the average molecular weight of the gaseous product before calculation of the weight of volatile product on the basis of the observed volumetric data. These indispensable values have been previously estimated on the basis of the author’s thesis [18].

### 2.3. Analytical methods

Gaseous products were analyzed using a gas chromatograph with a Molecular Sieve 13X column and a TCD detector at 40 °C using argon as carrier gas for analysis of hydrogen; and

a diatom Earth with di-*n*-butyl maleate column and a TCD detector at 40 °C using hydrogen as carrier for hydrocarbon gases analysis.

Liquid products were analyzed by a gas chromatograph with a DB-1 capillary column (60 m × 0.252 mm i.d., 0.25 μm film thickness) using a temperature program from 40 to 280 °C at a heating rate of 5 °C min<sup>-1</sup> and a FID detector. Specific gravity was determined by a float method. Average molecular weight of the liquid product was determined by the freezing point depression of benzene.

Reactor contents were analyzed with a gel permeation chromatograph (Waters 150C ALC/GPC) with two Shodex AT-806M/S columns (250 mm × 8 mm i.d.) in ODCB (0.1 ml min<sup>-1</sup>) at 140 °C and a RI detector calibrated by styrene oligomers. The sample was dissolved in ODCB at 140 °C for 1 h and passed through 0.5 μm filter before GPC analysis. Average molecular weight of the reactor contents was determined by the elevation of boiling point of toluene.

### 3. Results and discussion

#### 3.1. Rate of thermal degradation and characteristics of reactor

##### 3.1.1. Rate of thermal degradation

Fig. 3 shows plot of the cumulative weight of volatile products (gas + liquid) and the amount of reactor contents observed with the time during thermal degradation of polyethylene by continuous flow operation at 440 °C, 0.6 MPa. The cumulative curve gradually approaches a straight line, which indicates a steady state attained by this continuous flow operation. The slope of cumulative weight corresponds to the production rate of volatile products. Likewise, a plot of cumulative weight of the input material revealed a similar curve having the same slope as volatile products. The amount of reactor contents ( $\Delta w$ ) is equal to the difference between the cumulative input ( $w_{in}$ ) and the cumulative output ( $w_{out}$ ), i.e.

$$\Delta w = w_{in} - w_{out} \quad (1)$$

Fig. 4 shows the rate of volatilization observed during thermal degradation of polyethylene under elevated pressures and temperatures. The definition of the rate of volatilization is given by Eq. (2). The rate of volatilization is determined based on the production rate which corresponds to the slope of cumulative weight of volatile products, such as shown in Fig. 3, and the amount of reactor contents,  $\Delta w$ , given by Eq. (1).

$$\text{rate of volatilization (h}^{-1}\text{)} = \frac{\text{production rate (kg h}^{-1}\text{)}}{\text{amount of reactor contents (kg)}} \quad (2)$$

It is clear from Fig. 4 that the degradation pressure has substantial effect on the rate of volatilization as well as the degradation temperature.

Fig. 5 shows the observed rate of double bond formation in thermal degradation of polyethylene at various temperatures and pressures. As the raw polymer contains a negligible amount of double bonds, the rate of double bond formation is given by Eq. (3) under a steady state. The amount of C=C bonds in volatile was determined based on the iodine number

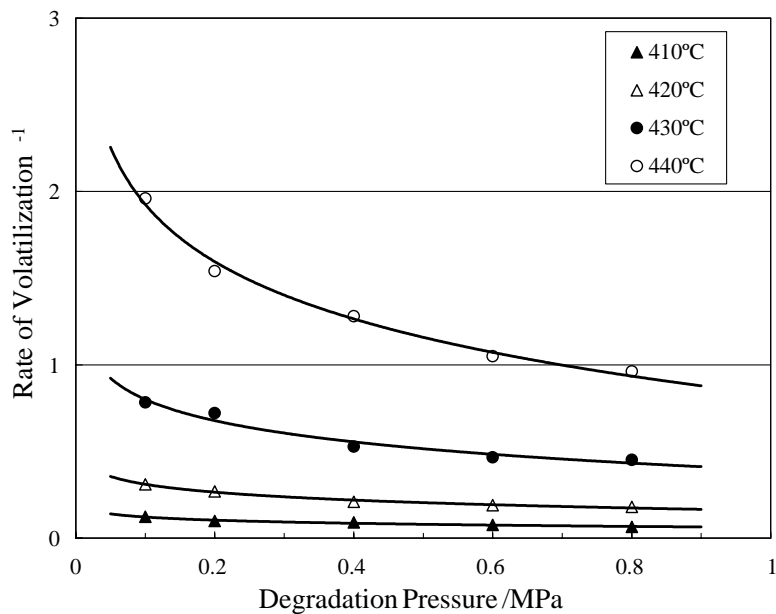


Fig. 4. Effect of temperature and pressure on the rate of volatilization.

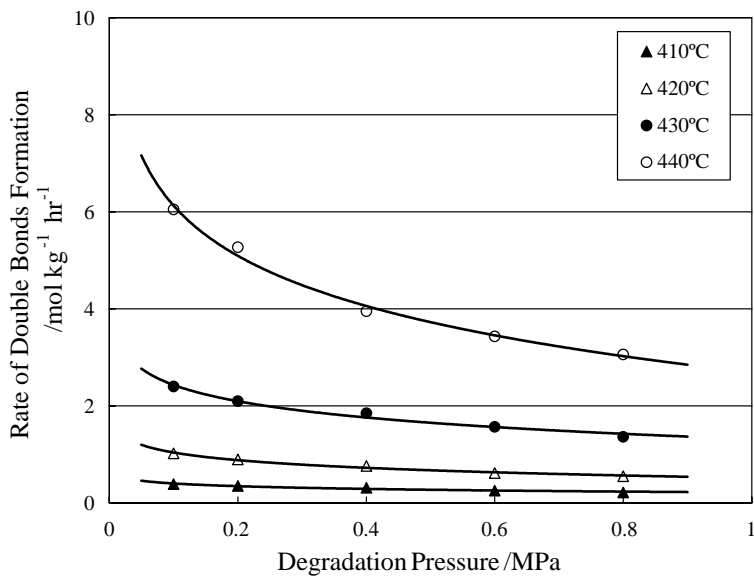


Fig. 5. Effect of temperature and pressure on the rate of double bond formation.

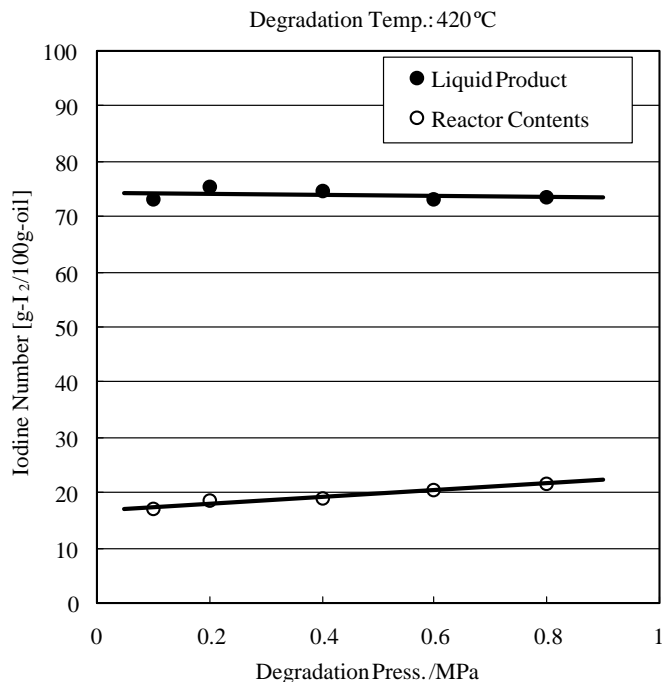


Fig. 6. Iodine number of the liquid product and reactor contents.

of liquid product and the gas chromatography data of gaseous product. Observed iodine numbers were plotted in Fig. 6 for the liquid product and the reactor contents of polyethylene degraded at 420 °C.

$$\text{rate of double bond formation (mol kg}^{-1} \text{ h}^{-1}) = \frac{\text{C=C bonds in volatile (mol h}^{-1})}{\text{amount of reactor contents (kg)}} \quad (3)$$

Fig. 5 shows that the degradation pressure also has substantial effect on the rate of double bond formation as well as the degradation temperature.

Based on Arrhenius plots of the rate of volatilization (Fig. 4) and the rate of double bond formation (Fig. 5), the activation energies of thermal degradation of polyethylene were calculated and plotted in Fig. 7. Generally speaking, when a physicochemical process has an activation energy of less than 40 kJ mol<sup>-1</sup>, a physical process takes a role of rate controlling step. On the contrary, when the activation energy is greater than 120 kJ mol<sup>-1</sup>, we conclude that a chemical reaction plays the role of rate controlling step in that process [19].

As the both of activation energies of thermal degradation of polyethylene are much higher than 120 kJ mol<sup>-1</sup>, as shown in Fig. 7, it is evident that the thermal degradation of polyethylene in this reactor system is a chemical reaction dominant process. All of the



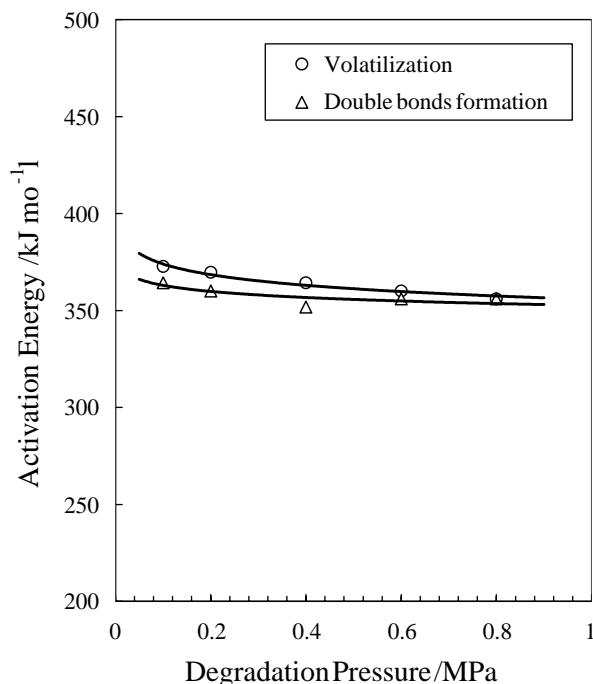


Fig. 7. Activation energies calculated on the basis of the rate of volatilization and the rate of double bond formation.

activation energies calculated from thermogravimetric analysis in the literature support this conclusion [20–23].

As shown in Figs. 4 and 5, the reaction pressure has significant effect on the thermal degradation rate of polyethylene. The double bond in degradation products is a direct measure for the scission of C–C links in polymer, because there exists a one to one correspondence between the scission of C–C links and the formation of double bonds during thermal degradation of polymers [1]. The observed pressure effect on the rate of double bond formation brings about a definite conclusion that the reaction pressure directly affects the scission rate of C–C links in polymers.

### 3.1.2. Characteristics of continuous flow reactor

The fact that there is a gas–liquid interface in the reactor leads to an important conclusion that the residence time in DVR is not an independent operation variable. Once we choose a temperature and a pressure for a degradation run, the whole behavior on thermal degradation of a given polymer, such as degradation rate, product compositions and so on, must be determined in the DVR system.

The definition of residence time in DVR is given by:

$$\text{residence time (h)} = \frac{\text{amount of reactor contents (kg)}}{\text{feed rate (kg h}^{-1}\text{)}} \quad (4)$$

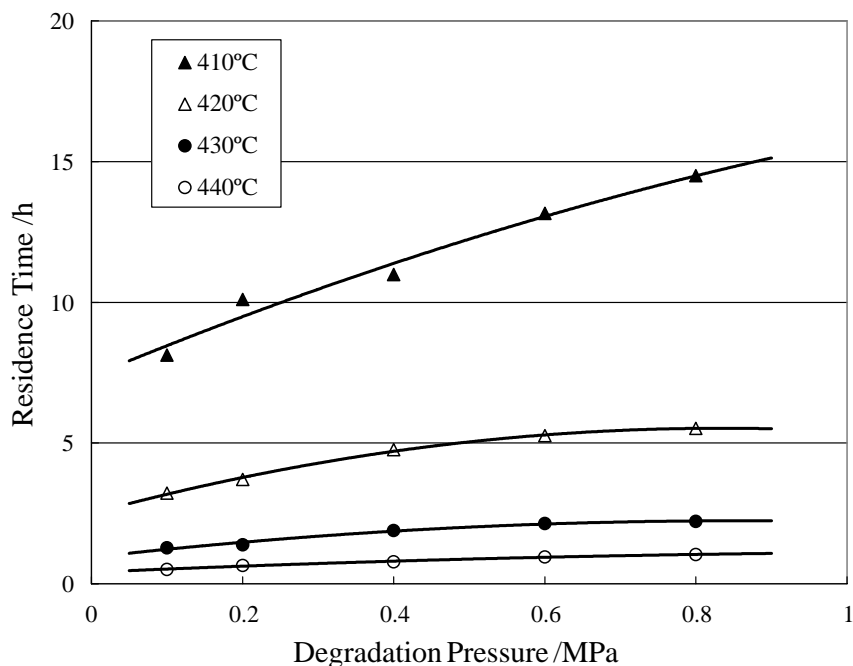


Fig. 8. Effect of temperature and pressure on the residence time in reactor.

In DVR, the feed rate of raw polymer is equal to the production rate of volatile products. Depending on this condition, Eqs. (2) and (4) make Eq. (5), i.e.

$$\text{residence time (h)} = \frac{1}{\text{rate of volatilization (h}^{-1}\text{)}} \quad (5)$$

Eq. (5) reveals the residence time in DVR is the reciprocal of the rate of volatilization. Moreover, the residence time in DVR is not an independent variable, but an observed value, which is to be determined at a fixed temperature and a pressure. Fig. 8 shows the observed residence time in DVR for thermal degradation of polyethylene, which corresponds to the reciprocal of the rate of volatilization shown in Fig. 4. The residence time depends on the reaction pressure and temperature in the same way as the rate of volatilization.

Therefore, the significance of residence time in DVR is different from that in a continuous flow mixed reactor for homogeneous reaction in which the retention value is independently chosen as an operation variable. The following consideration leads to the same conclusion.

In DVR, all kinds of behaviors involved in thermal degradation of polymers, e.g. rate of degradation, composition of products and so on, can be expressed by a function, such as:

$$X = f_0(P, T, \tau) \quad (6)$$

where  $X$  is a behavior involved in thermal degradation of a given polymer,  $P$  the reaction pressure,  $T$  the reaction temperature, and  $\tau$  the residence time.

For the rate of volatilization ( $r$ ), we introduce Eq. (7):

$$r = f_1(P, T, \tau) \quad (7)$$

Substituting Eq. (5) in Eq. (7) gives:

$$r = f_1\left(P, T, \frac{1}{r}\right) \quad (8)$$

Explicit expression for  $r$  is:

$$r = f_2(P, T) \quad (9)$$

Substituting Eq. (9) in Eq. (6) gives:

$$X = f_0\left(P, T, \frac{1}{f_2(P, T)}\right) = f_3(P, T) \quad (10)$$

Eq. (10) shows that the whole behavior on thermal degradation of a given polymer is to be determined, once we choose a temperature and a pressure for a degradation run. DVR is a system that gives intrinsic properties of a polymer on thermal degradation, as there are no independent variable other than temperature and pressure in the system.

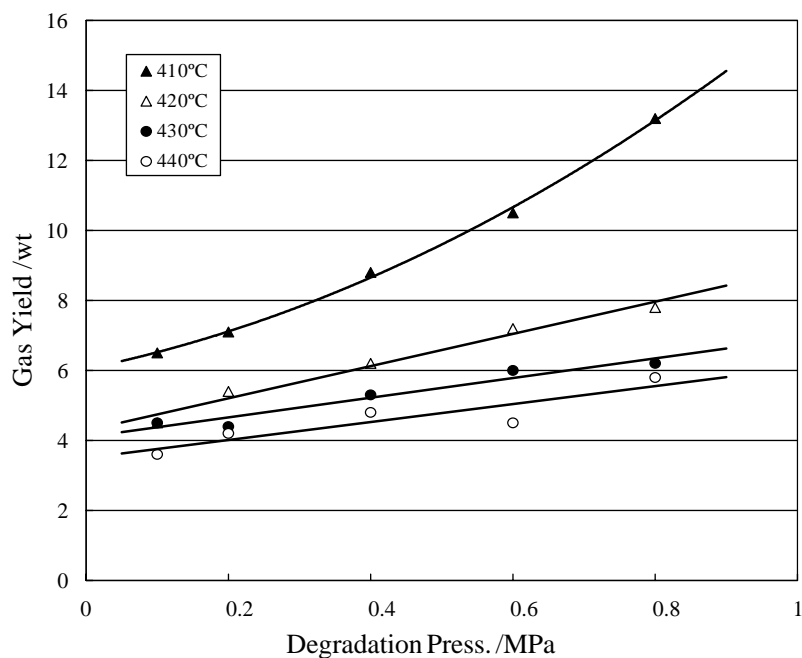


Fig. 9. Yield of the gaseous product, gas/(gas + liquid).

Table 2  
Composition of gaseous products

Component	Composition (mol%)			
	410 °C, 0.1 MPa	410 °C, 0.8 MPa	440 °C, 0.1 MPa	440 °C, 0.8 MPa
H <sub>2</sub>	4.9	5.2	3.0	2.1
CH <sub>4</sub>	16.6	20.5	8.9	19.5
C <sub>2</sub> H <sub>6</sub>	19.3	25.5	11.8	22.7
C <sub>2</sub> H <sub>4</sub>	6.8	3.3	7.1	5.0
C <sub>3</sub> H <sub>8</sub>	15.3	18.8	13.7	17.4
C <sub>3</sub> H <sub>6</sub>	17.8	12.4	16.5	13.8
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.1	0.2	0.3	0.4
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	4.8	5.0	8.4	6.9
1-C <sub>4</sub> H <sub>8</sub>	3.9	2.2	7.3	3.9
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	1.7	1.4	3.7	2.6
2-C <sub>4</sub> H <sub>8</sub>	0.9	0.7	0.1	0.1
1,3-C <sub>4</sub> H <sub>6</sub>	2.1	1.8	1.1	0.2
C <sub>5</sub> -	5.7	3.0	11.8	4.5
C <sub>6</sub> -	0.1	0.0	6.3	0.9
Average <i>M</i> <sub>n</sub>	36.3	33.9	45.4	36.8

### 3.2. Degradation products

#### 3.2.1. Gaseous product

Fig. 9 shows the yield of the gaseous product derived by thermal degradation of polyethylene. The yield of the gaseous product increases with the increase of pressure and decreases with the increase of temperature.

Table 2 shows the composition of the gaseous product. The gaseous product derived from polyethylene consisted of mainly methane, ethane, ethylene, propane, propylene, C4 components, and small amount of hydrogen. Above all, C2 (ethane, ethylene) and C3 (propane, propylene) were major components in the gaseous product.

The reaction pressure and temperature have remarkable effects on the composition of the gaseous product. The higher the temperature or the lower the pressure, the greater the amount of 1-olefins, such as ethylene, propylene and butene, although alkanes, such as methane, ethane and propane exhibit an opposite behavior. The average molecular weight of the gaseous product decreases with the higher pressure and increases with the temperature as shown in Fig. 10.

#### 3.2.2. Liquid product

Based on the condition that the input rate of raw polymer is equal to the output rate of volatile products in DVR, the yield of the liquid product in thermal degradation of polymers is given by:

$$\text{yield of liquid product (wt.\%)} = 100 - \text{yield of gaseous product (wt.\%)} \quad (11)$$

From Eq. (11) and the yield of the gaseous products shown in Fig. 9, the yield of the liquid product in this continuous flow operation for polyethylene was 86.8–96.4 wt.%,

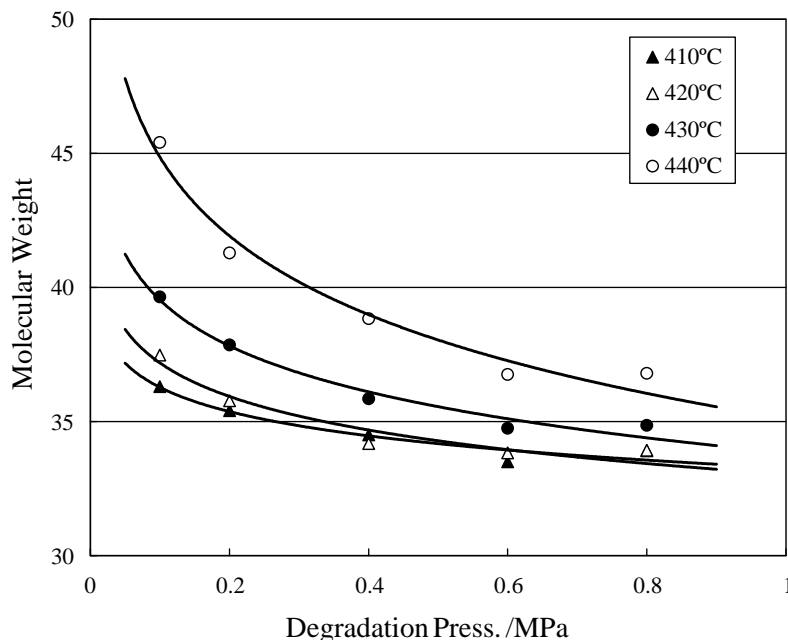


Fig. 10. Average molecular weight of the gaseous product.

depending on the reaction pressure and temperature. The liquid product from polyethylene was yellowish and clear oil. The carbon number distribution and the average molecular weight are shown in Figs. 11 and 12, respectively.

With the higher pressure or the lower temperature, the carbon number distribution of the liquid product shifts to the lower molecular weight side. Accordingly, the average molecular weight of the liquid product decreases with the higher pressure or the lower temperature.

The iodine number of the liquid product was previously shown in Fig. 6. The reaction pressure does not give any appreciable change of the iodine number of the liquid product in spite of decreasing of the molecular weight. This fact indicates that olefinic compounds in the liquid product increase in a similar manner to the gaseous product.

### 3.2.3. Reactor contents

Reactor contents were brown solid at ambient temperature, even though they melted at temperatures above 150 °C and became liquid at degradation temperature. A visual inspection of reactor contents of polyethylene during thermal degradation reveals a liquid generating a great deal of small bubbles in a similar manner to the distillation of kerosene [24].

Their molecular weight distribution and average molecular weight are presented in Figs. 13 and 14, respectively, and the iodine number was previously shown in Fig. 6. Figs. 13 and 14 demonstrate the reaction pressure has a significant effect on the molecular weight distribution of reactor contents.

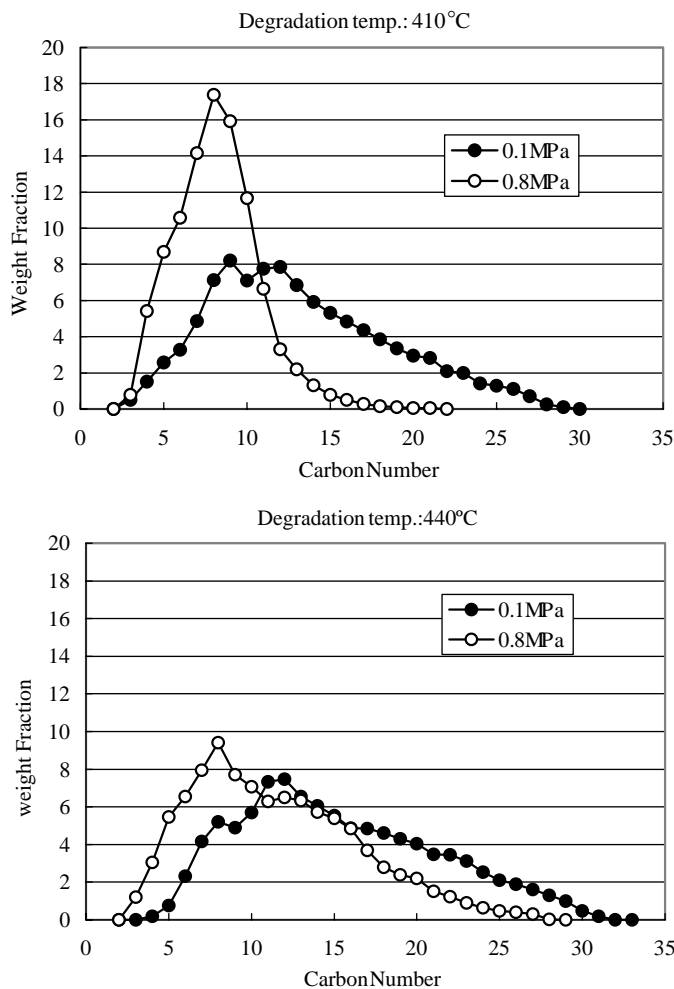


Fig. 11. Carbon number distributions of the liquid product.

The molecular weight distribution of reactor contents shifts to the lower molecular weight side with the higher pressure, and to the higher side with the higher temperature. Similarly, the average molecular weight of reactor contents decreases with the higher pressure and increases with the higher temperature.

### 3.3. Mechanistic considerations

#### 3.3.1. Pressure effect on thermal degradation of polymers

Based on the following considerations, we can conclude that the reaction pressure takes part in the reaction itself during thermal degradation of polymers:

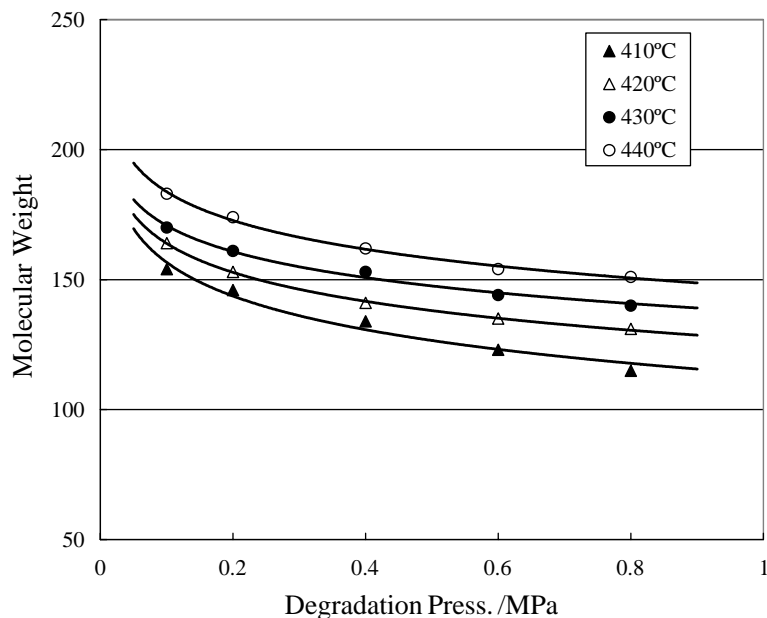


Fig. 12. Average molecular weight of the liquid product.

- (1) The rate of double bond formation decreases with the increase of reaction pressure, as shown in Fig. 5. Since there exists a one to one correspondence between the double bond formation and the scission of C–C links in polymers, we can conclude that the reaction pressure takes part directly in the scission of C–C links in polymers.
- (2) For the increase of reaction pressure from 0.1 to 0.8 MPa, the rate of volatilization decreases to about a half, as shown in Fig. 4. On the other hand, the average molecular weight of volatile products decreases to about five-sixth, based on the data shown in Figs. 9, 10 and 12. It thus follows that the molar base rate of volatilization, that is, the number of scission times, decreases to three fifth for the elevation of pressure from 0.1 to 0.8 MPa. We can conclude that the reaction pressure takes part directly in the scission of C–C links in polymers.
- (3) As mentioned in Section 3.1.1, the thermal degradation of polymers in the DVR system is a chemical reaction dominant process. Since there is no independent variable other than temperature and pressure in DVR as mentioned in Section 3.1.2, the observed fact that the reaction pressure has a significant effect on thermal degradation behavior of polyethylene under a fixed temperature, certifies that the reaction pressure is involved in the reaction itself during thermal degradation of polymers.

### 3.3.2. Two sorts of scission in thermal degradation of polymers

With the higher reaction pressure, the molecular weight distribution of reactor contents shifts to the lower molecular weight side, and with the higher temperature to the higher side, as shown in Figs. 13 and 14. This behavior of reactor contents in DVR is related to

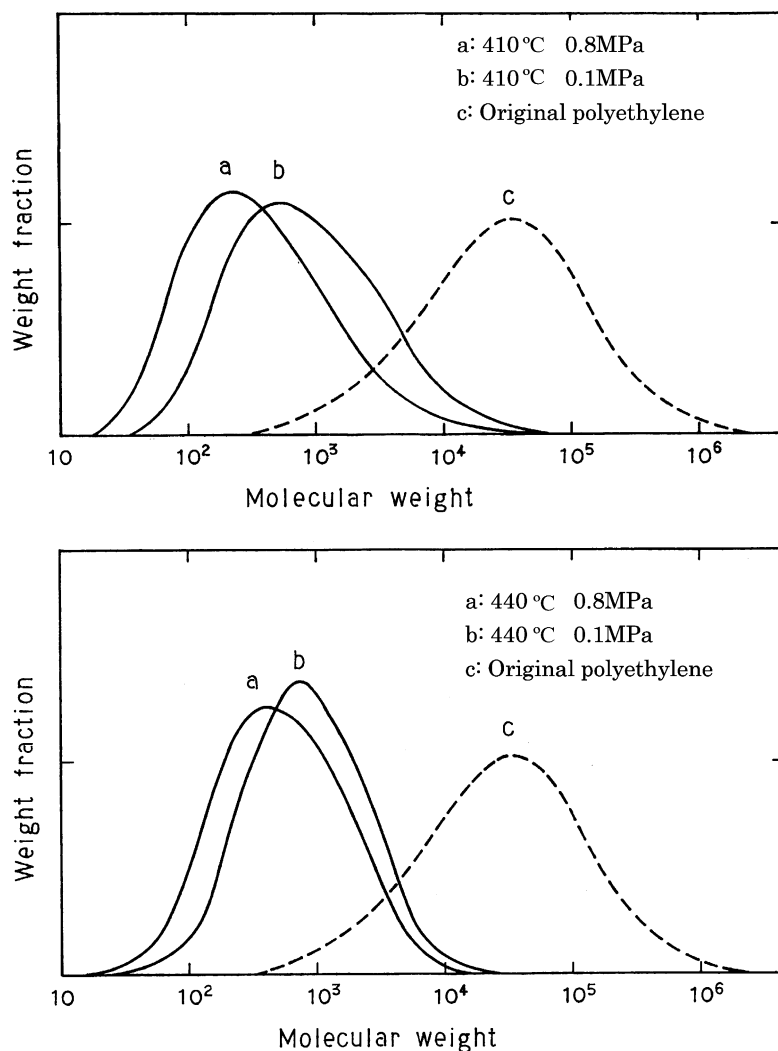


Fig. 13. Molecular weight distributions of reactor contents.

the mechanism that the thermal degradation of polymers consists of two sorts of scission which simultaneously occur in a manner mentioned in the preceding paper [13].

One is a random scission, and the other is a chain-end scission. The random scission of C–C links in polymers causes a molecular weight reduction of raw polymer increasing reactor contents, and the chain-end scission of C–C links causes a dissipation of reactor contents generating volatile products. The rate of random scission is proportional to the number of C–C links and the rate of chain-end scission is proportional to the number of molecules. It is the chain-end scission that the reaction pressure has an effect on. It takes place at a gas–liquid interface generating volatile products in such a manner as shown in



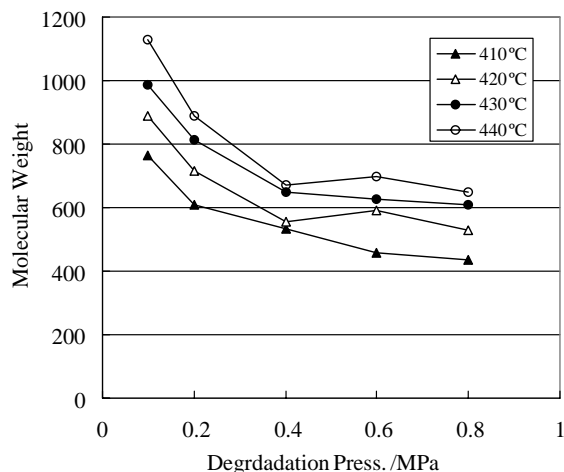


Fig. 14. Average molecular weight of reactor contents.

Fig. 1. On the other hand, the random scission does not exhibit any appreciable effect with pressure, since it takes place in liquid phase.

Arrhenius plots of the rate of volatilization observed at various pressures in the present work and the rate constant of random scission of polyethylene reported by Inoue et al. are shown in Fig. 15. The rate of chain-end scission is substituted by the rate of volatilization in Fig. 15, for the reason that a generation of volatile products during the chain-end scission corresponds to the volatilization of product.

Fig. 15 shows that the elevation of reaction pressure causes a decline in the rate of volatilization during the rate of random scission keeping constant under a fixed temperature. The relative increase in the rate of random scission to the rate of chain-end scission brings about a shift to the lower molecular weight side for the molecular weight distribution of reactor contents as shown in Figs. 13 and 14.

With the increase of reaction temperature, the distribution of reactor contents shifts to the higher molecular weight side as shown in Figs. 13 and 14. This behavior of reactor contents can be interpreted as follows.

As shown in Fig. 15, the activation energy of chain-end scission ( $370 \text{ kJ mol}^{-1}$ ) is larger than that of random scission ( $268 \text{ kJ mol}^{-1}$ ). Thus, for the elevation of temperature, the rate of chain-end scission increases more than that of random scission. As the dissipation rate of reactor contents caused by chain-end scission relatively exceeds the production rate of reactor contents caused by random scission, it brings about a shift to the higher molecular weight side for the distribution of reactor contents.

### 3.3.3. The behavior of liquid product

With the higher reaction temperature, the molecular weight distribution of liquid product shifts to the higher molecular weight side, and with the higher pressure it shifts to the lower side, as shown in Figs. 11 and 12. This behavior in thermal degradation of polymers

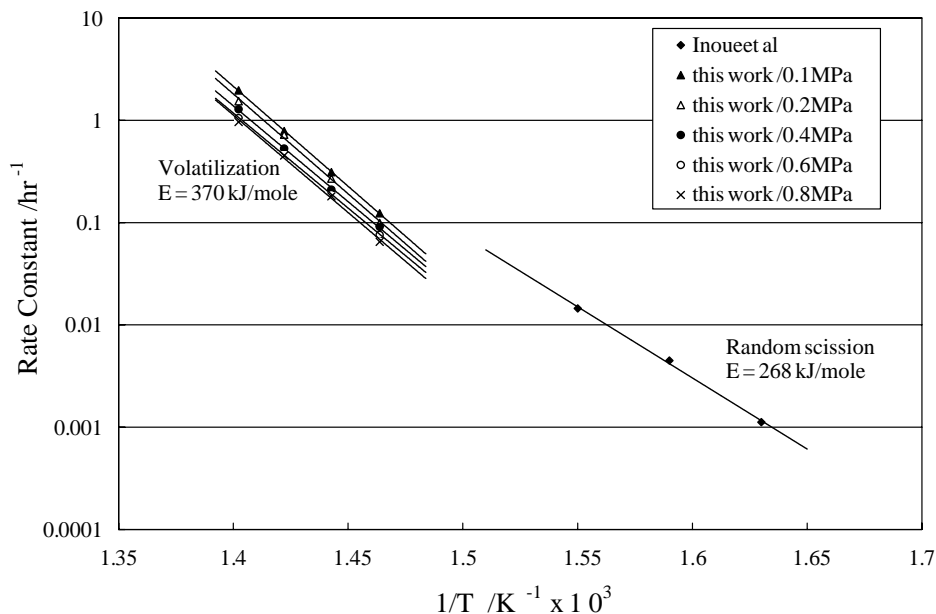


Fig. 15. Arrhenius plots of the volatilization rate observed at various pressures in this work and the rate constant of random scission of polyethylene reported by Inoue et al. [25].

is related to the chain-end scission which takes place at a gas–liquid interface generating liquid products in a manner as shown in Fig. 1.

With the higher reaction temperature, it generates the longer chain products, because it increases the kinetic energy to cause a vehement movement for chain-ends of oligomers and/or polymers constituting the reactor contents. On the contrary, with the higher reaction pressure, it generates the shorter chain products, because it suppresses the movement of chain-ends.

### 3.3.4. Temperature difference between gas and liquid phase

When a simple vaporization of a liquid occurs in DVR, there will not be an appreciable difference in temperature between vapor and liquid phase. In a process of vaporization, the change of state from liquid to vapor compensates the latent heat of vaporization. But for the thermal degradation of polymers in DVR, the change from the liquid (reactor contents) to the gas (volatile products) involves the change of substance as well as the state.

When we attempt to estimate an enthalpy change from state A to B in a system, we can choose any route going from state A to B according to Hess's law. In order to estimate the enthalpy change from reactor contents to volatile products in DVR, we choose a route along that reactor contents vaporize into gas phase and then decompose to volatile products.

For the resultant change of state from reactor contents to volatile products, the heat of vaporization is compensated by the change of state, but the heat of thermal degradation must be compensated by the heat capacity of volatile products. Exactly, there must exist

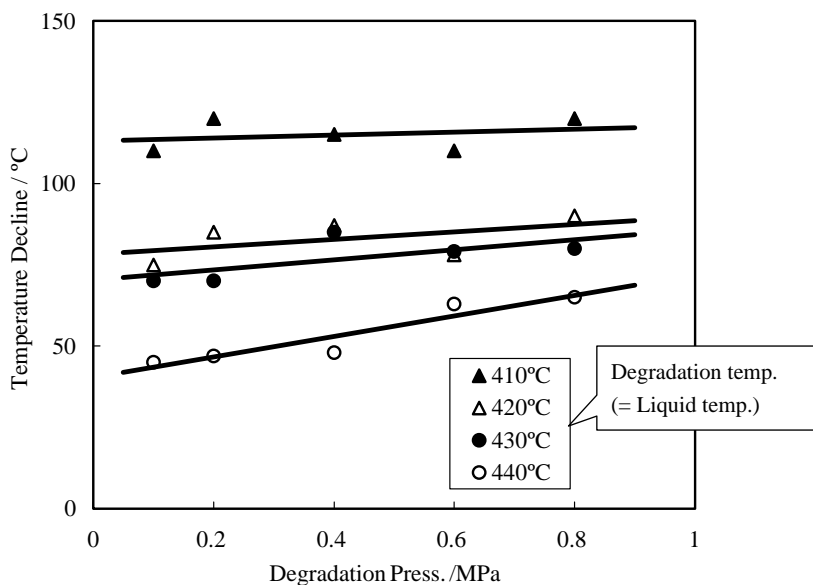


Fig. 16. Temperature decline from liquid to gas phase in continuous reactor.

a temperature decline from the liquid phase (reactor contents) to the gas phase (volatile products) to counterbalance the heat of thermal degradation.

Fig. 16 shows the observed decline in temperature from the liquid phase to the gas phase in DVR. Four thermocouples were installed at different levels in the reactor as shown in Fig. 2. During operation, the liquid level was kept in between thermocouple T2 and T3. Practically, we could know the liquid level by the temperature difference in thermocouple T2 and T3. Throughout the experimental run, thermocouples T3 and T4 showed the same temperature and thermocouples T1 and T2 did too at a lower level than T3 and T4.

Because the enthalpy change from reactor contents to volatile products in DVR involves not only the heat of vaporization but also the heat of thermal degradation, it is not enough for the heat of vaporization to compensate the change of state from liquid to gas. Thus, it brings about a temperature decline from reactor contents to volatile products.

As shown in Fig. 16, there appeared a significant difference in temperature between gas and liquid phase in DVR. Provided that the chain-end scission of C–C bonds takes place at a gas–liquid interface in working reactor, volatile products must lose as much kinetic energy (equivalent to temperature) as the heat of scission of C–C links. The observed temperature decline from liquid to gas phase supports definitely the mechanistic consideration previously mentioned by the authors in the preceding paper [13] and in this paper.

### 3.3.5. Decomposition in the gaseous portion of reactor

Iodine number indicates about the level of unsaturation (double bonds), i.e. the higher the iodine number, the higher the double bonds. It seems that there is no formation of double

bonds once the volatile products leave the gas–liquid interface, even with the increase of pressure from 0.1 to 0.8 MPa, as shown in Fig. 6.

The volatile products do not decompose during passing through the gaseous portion of reactor, because the rate of thermal degradation decreases with the increase of pressure, as shown in Figs. 4 and 5, even though the residence time for the volatile products in the gaseous portion of reactor increases with the increase of pressure.

#### 4. Conclusions

A thermal degradation of polyethylene was carried out in a stirred tank reactor by continuous flow operation under elevated pressures ranging from 0.1 to 0.8 MPa, in order to investigate the effect of pressure on the degradation rate and the product distribution. From the observed results and discussion, we can conclude as follows:

- The reaction pressure takes part directly in the scission of C–C links during thermal degradation of polymers.
- The thermal degradation of polymers consists of two sorts of scission, which simultaneously occur in reactor. One is a random scission, and the other is a chain-end scission. The random scission of C–C links in polymers causes a molecular weight reduction of raw polymer increasing reactor contents, and the chain-end scission of C–C links causes a dissipation of reactor contents generating volatile products. The rate of random scission is proportional to the number of C–C links and the rate of chain-end scission is proportional to the number of molecules. It is the chain-end scission that the reaction pressure has an effect on. It takes place at a gas–liquid interface generating volatile products in such a manner as shown in Fig. 1. On the other hand, the random scission does not exhibit any appreciable effect of pressure, since it takes place in liquid phase.
- Consequently, the volatilization of product during thermal degradation of polymers is a heterogeneous reaction in which the reactant is in a liquid phase and the product is in a gas phase.
- The observed temperature decline from liquid to gas phase in DVR supports the mechanistic consideration mentioned in the preceding paper [13] and in this paper.
- Hereafter, it is required to investigate the consistency between the macroscopic mechanism mentioned in this paper and the microscopic mechanism mentioned in the literature that is composed of initiation, depolymerization, back biting, radical transfer and termination.
- The elevation of pressure during thermal degradation provides a potential alternative to control the product distribution in a process for converting waste plastics into liquid hydrocarbons, which could be used as feedstock material.

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## References

- [1] W.G. Oakes, R.B. Richards, *J. Chem. Soc.* (1949) 2929.
- [2] R. Simha, L.A. Wall, *J. Phys. Chem.* 56 (1952) 707.
- [3] E. Kiran, J.K. Gillham, *J. Appl. Polym. Sci.* 20 (1976) 2045.
- [4] S.L. Madorsky, S. Straus, *J. Res. Natl. Bur. Stand.* 53 (1954) 361.
- [5] J.V. Schooten, P.W.O. Wijgo, *Thermal Degradation of Polymers*, Monograph no. 13, Society of Chemical Industry, London, 1961, p. 432.
- [6] T.E. Davis, R.L. Tobias, E.B. Peterli, *J. Polym. Sci.* 56 (1962) 485.
- [7] H. Staudinger, A. Steinhofner, *Ann. Chem.* 571 (1935) 35.
- [8] S.L. Malhotra, L. Hesse, L.P. Blanchard, *Polymer* 16 (1975) 81.
- [9] G. Audisio, F. Bertini, *J. Anal. Appl. Pyrolysis* 24 (1992) 61.
- [10] Y. Tsuchiya, K. Sumi, *J. Polym. Sci. A* 7 (1969) 813.
- [11] R.P. Lattimer, *J. Anal. Appl. Pyrolysis* 31 (1995) 203.
- [12] M.R. Grimbley, R.S. Lehrle, *Polym. Degrad. Stab.* 48 (1995) 441.
- [13] K. Murata, Y. Hirano, M.A. Uddin, Y. Sakata, *J. Anal. Appl. Pyrolysis* 65 (2002) 71.
- [14] K. Murata, T. Makino, *Nippon Kagaku Kaishi* (1973) 2414.
- [15] K. Murata, K. Sato, H. Teshima, *Kagaku Kagaku Ronbunshu* 7 (1981) 64.
- [16] K. Murata, K. Sato, *Kagaku Kagaku Ronbunshu* 8 (1982) 279.
- [17] K. Murata, K. Sato, *Nenryo Kyokaishi* 61 (1982) 776.
- [18] K. Murata, Doctor thesis, Tokyo University, 1984.
- [19] O. Levenspiel, *Chemical Reaction Engineering*, second ed., Wiley, New York, 1972, p. 491.
- [20] D.A. Anderson, E.S. Freeman, *J. Polym. Sci.* 54 (1961) 253.
- [21] R.M. Fuoss, I.O. Salyer, H.S. Wilson, *J. Polym. Sci. A* 2 (1964) 3147.
- [22] A.B. Mathur, V. Kumar, A.K. Nagpal, G.N. Mathur, *Indian J. Technol.* 19 (1981) 89.
- [23] H. Nishizaki, K. Yoshida, J.H. Wang, *J. Appl. Polym. Sci.* 25 (1980) 2869.
- [24] Y. Sakata, M.A. Uddin, K. Koizumi, K. Murata, *Polym. Degrad. Stab.* 53 (1996) 111.
- [25] R. Inoue, S. Ouchi, S. Yasuhira, *Kobunshi Kagaku* 13 (1955) 38.