Gasification of Polyethylene over Solid Catalysts (Part 2)*

—Gasification over Glass Beads by a Fixed Bed Tubular Flow Reactor—

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Summary: Fundamental gasification-degradation of polyethylene (PE) over glass beads was studied by the use of a fixed bed tubular flow reactor at 486~562°C, as the beginning in researches for direct catalytic gasification of PE by the flow system. Gasification of PE over glass beads proceeded stationarily without depending on reaction time in every reaction condition. The degree of gasification (R_{gF}) or the rate of it increased with contact time and exponentially with temperature. An empirical relationship among R_{gF} , contact time ($1/F$) and temperature was found to be:

$$R_{gF} = 1.56 \times 10^6 \exp\left(-\frac{32,500}{RT}\right) \left(\frac{1}{F}\right)^{0.467}$$

where F is the mass flow rate of PE melted.

Product composition ($\leq C_8$ -hydrocarbon fractions) shifted to smaller fractions with temperature rise, but the amount of methane was slightly 5.5% and 16% of all gaseous products at 486°C ($R_{gF}=0.023$) and 562°C ($R_{gF}=0.204$), respectively. Ratio of olefin to paraffin for $C_2\sim C_4$ fractions increased with the rise of temperature and $1/F$, and the ratio for C_4 fraction went up to 4 at 562°C and 22 min/g-PE. On the other hand, product composition and ratios of olefin to paraffin did not depend on reaction time in every condition.

1 Introduction

In the preceding paper¹⁾, catalytic gasification-degradation of polyethylene (PE) over various zeolites was studied with a batchwise reactor. The results suggested that X-type and Y-type zeolites and silica-alumina had higher activity and selectivity.

However, taking into considerations of industrial applications, controlling of contact time, and regenerations of deactivated catalysts, it is evident that a fixed bed flow reactor is superior to a batch reactor for such catalytic reactions as crackings of higher hydrocarbons.

In the present study, as the beginning in experimental works for direct catalytic gasification of PE by a conventional fixed bed flow reactor, gasification-degradation of PE over glass beads was carried out.

2 Experimental

2.1 Apparatus

Figure 1 shows a schematic diagram of the experimental apparatus, of which the principal

pieces consisted of a melter, neck, fixed bed tubular flow reactor and a trap, and were settled vertically.

The melter was made of a 3.0 cm i.d. Pyrex glass tubing 30 cm long. A branched pipe, which was used to evacuate gases in the melter and to charge nitrogen gas, was connected at a upper part of the melter. The melter was heated with heating wire wound around it. The neck was a section between the melter and the reactor and a 0.05 cm i.d. glass capillary 3.0 cm long, and the temperature of it was controlled within $\pm 1.0^\circ\text{C}$ of a given value. Mass flow rate of PE melted was controlled by the neck, its temperature and the pressure of nitrogen charged in the melter.

The fixed bed tubular flow reactor consisted of a 1.12 cm i.d. Pyrex glass tubing 13.5 cm long. The empty volume of the reactor was 15.6 ml and its void volume when 19.9 g of glass beads (average 0.41 cm ϕ) was packed was 8.27 ml. A helium stream carrying gaseous products in the reactor was introduced from a head of the reactor. Its flow rate at the inlet was 2.90 to 8.30 ml/min and was kept constant during a run. Variations in the flow rate at the outlet was followed by a soap film meter. The trap was also made of a 2.0 cm i.d. glass

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Fig. 1 Schematic Diagram of Fixed Bed Flow Reactor System

tubing 11.0 cm long and its temperature was kept at about 30°C. Gas sampler for gas chromatographs and the main path which stream of helium and product gases passed through was warmed with a flexible heater to avoid condensations of gaseous products.

2.2 Operations

About 60 to 70 g of PE was charged into the melter, in which the air was evacuated by a vacuum pump, replaced with nitrogen to avoid oxidation of PE, and then PE was heated up to about 300°C. After melting, gases containing in the fluid was evacuated until generation of bubbles disappeared. Again, nitrogen was charged into the melter and the pressure was kept constant (usually 0.3 kg/cm²·G) and was followed by a pressure gauge through a run.

Previous to the run, the reactor was heated up to a given temperature and the stream of helium with constant flow rate was passed through it. After these conditions were obtained, the neck was rapidly heated up to about 400°C. As soon as melted PE entered into the reactor, gases were rapidly formed by degradation and at the same time the flow rate of out gas increased quickly. The time when the quick increase began was realized as the beginning time of the reaction. Gasification-degradations of PE was carried out at 486~562°C for 2.5~3 hours.

Nonvolatile hydrocarbon fractions produced

were trapped and weighed for each 30 minutes, whereas volatile fractions were analyzed by two gas chromatographs.

2.3 Analysis

An active alumina TR column (0.4 cm ϕ $\times$ 450 cm) was used for analysis of C₁~C₄ fractions at 70°C and the cell current was 120 mA. For analysis of C₅~C₈ fractions an apiezon grease L column (0.4 cm ϕ $\times$ 200 cm) was used at 120°C and the cell current was 130 mA. Flow rates of helium carrier of both columns were 31.3 and 32.1 ml/min, respectively. Concentrations of fractions were determined on the basis of peak height of chromatograms and the relative mole responses in literature²⁾.

PE used was the same commercial sample as used in the preceding study¹⁾.

3 Results and Discussion

3.1 Determination of F and R_{GF}

A typical result is shown in Fig. 2. The total rate of formations of C₁~C₈ fractions or the rate of gasification of PE, including paraffin, olefins and isomers of each fraction, was calculated from concentrations of their fractions in out gas and the flow rate of out gas. The total rate of formations of liquid fractions*¹⁾ was determined as an average value by weighing of them taken out of the trap for each 30 minutes. The flow

*1 At room temperature, mixture of liquid fractions was waxen and showed a cream color. Analyses of their fractions were not carried out.

Fig. 2 Dependences of Rates of Formation of Total Gaseous Products and Liquid Products and R_{gF} on Reaction Time at 536°C and Flow Rate of He Carrier (F_{He}) = 2.90 ml/min

rate of melted PE (F) was given by sum of the rates of gasification and liquid fractions, and the time average values of it agreed with the rates of decrease of PE in the melter. Further, weight ratio (R_{gF}) of gaseous products to PE supplied at a given reaction condition represented the degree of gasification-degradation, *i.e.*, gasification of PE.

In Fig. 2, the rate of gasification and the total rate of formations of liquid fractions were constant without depending on reaction time, so was F , and consequently R_{gF} became constant.

3.2 Dependence of Product Composition on Reaction Time

Product compositions of gaseous products corresponding to the results in Fig. 2 are plotted against reaction time in Fig. 3, and an example of original data is shown in Table 1. M_i implies mole fraction of C_i fraction in all gaseous products, and α_i does ratio of olefin to paraffin of C_i fraction ($4 \geq i \geq 2$). All of M_i and α_i were independent of reaction time as found in Fig. 3.

From results in Figs. 2 and 3, it is evident that gasification of PE over glass beads proceeds stationarily from the first stage of the reaction at a given temperature and flow rate of melted

Fig. 3 Variations of M_i and α_i with Reaction Time at 536°C, $F=0.0741$ g/min, and $F_{He}=2.90$ ml/min

Table 1 A Typical Original Data*

Component	Concentration in Out Gas (vol%)	mol%	mol/min (STP) $\times 10^5$	g/min (STP) $\times 10^4$
CH ₄	6.43	11.8	1.76	2.82
C ₂ H ₆	6.15	11.2	1.68	5.06
C ₃ H ₈	5.23	9.6	1.43	6.31
<i>n</i> -C ₄ H ₁₀	3.37	6.2	0.92	5.33
C ₂ H ₄	10.30	18.9	2.82	7.90
C ₃ H ₆	9.38	17.1	2.56	10.79
<i>n</i> , <i>i</i> -C ₄ H ₈	4.62	8.4	1.26	7.09
C ₅	2.67	4.9	0.73	5.27
C ₆	3.58	6.6	0.98	8.43
C ₇ +C ₈	2.87	5.3	0.79	8.37
Total	54.6	100	14.9	67.4**

* Glass beads=19.9 g, Reaction temperature=536°C, Room temperature=17°C, Flow rate of He carrier in the reactor (F_{He})=2.90 ml/min, Flow rate of out gas=6.45 ml/min, Net flow rate of gaseous products=3.55 ml/min, Weight of liquid products per minute=2.02 g/30 min=6.74 $\times 10^{-2}$ g/min**;

** Flow rate of PE supplied (F)=6.74 $\times 10^{-2}$ + 67.4 $\times 10^{-4}$ g/min=0.0741 g/min.

PE.

Glass beads after the reactions showed a light blonde color, and carbon deposit was trace amount.

3.3 Effect of Flow Rate of Helium Stream

By changing the flow rate of helium stream (F_{He}) passing through the reactor, the rate of gasification and product composition are considered to be altered. Figure 4 shows dependences of the rate of gasification and the total formation rate of $C_1 \sim C_4$ fractions on F_{He} at $F=0.045$ g/min and 536°C. The two rates decreased with increasing in F_{He} . The decreases are estimated to result from the decrease in

Fig. 4 Effects of F_{H_0} on R_{gF} and Rates of Formation of Gaseous Products at 536°C and $F=0.0458$ g/min

Fig. 5 Dependence of R_{gF} on Reaction Temperature at $F_{H_0}=2.90$ ml/min and Different $(F)_{av}$

residence time or contact time of PE and the first degraded products, because the total formation rate of $C_1 \sim C_4$ fractions depended on F_{H_0} larger than the rate of gasification. However, none of α_1 depended almost on F_{H_0} .

3.4 Dependences of R_{gF} on Temperature and Contact Time

Dependences of R_{gF} on temperature were measured at three levels of F and at $F_{H_0}=2.90$ ml/min. The results are shown in Fig. 5. R_{gF} increased exponentially with temperature. Since R_{gF} corresponds to the rate of gasification and, as described above, is able to be considered as its initial value, apparent activation energy for the gasification at a constant value of F would be obtained. Arrhenius plots of R_{gF} are shown in Fig. 6. The slopes for three levels of F were

Fig. 6 Plots of Initial Rate of Gasification of PE, Constant k' of Eq. (2), and R_{gF} against $1/T$

Fig. 7 Variations of R_{gF} with Contact Time $1/F$ at $F_{H_0}=2.90$ ml/min

identical and $\Delta E=32.5$ kcal/mol was obtained.

Figure 7 shows dependences of R_{gF} on contact time $1/F$, which was used by considering the constancies of weight of glass beads and of void volume of the reactor.

If the gasification is first order reaction, the following equation would be satisfied.

$$\frac{dR_{gF}}{d(1/F)} = k(1 - R_{gF})$$

or

$$\ln\left(\frac{1}{1-R_{gF}}\right) = k\left(\frac{1}{F}\right) \quad (1)$$

where k is a rate constant.

However, although plots of $\ln\{1/(1-R_{gF})\}$ vs. $1/F$ were close to be linear, the lines were not drawn through the point of $R_{gF}=0$ and $1/F=0$. The reason would be considered to lie in the occurrences of further degradation of hydrocarbons produced in the earlier stage of degradation of PE.

Here, calculating the initial rates of gasification (v°) from extrapolations of $\Delta R_{gF}/\Delta(1/F)$ to $1/F \rightarrow 0$, $v^\circ = 0.37, 0.72, 1.32$, and 2.50×10^{-2} g/min were obtained at 486, 512, 536, and 562°C, respectively. These values satisfied Arrhenius equation (see Fig. 6) and gave the identical slope with R_{gF} vs. $1/T$ plots.

Further, plotting $\ln(R_{gF})$ vs. $\ln(1/F)$ in order to establish a relationship between their parameters, Fig. 8 was drawn^{*2}). Slopes of four lines were nearly equal (0.460~0.474) and an average value of 0.467 was obtained. Consequently, the following equation is established.

$$R_{gF} = k' \left(\frac{1}{F}\right)^{0.467} \quad (2)$$

where k' is constant. The values of k' obtained was 0.007, 0.015, 0.026, and 0.048 at 486, 512, 536, and 562°C, respectively. The plot of k' vs. $1/T$ is also shown in Fig. 6, and apparent activation energy based on the plot was identical with the value described above, too. So, the relationship among R_{gF} , $1/F$, and temperature is empirically represented by Eq. (3) in a simple form.

$$R_{gF} = 1.56 \times 10^6 \exp\left(-\frac{32,500}{RT}\right) \left(\frac{1}{F}\right)^{0.467} \quad (3)$$

Apparent activation energy for gasification of PE obtained here was close to 35 kcal/mol in the thermal degradation by a batch reactor¹). The difference was estimated to be related to difference in the range of fractions which were taken into account in the calculation of R_{gF} , i.e., in the batch reactor $C_1 \sim C_4$ fractions and in the present study $C_1 \sim C_8$ fractions. However, in the data stated above, apparent activation energy based on the total formation of $C_1 \sim C_4$ fractions was 32.6 kcal/mol. Consequently, since the difference in activation energy is small and

Reaction temperature— $\bigcirc$: 486°C, $\bigcirc$: 512°C, $\bullet$: 536°C, $\bigcirc$: 562°C

Fig. 8 Plots of $\ln(R_{gF})$ vs. $\ln(1/F)$

is evaluated to be due to that gasification of PE is promoted slightly by facility of heat transfer between fluid of PE and surface of glass beads, the gasification over glass beads would be estimated to be close to that in the thermal degradation, i.e., to proceed with a similar mechanism to the thermal degradation.

On activation energy of thermal degradation of PE, values of 68, 60~70, and 76.6 kcal/mol had been reported by Wall and Madorsky et al.^{3,7}), Oakes and Richards⁴), and Saito and Mitsui⁵), respectively. Comparing with these values, the value of 32.5 kcal/mol found by authors is too small, although the activation energy depends on molecular weight⁶) and amount of branching of PE³). As one of the causes, it would be estimated that when PE is melted and kept at about 300°C and also pass through the capillary keeping at about 400°C, mild degradations of PE occur already. Detailed works for the causes would be carried out in future.

3.5 Variation of Product Composition with Temperature

Variations of product composition and α_1 with temperature at $F=0.074$ g/min and $F_{H_2O}=2.90$ ml/min are shown in Figs. 9 and 10. As being expected, C_1 and C_2 fractions increased remarkably and others decreased with temperature. However, comparing with the results in the thermal degradation by a batch reactor¹), C_1 fraction was smaller remarkably, C_3 fraction was in the same order, C_4 fraction larger, and C_2 fraction was smaller only at lower temperature.

*2 The line at 486°C was drawn through points which were read in the line in Fig. 6 because R_{gF} at 486°C was very small and had larger experimental error.

Fig. 9 Dependence of M_i on Reaction Temperature at $(F)_{av} = 0.0735$ g/min and $F_{H_2} = 2.90$ ml/min

Fig. 10 Dependence of α_i on Reaction Temperature at $(F)_{av} = 0.0735$ g/min and $F_{H_2} = 2.90$ ml/min

Further, as found in **Fig. 10**, formations of olefins increased larger with temperature than that of the corresponding paraffins. The facts would be easily understood by considering that the degrading PE to smaller fractions results in the insufficient state of hydrogen atoms.

From these results, in order to recover more useful gaseous petrochemical raw materials, i.e., olefins, from PE, fixed bed flow reactor processes are evaluated to be superior to batch reactor operations, and at moderately higher temperature olefins would be obtained in good yield.

Fig. 11 Variations of M_i and α_i with Contact Time $1/F$ at 562°C and $F_{H_2} = 2.90$ ml/min

3.6 Variation of Product Composition with Contact Time

Relation between product composition or α_i and contact time is shown in **Fig. 11**. With contact time, $C_3 \sim C_8$ fractions decreased, C_1 and C_2 fractions increased gradually, and further α_3 and α_4 increased sharply and α_2 did mildly in linear forms. These results are attributable to that hydrocarbons produced in the earlier stage of degradation of PE are further degraded to smaller hydrocarbon molecules with contact time.

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