

Research in Thermal Cracking Properties of Waste Plastics

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Abstract:

Plastics generated as municipal solid waste are represented by polyethylene, polypropylene, polystyrene, and polyvinyl chloride. The thermal cracking properties of these waste plastics were studied to clarify their Arrhenius factors, among other things. The results of thermal cracking experiments conducted using an electric furnace confirmed that polyethylene, polypropylene, and polystyrene are materials suited for liquefaction into oil.

1. Introduction

On June 16, 1995, the Japanese government promulgated the new "Law for Promotion of Source-Separated Collection and Recycling of Containers and Packages (abbreviated to the Container and Package Recycling Law)" to reduce the generation of municipal solid waste (MSW) and to encourage the recycling of MSW. The law targets the recycling of solid wastes, such as bottles, cans, paper, and plastics. Liquefaction has potential as a technology for converting waste plastics into oil. Much time and labor have been expended in developing this technology prior to full enforcement of the law in June 2000.

In 1990, Nippon Steel's Plant & Machinery Division started developing a plant to produce oil from source-separated plastic from MSW collected in Okegawa City, Saitama Prefecture. Furthermore, it ascertained the viability of the technology. This paper contains results of research conducted into the thermal cracking properties of plastics and outlines findings gained from developing waste plastic liquefaction technology.

2. Properties of Waste Plastics

2.1 Composition of waste plastics

General-purpose plastics used in our daily lives are mostly thermoplastics and usually end up as MSW. Table 1 shows the percentage of waste plastics by type as the average values of sur-

veys conducted by five local governments.

Thermoplastics, or polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC), account for 96% of the waste plastics. The "Others" category includes polyethylene terephthalate (PET), acrylonitrile-butadiene-phenylethylene (ABS), and polyvinylidene chloride (PVDC). Since PET beverage bottles have been discarded in increasing amounts in recent years, the "others" category now exceeds 10%.

2.2 Thermal properties of plastics

The thermal cracking of plastics occurs at high temperatures of about 400°C and involves many concurrent elementary reactions. This makes it difficult to classify plastics on a uniform basis. In Table 2, plastics are classified according to their characteristic thermal cracking pattern¹⁾.

Thermal cracking splits the main chain (C-C bond) of a gas-producing-type plastic, reduces its molecular weight, and finally decomposes it into oil and gas products at room temperature. The main chain may be separated by random decomposition or depolymerization. Random decomposition severs the main chain

Table 1 Distribution ratios of waste plastics by type

| Type | Ratio (wt%) |
|--------------------------------|-------------|
| Polyethylene and Polypropylene | 60 |
| Polystyrene | 23 |
| Polyvinyl chloride | 13 |
| Others | 4 |

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randomly. PE and PP are typical examples. Depolymerization breaks a weakly bonded main chain and successively splits monomers at their chain ends. PS and polymethyl methacrylate (PMMA) are typical examples.

When they reach the thermal cracking temperature, these plastics form monomers and dimers, but not intermediates, so that residues are high in the degree of polymerization and do not change.

Thermal cracking eliminates a side chain of lower bond dissociation (for example, C-Cl bond) in a plastic of the carbonization residue type. Thermal cracking then causes the decomposition, cyclization and other secondary reactions of the plastic, and carbonizes all of its molecules. PVC is a typical example. The physical properties, thermal cracking patterns, and liquefaction adaptability of general-purpose plastics are given in Table 3.

Table 2 Thermal cracking patterns of plastics

| | | |
|---------------------------------------|--|--|
| Thermal cracking patterns of plastics | Gas producing type (main chain severed) | Random decomposition type { Polyethylene, polypropylene, polyether, polyamide, polyester, polycarbonate, etc. } |
| | | Depolymerization type { Polymethyl methacrylate, polyaldehyde, polystyrene, poly- α -methyl styrene, polytetrafluoroethylene, etc. } |
| | Carbonization residue type (main chain) | Main-chain carbonization type (crosslinked, cyclized, aromatized, and polyene-forming polymers) { Polyacrylonitrile, phenol resin, and malamine resin } |
| | | Side-chain elimination type { Polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, etc. } |

Table 3 Properties of general-purpose plastics

| Plastic | ⊙ Polyethylene (PE) | ⊙ Polypropylene (PP) | ⊙ Polystyrene (PS) | △ Acrylonitrile-butadiene-styrene (ABS) resin | △ Polyvinyl chloride (PVC) | △ Polyvinylidene chloride (PVDC) | △ Polyethylene terephthalate (PETP) |
|---------------------------------|---|--|---|--|---|---|---|
| Classification | Polyolefin | Polyolefin | Polystyrene | Polystyrene | Vinyl | Vinylidene | Polyester |
| Structural formula of monomer | $[-CH_2-CH_2-]_n$ | $\left[\begin{array}{c} -CH_2-CH- \\ \\ CH_3 \end{array} \right]_n$ | $\left[-CH_2-CH- \right]_n$ | $\left[\begin{array}{c} HH \ HH \ HH \ H \\ \ \ \ \\ -C-C-C=C-C-C- \\ \ \ \ \\ HCN \ H \ H \ \text{Benzene ring} \end{array} \right]_n$ | $\left[-CH_2-CH- \right]_n$ | $\left[\begin{array}{c} H \ Cl \\ \ \\ -C-C- \\ \ \\ H \ Cl \end{array} \right]_n$ | $\begin{array}{c} O \ O \\ \ \\ HO-C \oplus \ C-OH \\ \\ \text{Terephthalic acid} \\ + \\ HO-C_2H_4-OH \\ \\ \text{Ethylene glycol} \\ \downarrow \\ \begin{array}{c} -H_2O \\ O \ O \\ \ \\ -O-C \oplus \ C-O-C_2H_4-O- \end{array} \end{array}$ (Ester bond) |
| Molecular weight of monomer (n) | 28 (4,300-12,000) | 42 (2,000-3,500) | 104 (1,500-3,500) | 197 | 62.5 (400-1,600) | 97 | 208 |
| Specific gravity | 0.91-0.965 | 0.902-0.906 | 1.04-1.1 | 1.01-1.07 | 1.3-1.4 | 1.7-1.8 | 1.06-1.46 |
| Thermal cracking pattern | A1 Random decomposition type | A1 Random decomposition type | A2 Decopolymerization type | A2 Decopolymerization type | B2 (Zipper reaction) Side-chain elimination type (Cyclization and condensation polymerization) | B2 Side-chain elimination type (Cyclization and condensation polymerization) | A1 Ester decomposition Decarbonization reaction |
| Caloric value (kcal/kg) | 11,040 | 11,040 | 9,680 | 8,424 (~9,200) | 4,230 | 2,000 (~2,600) | 5,500 |
| Product use | Film (food packaging), containers, toys, sundry goods, electric wire covering | Film, pipe, rope, containers, electric appliances, sundry goods | Transparent formed parts, sheeting, sundry goods, toys, stationery, TV parts, sponges, containers | Floppy disks, cassette tapes, automotive dashboards, trunks | Film, leather, sheet, pipe, sponges, plating, sundry goods, electric wire covering, toys | Saran wrap and Kure wrap (low gas permeability), ham and sausage packages, nets, filter cloth | PET bottles, Teiron fiber (shirts and cloth), cassette tapes, films, wrappers, engineering plastics |

A Gas-producing type (Main chain scission type) — A1 Random decomposition type
 B Random decomposition type (Main chain non-scission type) — B1 Main-chain carbonization type
 — B2 Side-chain elimination type
 ⊙: Best suited for liquefaction
 △: Acceptable if only a few percent mixed in

3. Basic Thermal Cracking Experiments

To grasp the thermal cracking reaction rate of plastics, experiments were conducted using a thermobalance. The experimental procedure and results are described below.

3.1 Experimental procedure

3.1.1 Samples

Four types of general-purpose plastics, PE, PP, PS, and PVC, were used as samples. Both commercial pellets and waste plastics were used. Each sample was finely shredded, cryogenically ground with liquid nitrogen and vacuum dried for about 2 hours. Only material of the desired particle size was used as an experimental sample. The types and average particle sizes of the samples are shown in Table 4. An average particle size of 100 μm or less is thought to be appropriate because particles of this size are free from the effects of such factors as thermally cracked gas transfer and diffusion, heat transfer, and expansion. PP, PS and PVC were difficult to pulverize, and particles about 1.5 times larger than 100 μm were used as the PP, PS and PVC samples.

3.1.2 Experimental apparatus

Fig. 1 shows the thermobalance. Using the thermobalance,

Table 4 Types and particle sizes of samples

| Commercial pellet | Waste plastic (name) | Average particle size of sample (μm) |
|----------------------------------|------------------------------------|---|
| Low-density polyethylene (LDPE) | Packaging PE sheet (PE sheet) | 56 |
| High-density polyethylene (HDPE) | | 65 |
| Polypropylene (PP) | Packaging PP sheet (PP sheet) | 135 |
| Polystyrene (PS) | Volume-reduced PS trays (PS chips) | 156 |
| Polyvinyl chloride (PVC) | Egg cartons (PVC) | 144 |

the change in the weight of a sample is continuously measured while heating the sample under certain conditions. The weight loss characteristic of each plastic can be determined from the thermogram (TG curve) thus obtained.

The principle of this device is described as follows. The spring contracts as the sample decreases in weight. The contraction of the spring deflects the moving armature. The deflection of the moving armature is detected by the solenoid coil. An electric current is induced to flow in the solenoid coil to return the moving armature to the original position. The weight loss of the sample in proportion to the magnitude of this current is automatically measured and recorded.

3.1.3 Experimental conditions

(1) Thermal cracking temperature

Since none of the plastics revealed weight loss at temperatures of 500°C and above in preliminary thermal cracking experiments, the thermal cracking temperature range was set at room temperature to 550°C.

(2) Sample size

To grasp the effect of sample size on mass transfer, 5-mg and 25-mg samples were comparatively investigated.

(3) Heating rate

Plastics are extremely poor in thermal conductivity, which is approximately 1/400 to 1/500 of that of metals. The heating rate is considered to influence the thermal cracking properties of the plastics. The thermal cracking properties were thus compared at three heating rates of 5°C/min, 20°C/min, and 50°C/min.

(4) Atmosphere gas

The thermal cracking of plastics is generally a solid-phase decomposition reaction. There is the possibility that their thermal cracking causes a secondary gas-solid phase reaction under the influence of radicals in the gas evolved. To grasp the thermal cracking properties of a sample, it is necessary to rapidly remove the formed gas out of the system. The experiments were conduct-

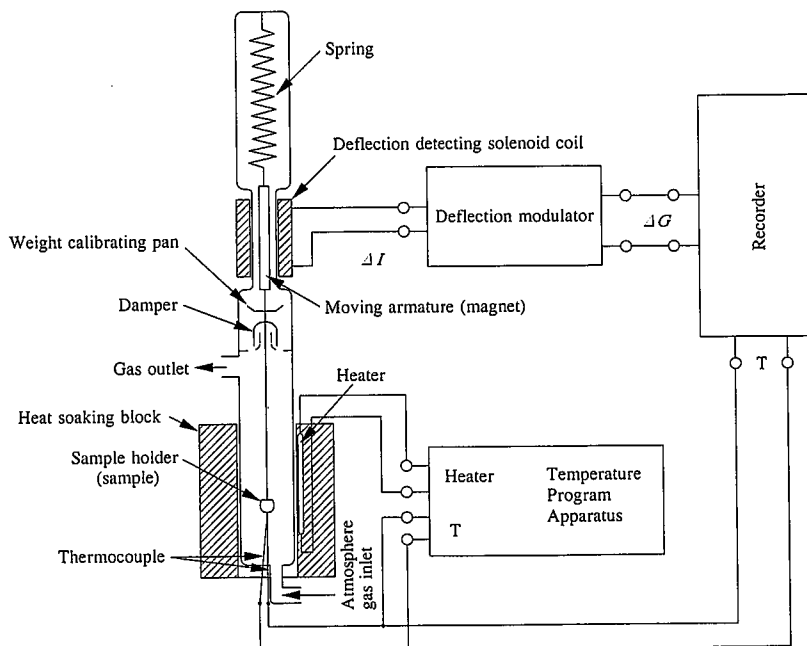


Fig. 1 Thermobalance

ed in a nitrogen stream at 50 mL/min:

3.1.4 Hypothesis on thermal cracking reaction rate equations

Plastics are available in a wide variety of types. It is difficult to accurately grasp reaction rate equations under the influence of a three-dimensional microstructure that is not uniform for plastics. This article analyzes the experimental data on the two basic assumptions that the thermal cracking of plastics can be described by a rate equation that is linearly proportional to the amount of unreacted material and that the Arrhenius equation holds.

Several methods are proposed for K_{r0} (reaction frequency factor) and E (activation energy), both of which are the Arrhenius factors, by using these assumptions and the TG curves. This paper uses a method based on the integral curve of Coats and Redfern²⁾.

According to the above assumptions, the following equations hold:

$$\frac{dx}{dt} = K_r (x^* - x) \quad \dots\dots(1)$$

$$K_r = K_{r0} \exp\left(-\frac{E}{RT}\right) \quad \dots\dots(2)$$

where x = percent conversion at time $t = t$; x^* = percent conversion at time $t = \infty$; K_r = true thermal cracking reaction rate; K_{r0} = reaction frequency factor; E = activation energy; R =

gas constant; and T = reaction temperature.

From Eqs. (1) and (2),

$$\int_0^x \frac{dx}{x^* - x} = \int_0^t K_{r0} \exp\left(-\frac{E}{RT}\right) dt \quad \dots\dots(3)$$

Assuming that the heating rate of plastics is constant at $m = \frac{dT}{dt}$ and $m = \frac{E}{RT} \gg 1$, the integration of Eq. (3) yields Eq. (4). The following discussion makes use of Eq. (4).

$$\frac{x^* - x}{x^*} = \exp\left\{-\frac{K_{r0} R T^2}{mE} \times \exp\left(-\frac{E}{RT}\right)\right\} \quad \dots\dots(4)$$

3.2 Experimental results

3.2.1 TG curves

The TG curves of plastics obtained as experimental results are too numerous to completely present here. Representative TG curves are shown in Figs. 2(a) to 2(d). PE, PP, PS, the commercial pellets and waste plastics exhibit extremely similar TG curves. Under the influence of contamination from additives and fillers, the waste PVC plastic had more residues that were not decomposed than the commercial PVC pellets.

The temperature at which a 5% weight decrease occurs is called the thermal cracking start temperature T_s , the temperature when the differential curve of TG (DTG) peaks is called the ther-

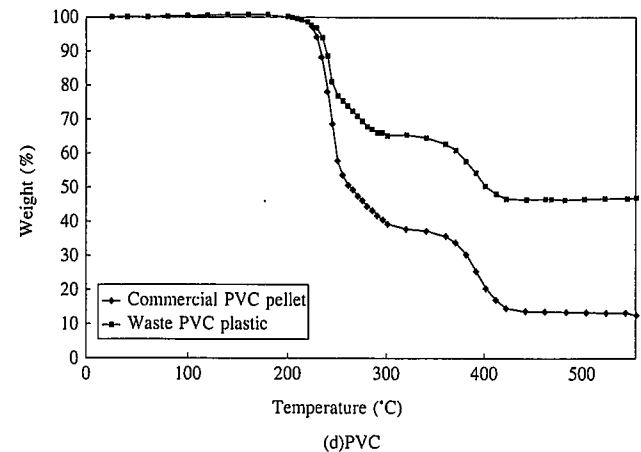
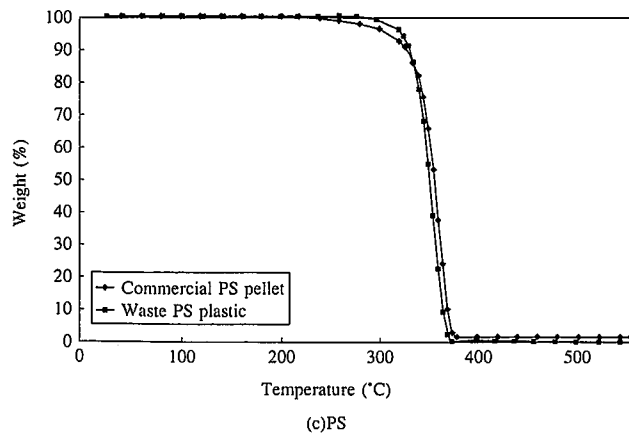
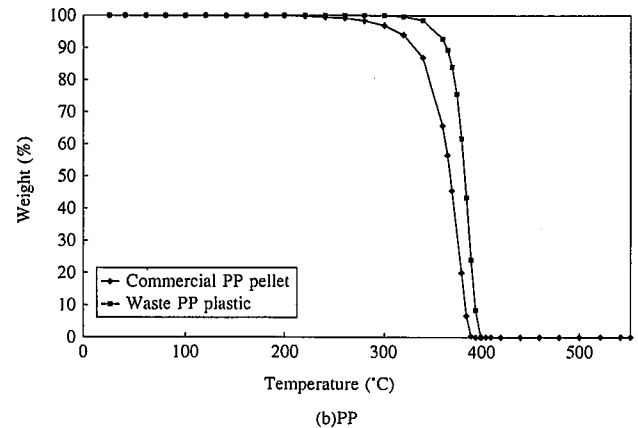
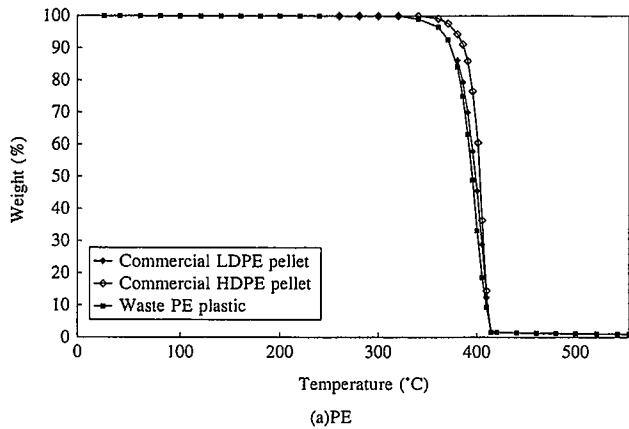


Fig. 2 TG curves of commercial pellets and waste plastics

Table 5 Thermal cracking characteristic temperatures of plastics

| Sample size: 25 mg (Unit: °C) | | | | | Sample size: 5 mg (Unit: °C) | |
|-------------------------------|-------------------|---------------|-------------------|---------------|------------------------------|-------------------|
| [T ₁] | 5°C/min | | 20°C/min | 50°C/min | 5°C/min | 50°C/min |
| | Commercial pellet | Waste plastic | Commercial pellet | Waste plastic | Commercial pellet | Commercial pellet |
| LDPE | 360 | 360 | 390 | 410 | 330 | 370 |
| HDPE | 380 | - | 400 | 420 | 340 | 410 |
| PP | 330 | 360 | 350 | 380 | 270 | 370 |
| PS | 320 | 320 | 340 | 360 | 220 | 340 |
| PVC-A | 230 | 320 | 250 | 260 | 210 | 270 |
| PVC-B | 370 | 340 | 370 | 380 | 360 | 380 |
| [T _p] | | | | | | |
| LDPE | 406 | 396 | 421 | 441 | 383 | 429 |
| HDPE | 407 | - | 429 | 439 | 388 | 446 |
| PP | 378 | 388 | 406 | 425 | 351 | 424 |
| PS | 362 | 358 | 386 | 416 | 336 | 394 |
| PVC-A | 242 | 241 | 265 | 282 | 230 | 286 |
| PVC-B | 391 | 392 | 415 | 424 | 387 | 427 |
| [T ₂] | | | | | | |
| LDPE | 420 | 420 | 440 | 460 | 400 | 440 |
| HDPE | 420 | - | 440 | 460 | 400 | 460 |
| PP | 390 | 400 | 420 | 440 | 360 | 450 |
| PS | 380 | 370 | 410 | 440 | 350 | 420 |
| PVC-A | 300 | 280 | 300 | 330 | 300 | 330 |
| PVC-B | 420 | 440 | 440 | 450 | 410 | 470 |

Table 6 Arrhenius factors for plastics in thermal cracking reactions

| Sample size: 25 mg (Unit: s ⁻¹) | | | | | Sample size: 5 mg (Unit: s ⁻¹) | |
|---|-----------------------|-----------------------|-----------------------|-----------------------|--|-----------------------|
| [K _a] | 5°C/min | | 20°C/min | 50°C/min | 5°C/min | 50°C/min |
| | Commercial pellet | Waste plastic | Commercial pellet | Commercial pellet | Commercial pellet | Commercial pellet |
| LDPE | 1.34×10 ²¹ | 1.35×10 ¹⁶ | 1.29×10 ²⁰ | 1.59×10 ²¹ | 1.81×10 ⁴ | 6.13×10 ¹³ |
| HDPE | 4.26×10 ²⁹ | - | 2.66×10 ³⁰ | 4.44×10 ²⁹ | 2.09×10 ¹¹ | 1.07×10 ³¹ |
| PP | 8.03×10 ¹³ | 1.87×10 ¹⁸ | 1.52×10 ¹³ | 93.5×10 ¹⁶ | 3.75×10 ⁵ | 9.76×10 ¹⁴ |
| PS | 1.12×10 ¹⁷ | 1.09×10 ¹² | 2.55×10 ¹⁵ | 9.24×10 ¹³ | 81.64 | 9.59×10 ¹⁴ |
| PVC-A | 7.85×10 ⁹ | 7.46×10 ¹⁰ | 1.31×10 ¹⁹ | 6.88×10 ¹¹ | 2.26×10 ⁸ | 3.46×10 ¹² |
| PVC-B | 4.40×10 ¹¹ | 1.24×10 ¹⁰ | 1.26×10 ¹² | 8.73×10 ¹² | 2.09×10 ¹⁶ | 4.27×10 ¹⁰ |
| [E] | | | | | | |
| LDPE | 71.93 | 56.62 | 69.01 | 72.96 | 21.41 | 48.20 |
| HDPE | 98.36 | - | 102.10 | 100.92 | 41.75 | 105.56 |
| PP | 47.83 | 60.04 | 46.24 | 58.30 | 22.91 | 52.13 |
| PS | 55.84 | 41.71 | 51.56 | 48.06 | 13.27 | 49.84 |
| PVC-A | 29.96 | 32.01 | 51.90 | 34.60 | 25.89 | 36.57 |
| PVC-B | 43.09 | 38.67 | 46.92 | 45.97 | 56.98 | 39.22 |
| Correlation coefficient | | | | | | |
| LDPE | 99.8 | 98.4 | 99.5 | 99.6 | 91.5 | 99.6 |
| HDPE | 99.0 | - | 99.4 | 99.5 | 97.0 | 98.6 |
| PP | 99.8 | 98.3 | 98.8 | 98.3 | 97.3 | 99.4 |
| PS | 99.9 | 96.3 | 99.8 | 99.2 | 92.3 | 99.5 |
| PVC-A | 96.0 | 98.4 | 98.4 | 92.7 | 97.7 | 95.6 |
| PVC-B | 99.8 | 98.7 | 99.9 | 99.9 | 96.2 | 98.1 |

mal cracking peak temperature T_p , and the temperature at which the weight loss is 0.1% or less is called the thermal cracking end temperature T_e . These temperatures are generically defined as the thermal cracking characteristic temperatures. The thermal cracking characteristic temperatures of the plastics are summarized in Table 5 according to these definitions. Under all experimental conditions, the thermal cracking peak temperature is the highest for PE (396 to 441°C), followed by PP (378 to 425°C), PS (358 to 416°C), and PVC (241 to 282°C).

3.2.2 Arrhenius factors

The Arrhenius factors K_0 and E can be calculated using the observed values of x^* , x , T and m obtained from the TG curves and Eq. (4). Using the least square approximation of the measurements, the Arrhenius factors were calculated for the plastics under the specific experimental conditions. The results are given in Table 6.

3.2.3 Discussion

(1)Sample size

With a 5-mg sample, the thermal cracking start temperature and thermal cracking end temperature are low, the sample is more liable to be affected by differences in the heating rate, and there is a greater variability of data.

With a 25-mg sample, the correlation coefficient is extremely high at 0.98 to 0.999 or more, except for PVC, and can be accurately evaluated as hard data. This suggests that the effect of nonuniform reaction due to hot spots, among other things, is high for the 5-mg sample and less for the 25-mg sample.

Generally speaking, the greater the sample size, the greater the absolute value of thermal change, favoring the detection of minute thermal change. Plastics are extremely poor in thermal conductivity. With a sample of a few hundred milligrams, for example, the temperature distribution and gas partial pressure distribution in the sample bed becomes uneven. As a result, it is thought that the thermal change does not uniformly take place in the sample bed. This means that the appropriate sample size is about 25 mg.

(2)Heating rate

As evident from Table 5, increasing the heating rate from 5°C/min to 50°C/min shifts all of the thermal cracking characteristic temperatures T_s , T_p , and T_e to the high end of the temperature range.

Among the probable causes for this situation are: (1) the heat transfer is not fast enough for a heat buildup; (2) the thermocouples are faulty; and (3) a reaction intermediate forms, changing the thermal cracking energy. The experiments involved taking measurements at three heating rate levels of 5°C/min, 20°C/min, and 50°C/min. The Arrhenius factors are not significantly differ-

ent between the three heating rates, and there appear to be no problems if the heating rate falls within this range. Since a lower heating rate is considered to be better suited to simulate a situation closer to thermal equilibrium, a heating rate of about 5 °C/min is judged to be appropriate.

(3)Arrhenius factors

The Arrhenius factors obtained with the sample size of 25 mg and heating rate of 5 °C/min are discussed below.

The activation energy experimental values that occur in the thermal cracking reaction of the plastics are compared in Table 7 with those found in the literature. The activation energy values determined by the thermogravimetric analysis of the commercial pellets and waste plastics are considerably close to the literature values and can be considered as approximately correct data. As can be seen from its TG curves, PVC is thermally cracked in a two-step reaction. The first step (PVC-A) yields the value of E in the dehydrochlorination reaction, and the second step (PVC-B) produces the value of E in the cyclization and condensation reaction.

No published data is available on the frequency factor and therefore it remains uncertain. Generally speaking, the frequency factor in the C-C bond main-chain scission reaction for naphtha cracking is reported to be of the order of 1,010 to 1,020⁹. Except for HDPE, the frequency factor experimental values are 109 to 1,017 and 1,010 to 1,018 for the commercial pellets and waste plastics, respectively. Each range can be considered approximately correct data. These results show that the thermal cracking reaction rate data of the waste plastics are similar to those of the commercial pellets.

3.3 Reaction time

The Arrhenius plots of the commercial pellets and waste plastics were obtained by using the Arrhenius factors K_0 and E and Eq. (2). The Arrhenius plots are shown in Figs. 3 and 4. Assuming the thermal cracking temperature of 410°C, K₀ was obtained from Figs. 3 and 4, the relationship between the percent

Table 7 Activation energy of plastics

| | Experimental value (25 mg, 5°C/min) | | Literature value |
|-------|-------------------------------------|---------------|------------------|
| | Commercial pellet | Waste plastic | |
| LDPE | 71.93 | 56.62 | 72 ³⁾ |
| HDPE | 98.36 | - | |
| PP | 47.83 | 60.04 | 58 ³⁾ |
| PS | 55.84 | 41.71 | 55 ³⁾ |
| PVC-A | 29.96 | 32.01 | 34 ⁴⁾ |
| PVC-B | 43.09 | 38.67 | |

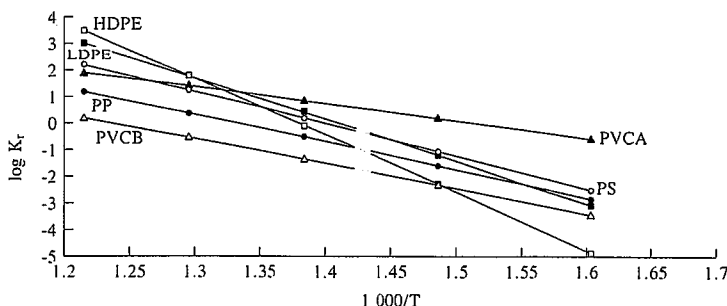


Fig. 3 Arrhenius plots of commercial pellets

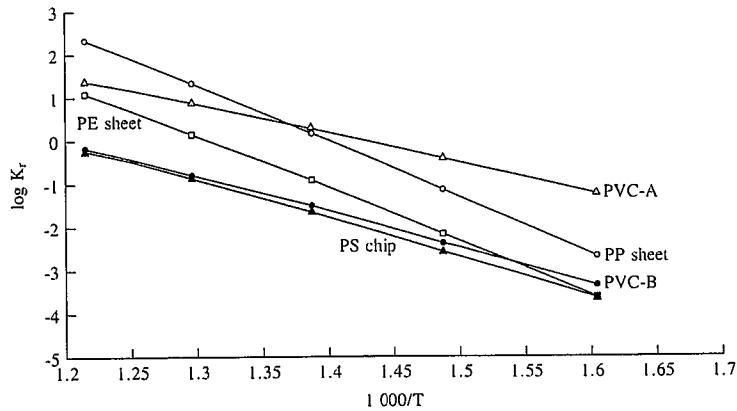


Fig. 4 Arrhenius plots of waste plastics

conversion and the reaction time could be calculated from the values of K_r . The results are shown in Tables 8 and 9.

For PVC, the first-step reaction or dehydrochlorination occurred near 300°C, the second-step reaction mainly consisted of cyclization and condensation, and the oil yield was extremely low. For these reasons, PVC was excluded from the study, and the reaction time for PE, PP and PS was calculated. According to the results, the true thermal cracking reaction finish time at the

percent conversion of 99% ranged between 31 and 336 seconds for the commercial pellets PS and HDPE, respectively, and ranged between 41 and 458 seconds for the waste plastics PP and PE, respectively. This means that when the waste plastics PE, PP, and PS are thermally cracked under ideal conditions in which there is no mass transfer effect, they are almost completely gasified in a very short time of 1 to 8 minutes.

This finding suggests that the method whereby the waste plastic feed is thermally cracked rapidly in a once-through heating furnace may be adopted in addition to the conventionally considered slow thermal cracking method, which involves heating furnace recirculation and tank retention.

It is necessary to make a final judgment regarding the adoption of the rapid thermal cracking method by using overall thermal cracking reaction rate data, including mass transfer.

Table 8 Relationship between conversion and reaction time of commercial pellets

| Type | LDPE | HDPE | PP | PS |
|----------------|-----------------------------|--------|-------|-------|
| K_r | 0.125 | 0.0137 | 0.039 | 0.148 |
| T (°C) | 410 | 410 | 410 | 410 |
| x (conversion) | t (reaction time) (Unit: s) | | | |
| 0.99 | 37 | 336 | 118 | 31 |
| 0.9 | 18 | 168 | 59 | 15 |
| 0.8 | 13 | 117 | 41 | 11 |
| 0.7 | 9.6 | 88 | 31 | 8.1 |
| 0.6 | 7.3 | 67 | 23 | 6.2 |
| 0.5 | 5.5 | 51 | 18 | 4.7 |
| 0.4 | 4.1 | 37 | 13 | 3.4 |
| 0.3 | 2.9 | 26 | 9.2 | 2.4 |
| 0.2 | 1.8 | 16 | 5.7 | 1.5 |
| 0.1 | 0.8 | 7.7 | 2.7 | 0.7 |

Table 9 Relationship between conversion and reaction time of waste pellets

| Type | PE sheet | PP sheet | PS chip |
|----------------|-----------------------------|----------|---------|
| K_r | 0.01 | 0.112 | 0.0482 |
| T (°C) | 410 | 410 | 410 |
| x (conversion) | t (reaction time) (Unit: s) | | |
| 0.99 | 458 | 41 | 96 |
| 0.9 | 229 | 21 | 48 |
| 0.8 | 160 | 14 | 33 |
| 0.7 | 120 | 11 | 25 |
| 0.6 | 91 | 8 | 19 |
| 0.5 | 69 | 6 | 14 |
| 0.4 | 51 | 5 | 11 |
| 0.3 | 35 | 3 | 7 |
| 0.2 | 22 | 2 | 5 |
| 0.1 | 10 | 1 | 2 |

4. Thermal cracking Experiments with Electric Furnace

The amounts of gas and oil generated by the thermal cracking of waste plastics were confirmed with an electric furnace. The experiments are described below.

4.1 Experimental procedure

4.1.1 Samples

Each waste plastic was finely shredded, cryogenically ground in liquid nitrogen and vacuum dried for about 2 hours. Only material of the desired particle size was used in the experiments.

4.1.2 Experimental apparatus

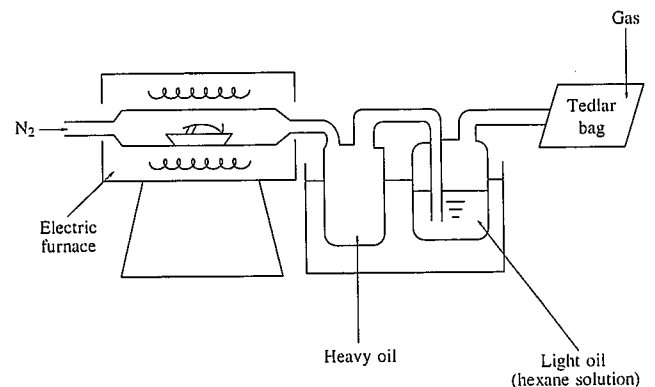


Fig. 5 Thermal cracking apparatus

Fig. 5 shows the experimental apparatus. Thermal cracking products were determined by using a simple thermal cracking device comprising a commercial electric furnace to which a gas collection line was connected.

4.1.3 Experimental conditions

A certain sample size is required to weigh the thermal cracking products. Since the sample size of 25 mg does not allow accurate weighing, 500-mg samples were used instead.

In preliminary thermal cracking experiments, a large amount of undecomposed plastic remained after heating 500-mg samples at 400°C. In the main experiments, each sample was heated to 500°C for 60 minutes or more. Nitrogen was supplied at a rate of 700 mL/min as atmosphere gas.

4.2 Experimental results

Table 10 shows the generation and composition of the thermal cracking products of the plastics excluding PVC. Nearly 100% of the PE sheet, PP sheet, and PS chips are all thermally cracked, and the residues formed amounted to an extremely small 0.3 to 0.65 wt%. This means that these plastics are materials suited for liquefaction by thermal cracking. The simple experimental apparatus did not allow accurate measurement of the oil yield, and the related data are omitted here. The oil yield was about

70%. With PVC, the scission of the main chain after the dehydrochlorination reaction causes gasification. At the same time, the cyclization and condensation reactions proceed. Eventually graphite is formed. For this reason, PVC generates more residue than the other plastics. Since the plastics greatly differ in thermal properties, the amounts of their thermal cracking products are not given here.

The thermal cracking products identified by gas chromatography are olefin and paraffin for the polyolefins PE and PP, and are styrene monomer, dimer, trimer, polycyclic aromatic compounds and alkylbenzene for PS due to depolymerization.

5. Thermal Properties of Other Plastics

Besides the plastics mentioned previously, MSW also contains PET, ABS, acrylonitrile styrene (AS) and many thermosetting resins in trace amounts. The thermogravimetric results of these plastics are shown in Fig. 6.

An increasing volume of PET bottles are now discarded each year. PET bottles account for nearly 10% of the plastics source-separated and collected. As shown in Table 3, PET is produced by polymerizing the ester bonds of terephthalic acid and ethylene glycol. Its thermal cracking pattern is of the random decomposition type, and its thermal cracking causes the ester decomposition reaction, resulting in the crystalline component terephthalic acid. As shown in Fig. 6, it has a low gasification rate, and generates much residue. Given the possibility of such problems as line plugging and combustion interference, it is necessary to grasp the thermal behavior of PET qualitatively and quantitatively and to take appropriate measures against these problems.

Thermosetting resins are found in MSW to an extremely small degree and are considered to have little or no effect on the thermal cracking properties of waste plastics. The thermosetting resins have a thermosetting-type thermal cracking pattern. The thermosetting resins are not thermally cracked and remain as

Table 10 Thermal cracking products of waste plastics (wt%)

| | PE sheet | PP sheet | PS chip |
|---------------------|--------------------|--------------------|--|
| Gas + oil | 99.35 | 99.7 | 99.36 |
| Product composition | Olefin Paraffin | Olefin Paraffin | Styrene monomer Dimer Oligomer Polycyclic aromatic series Alkylbenzene |
| Residue | 0.65 | 0.3 | 0.64 |

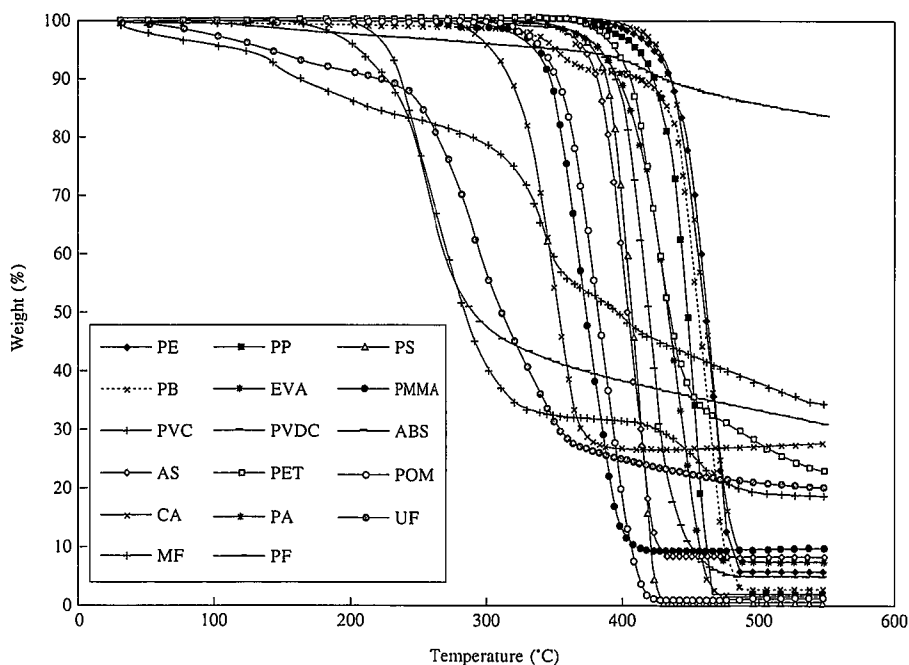


Fig. 6 TG curves of other plastics

residue in the system. Many of the thermosetting resins contain nitrogen in their molecular structure and are known to form trace amounts of harmful gases, such as hydrogen cyanide (HCN) and ammonia (NH₃). Since the thermosetting plastics are not suited for liquefaction, care should be exercised when they are present in high concentrations.

6. Conclusions

As waste plastics, PE, PP, PS, and PVC form a substantial portion of MSW. Basic thermal cracking experiments were conducted with commercial pellets and waste plastics, and the true thermal cracking rate equations of specific plastics were established. The results suggested the feasibility of a process for rapid liquefaction by thermal cracking. Thermal cracking experiments with an electric furnace confirmed that PE, PP, and PS are suitable for liquefaction.

The thermal properties of commingled plastics were partly clarified. These data will be presented on another occasion.

The basic thermal cracking experiments discussed in this study were conducted at the Heat-Fluid Processing & Environment Research Center, Process Technology Research Laboratories, Technical Development Bureau. They were part of a research project commissioned by the Plant & Machinery Division.

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