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Effects of hydrogen chloride on the pyrolysis of polyethylene: pyrolysis kinetics

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Abstract

The pyrolytic reaction of chlorinated plastics such as poly(vinyl chloride) (PVC) releases hydrogen chloride (HCl). The HCl released from the pyrolysis, in turn, may affect the mechanisms of the pyrolytic reactions. In this study, the pyrolysis of high-density polyethylene (HDPE), being the principal component of plastics in the municipal solid waste (MSW), was carried out in the thermal gravimetric analysis (TGA) reaction system containing HCl gas. The results indicated that HCl inhibited the pyrolytic reaction of HDPE. The activation energies, pre-exponential factors, and reaction orders of the reactions corresponding to the various concentrations of HCl (C_{HCl}) were obtained in the range of the experimental conditions. The results of this study are useful for the utilization of HDPE as an energy resource and for determining the thermal degradation rate of HDPE in an incinerator. © 1998 Elsevier Science B.V.

Keywords: Pyrolysis; Polyethylene; Hydrogen chloride

Abbreviations: A, Pre-exponential factor of Arrhenius-term, 1/s; C_{HCl}, Concentration of HCl, ppm; E, Activation energy, kcal/mol; k, Arrhenius reaction rate constant, 1/s ($A\exp[-E/(RT)]$); n, Reaction order; R, Universal gas constant, kcal/(mol K) (1.987×10^{-3}); R_1^2, R_2^2, R_3^2, Coefficients of determination at β of 1, 2, 5 K/min ($1-[\Sigma(y-\hat{y})^2/\Sigma(y-\breve{y})^2]$); T, T_0, Pyrolysis temperatures at time t, and at the beginning ($t=0$) of pyrolysis, K; t, Pyrolysis time, s ($[T-T_0]/\beta$); W, W_0, Total masses of residual sample at time, t, and of initial sample, mg; X, Conversion at time t ($1-W/W_0$); y, Experimental value of residual mass fraction at specified T; $\hat{y}$, Computed value of residual mass fraction at specified T; $\breve{y}$, Arithmetic average of experimental values of residual mass fraction at specified T; β, Heating rate, K/min ($\mathrm{d}T/\mathrm{d}t$); β_1, β_2, β_3, β at 1, 2, 5 K/min, K/min

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1. Introduction

Polyethylene (PE) is the principal component contributing to the municipal solid waste (MSW) of Taiwan. The quantities used in packing materials and PE cans have been 213 400–257 900 MT/yr through the years 1986–1994 [1]. Based on the current recycling frameworks promoted by ROCEPA (Environmental Protection Administration, Republic of China in Taiwan), the waste PE has been one of the significant resources. Typically, the calorific values of waste PE are 7000–11 000 kcal/kg. The conversion of waste PE to marketable fuels has become a noble goal not only from an economic but also from an environmental standpoint.

Studies on the pyrolysis of PE have been performed by many researchers. These studies were concerned mostly about the thermal degradation of PE in the absence of hydrogen chloride (HCl) and focused on the analyses of products [2–5], the mechanisms of reactions [6,7] and the pyrolysis kinetics [8–10]. Also, the pyrolysis kinetics and the thermal stabilities of principal components of MSW have been explored in the nitrogen environment [11–13]. The pyrolysis of six principal plastic materials of MSW and their mixtures were investigated with a thermal gravimetric analysis (TGA) reaction system at various heating rates (β) of 1, 2, and 5 K/min [12]. The results indicated that the order of thermal stability of the examined plastics was high-density polyethylene (HDPE) > LDPE > PP > ABS > PS > poly(vinyl chloride) (PVC). The degradation temperatures corresponding to the principal mass changes were 675–750 K for PE, 625–750 K for PP, 600–725 K for ABS, 600–700 K for PS, and 500–620 K and 700–750 K for PVC, respectively. Interestingly, the process of PVC pyrolysis under the experimental conditions consisted of two significant and distinct mass change stages [12,13]. The evolution of HCl played an important role in the low temperature range (500–620 K). Since the pyrolyses were carried out in the system with constant heating rates, the HCl had been purged out from the system before the pyrolysis reactions of other components of plastic mixtures began. In the purging case, the effects of HCl on the reactions were not seen for the pyrolysis of plastic mixture, but significant for that of paper mixture [14]. However, the systems of the real pyrolytic processes are controlled at isothermal condition with the evolved gases contacting with the solid samples. The HCl released from the pyrolysis of chlorinated plastics, e.g. PVC, may affect the mechanisms of the pyrolytic reactions and the composition of products for the pyrolysis of plastics of MSW.

It is thus the aim of the present work to investigate the effects of HCl on the pyrolysis of HDPE. The pyrolytic experiments were carried out in a TGA reaction system and over a wide temperature range (up to 800 K). The activation energies, pre-exponential factors, and reaction orders of the reactions corresponding to the pyrolysis reactions of HDPE in various C_{HCl} were obtained in the entire range of the experimental conditions.

2. Experimental

2.1. Materials

Commercial-grade HDPE was used in this study. It was supplied by the USI Far East of Taiwan, with the properties as listed in Table 1. The HCl gas and N_2 gas were

Table 1
Some properties of HDPE used in this study [12]

	Test method	Value/property
Manufacture		USIFE
Grade		LH606
Melt index (g/10 min)	D1238	6.0
Density (g/cm)	D1505	0.961
Vicat softening temperature (K)	D1525	400
Melting point (K)	DTA	407
Tensile strength (kg/cm^2)	D638	310
Tensile elongation (%)		600
C (%)	EA	86.09
H (%)	EA	12.99
O (%)	EA	ND[a]
N (%)	EA	ND
S (%)	EA	0.28
Cl (%)	EA	ND

[a] Not detected.

purchased from the San Fu Chemical and the Ching Feng Harng of Taiwan, respectively, and had a purity of 99.99%.

2.2. Pyrolysis apparatus and procedures

The process flow diagram of the experimental system for the pyrolysis of HDPE is illustrated in Fig. 1. A Sartorius R-200D electrical balance (Sartorius, Germany; with

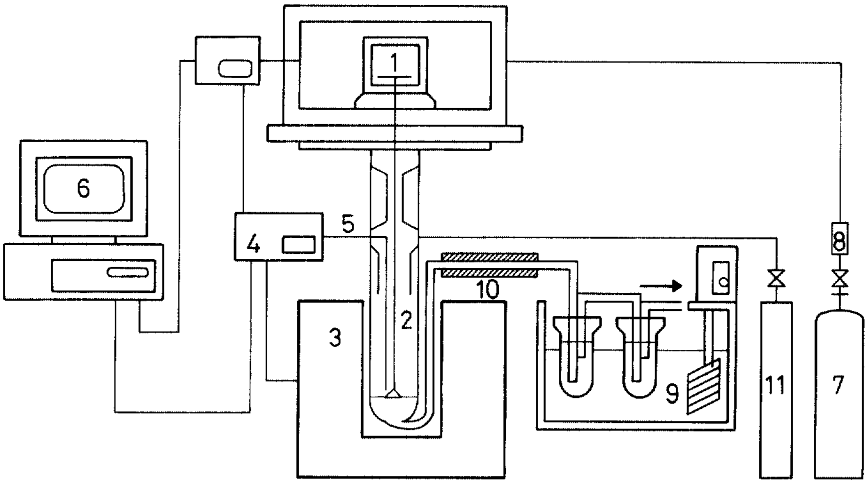

Fig. 1. Thermal gravimetric analysis reaction system. (1) Electrobalance; (2) Shell and tube reactor; (3) Furnace; (4) Power supply and temperature controller; (5) K-type thermocouple; (6) Computer for data processing; (7) Nitrogen; (8) Flow meter with needle valve; (9) Ice bath with impingers; (10) Heater; (11) HCl dilution system.

0.01 mg readability, ≤ ±0.02 mg reproducibility, and RS232 interface) was used. A sample of known mass was placed on a small quartz disk (with 2 cm diameter and 1 mm thickness). The disk was hung on the suspension wire (made of platinum with 0.18 mm diameter) of the balance and enclosed in a quartz shell and tube reactor. The outer shell was 27 cm long with a 3.8 cm inside diameter. The inner tube was 22 cm long with a 1.2 cm inside diameter. The N_2 at a high flow rate was first introduced into the rear channel of the balance protector for 1 h so as to purge out the residual oxygen and was then switched off. The carrier gas of N_2 with desired C_{HCl}, which was premixed in the HCl dilution system, was introduced into the inner tube of the reactor. After about 2 h, the reactor was placed in the furnace (HAS 100/250G with 1280 W), which had been preset to a specified heating rate (1, 2, or 5 K/min). When the control units (Eurotherm 815S with RS232 interface) were all ready, the experimental run was begun. At the same time, the variations of the mass of sample and of the reaction temperature (probed with a K-type thermocouple) during the entire pyrolysis process were recorded at time intervals of 10 s by the data-processing unit (IBM PC-AT 286 with RS232 interface). The pyrolysis process was operated under atmospheric pressure. The effluent stream leaving the outlet of the outer shell was absorbed by the 0.1N NaOH solution before it was vented to a fume hood. When the pyrolysis was finished, the furnace, the control-recording units and the HCl gas were turned off. The carrier gas of pure N_2 was kept flowing until the temperature of reactor was cooled below 373 K.

The samples were dried to constant mass at 378 K before starting the temperature change at a specified heating rate. Several carrier gas flow rates and sample masses were investigated to eliminate the effects of resistances caused by the heat and mass transfer. At a sufficiently high flow rate of nitrogen, the gas film resistance to heat and mass transfer can be considered to be negligible. The results indicated that a nitrogen flow rate of 100 cm^3/min (at 101.3 kPa and 293 K) was appropriate. Hence, the carrier gas flow rate of 100 cm^3/min was employed for all experimental runs. In a similar way, one found that the influence of sample mass between 2 and 20 mg on the reaction was

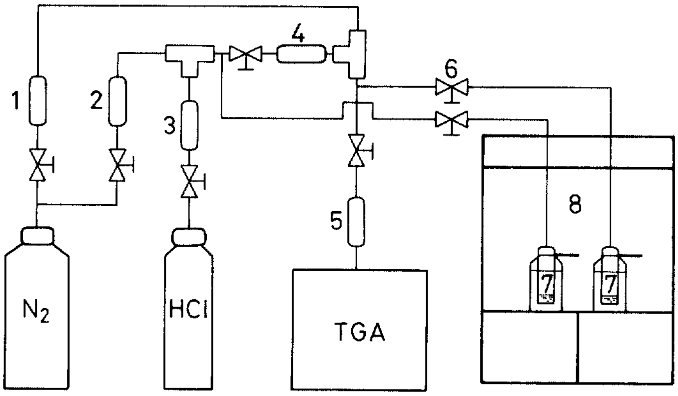

Fig. 2. HCl dilution system. (1–5) Flow meters with needle valves; (6) Needle valve; (7) 0.1N NaOH solution; (8) Fume hood.

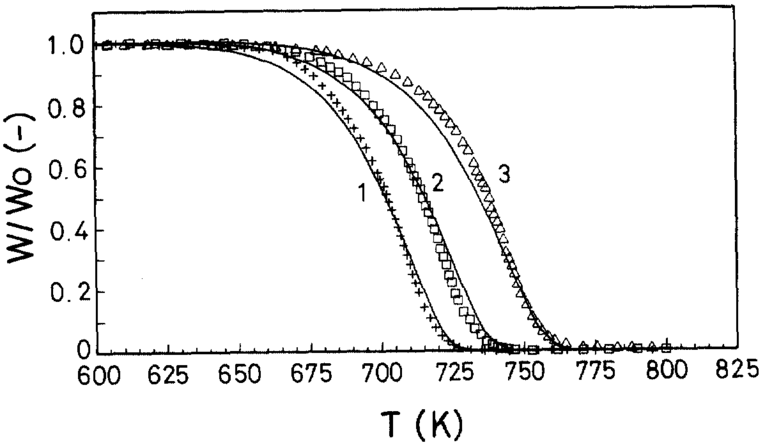

Fig. 3. Comparison of W/W_0 predicted from computed kinetic parameters, with experimental data at various β for pyrolysis of HDPE in N_2. 1, 2, 3: $\beta = 1$, 2, 5 K/min. +, □, △: Experimental; —: computed. $R_1^2 = 0.98$, $R_2^2 = 0.99$, $R_3^2 = 0.97$.

negligible. Hence, a sample mass of 4 ± 0.1 mg was employed for all the experimental runs yielding kinetic data.

In general, there were thermal gradients between the sample and the environment which may change during the reaction, along the longitudinal and radial directions of the TGA furnace. For this reason, the recorded temperature may not exactly match the real sample temperature. From the experimental results, the longitudinal temperature gradient was less than 0.5 K/mm for all three heating rates, and the radial temperature gradients

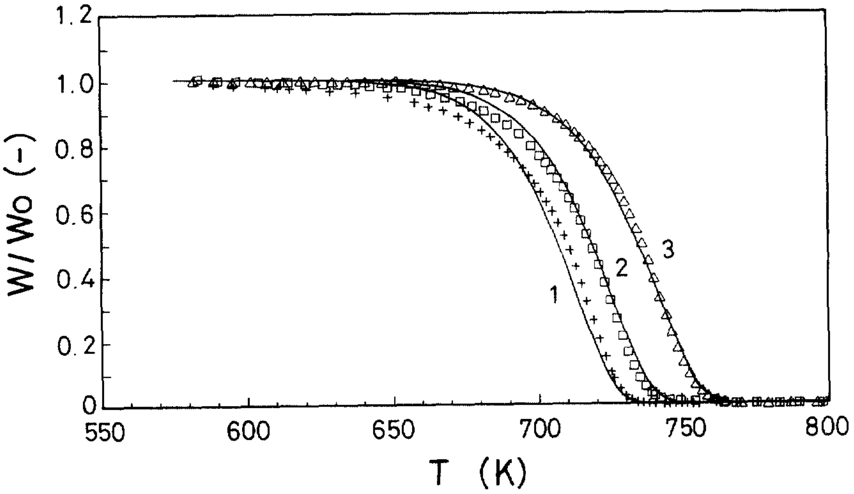

Fig. 4. Comparison of W/W_0 predicted from computed kinetic parameters, with experimental data at various β for pyrolysis of HDPE in HCl (500 ppm). 1, 2, 3: $\beta = 1$, 2, 5 K/min. +, □, △: Experimental; —: computed. $R_1^2 = 0.98$, $R_2^2 = 0.98$, $R_3^2 = 0.98$.

were about 0.33, 0.36, and 0.44 K/mm for the β of 1, 2, and 5 K/min, respectively. Thus, in this study, the sample was well spread and homogenized around the center of disk, and the temperature was measured at 3 mm radially near the disk center and 2 mm longitudinally above the sample for all experiments. The sample temperature was adequately represented by the measured temperature.

2.3. Preparation of the carrier gas containing HCl

The concentrations of HCl were prepared according to the typical range seen in an uncontrolled equipment incinerator. In this study, the HCl concentrations of 0, 500, 750, 1000, 3000, and 5000 ppm (in volume) were prepared from the pure HCl gas diluted by N_2 gas. For a satisfactory preparation of HCl concentrations, a two-step dilution system was set up. The flow diagram is illustrated in Fig. 2. (A large amount of N_2 will be consumed for one step dilution, while several flow controlled units will be used for multi-step dilution.) Because HCl is a corrosive gas, the tubes used in the system are made of teflon. The tees are made of 316 stainless steel. (Stainless steel, noted to be a better anticorrosive material than other metals, also slightly corroded in the HCl environment.) The HCl concentrations were checked by the direct detecting tube and titration method.

3. Pyrolysis kinetics

3.1. Effects of heating rate on pyrolysis

The residue with mass, W, after pyrolysis was expressed on a normalized basis (W/W_0, residual mass fraction). The variations of W/W_0 with reaction temperature (T)

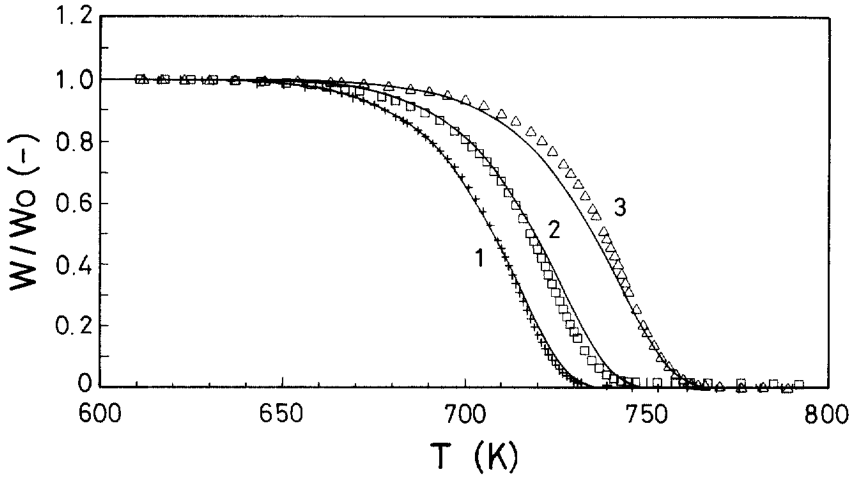

Fig. 5. Comparison of W/W_0 predicted from computed kinetic parameters, with experimental data at various β for pyrolysis of HDPE in HCl (750 ppm). 1, 2, 3: $\beta = 1$, 2, 5 K/min. +, □, △: Experimental; —: computed. $R_1^2 = 0.99$, $R_2^2 = 0.98$, $R_3^2 = 0.96$.

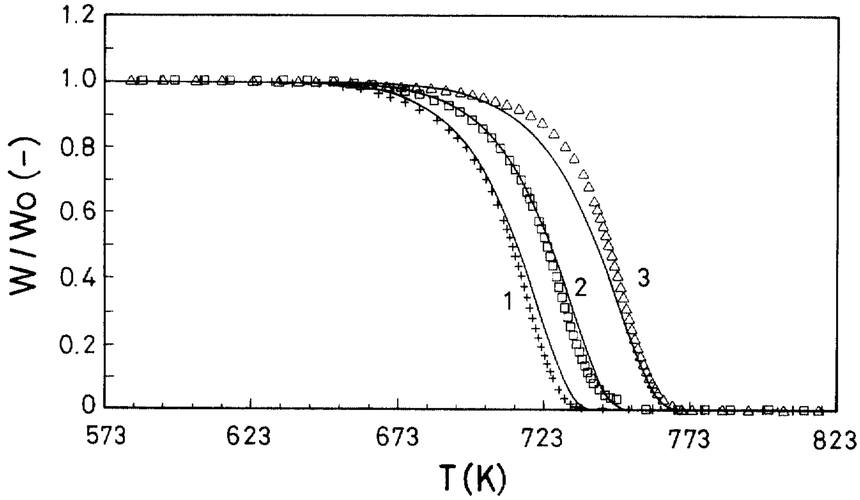

Fig. 6. Comparison of W/W_0 predicted from computed kinetic parameters, with experimental data at various β for pyrolysis of HDPE in HCl (1000 ppm). 1, 2, 3: $\beta = 1, 2, 5$ K/min. +, □, △: Experimental; –: computed. $R_1^2 = 0.98$, $R_2^2 = 0.98$, $R_3^2 = 0.97$.

for HDPE pyrolysis in various C_{HCl} are presented in Figs. 3–7. From the TGA curves yielded at three different β of 1, 2, and 5 K/min, it was noted that no residue remained for any HCl concentration. The time required for the reactant to reach a given temperature is longer for the lower heating rate than for the higher one. Generally, this will result in a lower residual mass fraction. Therefore, the residual curve of the lower heating rate is left to that of the higher heating rate.

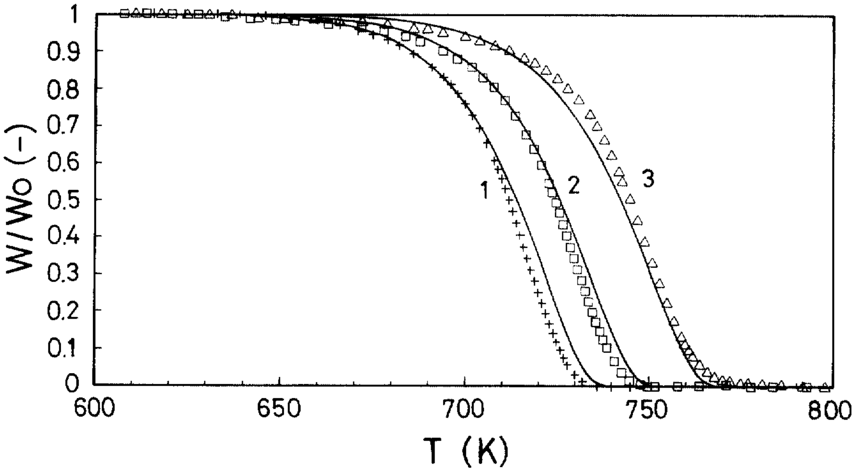

Fig. 7. Comparison of W/W_0 predicted from computed kinetic parameters, with experimental data at various β for pyrolysis of HDPE in HCl (5000 ppm). 1, 2, 3: $\beta = 1, 2, 5$ K/min. +, □, △: Experimental; –: computed. $R_1^2 = 0.97$, $R_2^2 = 0.97$, $R_3^2 = 0.96$.

Table 2
Kinetic parameters for HDPE pyrolysis in different C_{HCl}

C_{HCl} (ppm)	E (kcal/mol)	n	A (1/s)	r[a]
0	47.9	0.61	4.92×10^{11}	0.99
500	57.9	0.78	5.54×10^{14}	0.99
750	54.1	0.78	3.69×10^{12}	0.99
1000	59.4	0.66	9.66×10^{14}	0.98
5000	57.3	0.60	2.12×10^{14}	0.99

[a] Correlation coefficients accounting the Arrhenius' plots.

3.2. Kinetic parameters

Some common methods used for dealing with the pyrolysis data have been developed and employed by previous investigators [11,12,15–17]. These methods were primarily based on the general formulation of solid waste pyrolysis, $\mathrm{d}X/\mathrm{d}t = k(1\text{-}X)^n$. $\mathrm{d}X/\mathrm{d}t$ is the instantaneous reaction rate, X is the degree of conversion, n is the reaction order, k is the reaction rate constant depending on the pyrolysis temperature (T) according to the Arrhenius relationship.

The differential method for determining the activation energies (E) is employed in this study. Since the values of E were different at various reaction extents, there was a need to get a representative value for calculating reaction orders and pre-exponential factors. The value of activation energy was obtained by taking arithmetic average over the conversion range of $X = 0.2$–0.8. The reaction order (n) was determined by plotting $\ln[(\mathrm{d}X/\mathrm{d}t)/\exp(-E/(RT))]$ vs. $\ln(1-X)$. The activation energy and pre-exponential factor can be further revised by the use of temperature dependence of the reaction rate constant, i.e. Arrhenius' law. The results are listed in Table 2.

In order to verify the applicability of the obtained kinetic parameters, a comparison of the computed values of residual mass fraction with the experimental data was made as given in Figs. 3–7. The coefficients of determination, R_1^2, R_2^2, and R_3^2 (computed at the range of 5–95% of the residual mass fraction W/W_0) of these curves of β_1, β_2, and β_3 were about 0.96–0.99 for the various C_{HCl}. The agreement is quite satisfactory. This was also supported by the good correlation coefficients in the Arrhenius' plots as shown in Table 2.

4. Discussion

The TGA curves for the pyrolysis of HDPE at β of 5 K/min and in various C_{HCl} are shown in Fig. 8. When the C_{HCl} were between 0 and 500 ppm, the curves of residual mass fraction for the pyrolysis of HDPE were about the same. The influence of HCl was not obvious as $C_{HCl} < 500$ ppm. When the values of C_{HCl} were between 500 and 1000 ppm, the curves of residual mass fraction of HDPE pyrolysis were influenced moving to the higher temperature region. This indicated that HCl inhibited the pyrolytic reaction of HDPE, resulting in the lower conversion of HDPE. Furthermore, as C_{HCl} were between 1000 and 5000 ppm, the curves of residual mass fraction were not different.

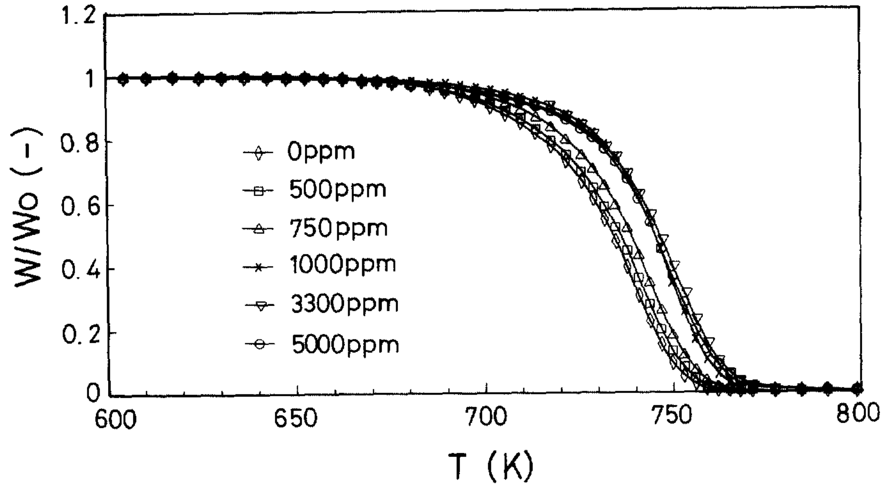

Fig. 8. Residual mass fractions (W/W_0) for pyrolysis of HDPE at various C_{HCl} at β of 5 K/min. W, W_0: masses of residues at temperature T and initial sample, respectively.

The variations of instantaneous reaction rates ($\mathrm{d}X/\mathrm{d}t$, $X = 1 - W/W_0$) with temperature under the β of 5 K/min and in various C_{HCl} are shown in Fig. 9. The peak rates and the shape of rate curves are about the same for the different C_{HCl}. However, the pyrolysis temperatures corresponding to the peak rates were different for the different C_{HCl}. A higher C_{HCl} would shift the reaction rate to a higher temperature range. This greatly supported the suggestion that HCl inhibited the pyrolysis reaction of HDPE.

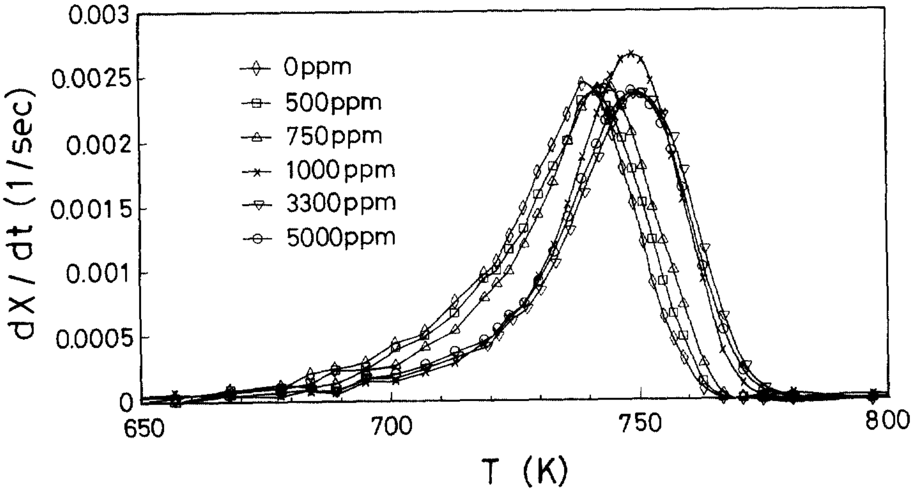

Fig. 9. Variation of $\mathrm{d}X/\mathrm{d}t$ with T at β of 5 K/min for pyrolysis of HDPE in various C_{HCl}.

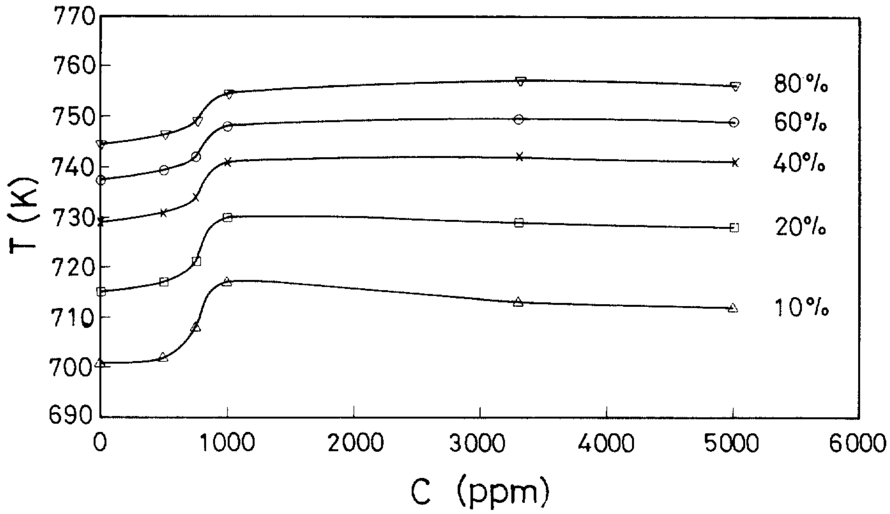

Fig. 10. Variation of T with C_{HCl} at various X of HDPE pyrolysis at β of 5 K/min. X: 80%, 60%, 40%, 20%, 10%.

The variations of T with C_{HCl} at various conversions (X) of HDPE pyrolysis at β of 5 K/min are shown in Fig. 10 (other relationships, such as X vs. C_{HCl} at various T, etc., can be also generated from Fig. 8). To reach the same conversion, the pyrolysis temperatures were different for various C_{HCl}. For instance, the differences in temperature were about 1–2 K for $C_{HCl} = 0$ and 500 ppm, about 5–7 K for $C_{HCl} = 0$ and 750 ppm, and about 12–14 K for $C_{HCl} = 0$ and 1000 ppm, respectively. The results should be useful in pyrolytic system design or in determining the incineration temperature for an incinerator.

The effects of C_{HCl} on the pyrolysis of HDPE have been investigated. The computed results from the obtained kinetic parameters gave a good agreement with the experimental data. However, further works would be helpful to the practical applications in pyrolysis/incineration processes. Such works may include: (1) to analyze the detailed pyrolysis products (solid residues/products, liquid oils, and gaseous materials) for the HDPE pyrolysis in various C_{HCl} (the results will be discussed in the later paper); (2) to deduce a representative rate equation including the C_{HCl} term; (3) to investigate the effects of HCl on the pyrolysis of other plastic materials of MSW.

5. Conclusions

Pyrolysis experiments of HDPE in various C_{HCl} were carried out in a TGA reaction system at the β of 1, 2, and 5 K/min. The corresponding activation energies, pre-exponential factors, and reaction orders were determined corresponding to the various C_{HCl}. The pyrolysis of HDPE in various C_{HCl} can be adequately described by the obtained kinetic parameters. The effects of HCl on the conversion and pyrolysis temperature of HDPE pyrolysis were discussed in detail. The results of this study may provide useful data for the design of HDPE processing system including pyrolysis and incineration.

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