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A basic test method for the study of explosion treatment of waste chemicals from laboratories

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Abstract

As a part of the research on the explosion treatment of waste chemicals from laboratories, a basic test method, which will provide the basis for our future research, was developed. First, the basic explosive, the scale of the explosion chamber and the assembly of the sample were decided. Then, measurement of detonation velocity was carried out, and the relationship between the quantity of explosive and the state of detonation propagation was obtained. A quantitative method for evaluating the decomposability of organic chemicals under explosion treatment was investigated. The results indicate that evaluating the explosion decomposability of organic chemicals from the gasification ratio could be used as a basic method provided that the excessive oxygen is approximately 62 mol% or higher. Finally, examinations of the possible effects of the quantity of explosive and conditions of atmosphere on the explosion decomposition of the model substance were conducted, and the basic test conditions regarding the quantity of explosive and condition of atmosphere were decided. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Explosion treatment; Explosion disposal; Unknown chemicals; Waste chemicals; Hazardous waste

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1. Introduction

In some chemical laboratories, there exist some unlabeled bottles of unknown origin which have accumulated for many years [1,2]. The problems of clean up of these unknown chemicals were recognized about 30 years ago, however, a fundamental solution has not yet been established [1,3,4]. Prior to the disposal of unknown chemicals, their identification by means of chemical analysis is essential. However, the possible presence of combustible, explosive and/or harmful substances among these unknown chemicals means that accidents may occur during the analysis process even when the bottles are manually opened [1,5]. In addition, the work to identify various unknown chemicals suggests a high cost because of the diversity and complexity of the analysis methods involved. It is also possible that there exist some unknown chemicals which defy efforts to identify them by various analyses, and cannot be disposed of [3,4,6–8]. This situation necessitates the development of a system to dispose of unknown chemicals in both an economical manner and with a low risk of ignition, explosion and/or harmful consequences.

Since 1993 when the present authors faced the challenge of disposing of unknown chemicals at Faculty of Engineering, The University of Tokyo, we have examined the problems associated with the analysis and disposal of these chemicals, and have tried to develop a explosion treatment method to disposal of unknown chemicals, together with their original containers, utilizing the explosive reaction of explosives [3,9].

In our previous research work, several explosible chemicals such as dibenzoyl peroxide were used as model substances, and were exploded with a commercial explosive in a relatively large explosion chamber (about 210 l). Since the analysis results showed that the original model substances and their explosive atomic groups were not found in the explosion residues, explosibility of model substances could be substantially decreased by the explosion treatment [10]. The next step was to use a small scale explosion chamber (about 230 ml) and primary explosive which can completely explode even with a small quantity. The model substance was naphthalene, known for its strong resistance to thermal decomposition. The purpose of the test was to examine the possibility of assessing the decomposition ratio without recovering the total amount of residue as such recovery would pose a major difficulty in the larger scale explosion treatment tests. It was found that under the certain explosion test conditions, the ratio of decomposition could be estimated based on the quantitative analysis results of the carbon contents of gaseous products [11].

Some study reports on the explosion treatment of chemicals are also available. In 1983, Takei et al. [1,12] of The University of Tokyo reported a case of explosion, where in a project disposal of waste explosive chemicals, some unknown chemicals of small quantities were stuck around a high performance explosive and exploded. However, the details about the decomposition ratio and post-explosion products are not reported. Other studies reported from 1994 to 1997 feature the explosion treatment of organic chlorine compounds and freon 113 [13–16]. In these studies, metal oxidants were used as additives, and explosion tests were conducted in the explosion chambers of 1–6.5 l. The reports said that the organic chlorine compounds and Freon 113 were rendered harmless as chlorine and fluorine atoms were fixed in the form of CaCl_2 , MnF_2 and others.

This paper describes the findings of our recent study on a basic test method about the explosion treatment, which will provide the basis for our future research on the application extent of the explosion treatment of waste chemicals as well as the problems associated with this method.

2. Experimental

The explosion tests for this study were carried out at the explosive experiment installation of National Institute of Materials and Chemical Research, Japan.

2.1. Materials

A slurry explosive (Super Energel manufactured by Nihon Koki) was used as the basic explosive of our study in consideration of follows.

1. It has excellent handling safety and is inexpensive.
2. Shaping and density adjustment of the explosive can be easily conducted.
3. As its oxygen balance is almost zero, it is easy to set the explosion test conditions.
4. Because of its inclusion of aluminium, it may be possible to estimate the recovery ratio of solid residue by means of analysing the aluminium content of the solid residue after the explosion test.

Number 6 electric detonators were used to initiate the slurry explosive.

Naphthalene was selected as model substance for chemicals to be decomposed by the explosive treatment. Naphthalene is a polycyclic aromatic compound and is known to be difficult to be decomposed among organic chemicals [17,18]. It also has the advantage of easy handling because it is powdery solid.

2.2. Explosion test apparatus

The scale of explosion test chamber was discussed based on our previous studies [10,11], and an explosion chamber with the volume of approximately 210 l was thought to be appropriate. Fig. 1 is an illustration of the explosion test apparatus. The explosion chamber, manufactured by Asahi Chemical Industry, has a airtight double-container structure with a revolving door. Electrodes for blasting explosive, piping for adjustment of atmosphere inside the chamber and for gas sampling, pressure and temperature sensors were installed to the chamber. The volume of the chamber actually measured was 196.8 l.

2.3. Test methods

2.3.1. Assembly of sample

Assembly of the sample used for the test is shown in Fig. 2. The model substance was filled in a glass sampling bottle on the assumption that waste chemicals are primarily discharged in glass bottles. The sampling bottle is about 15 cm³ in volume, and its polyethylene cap is 0.850 g in weight. The explosive was shaped to a form of

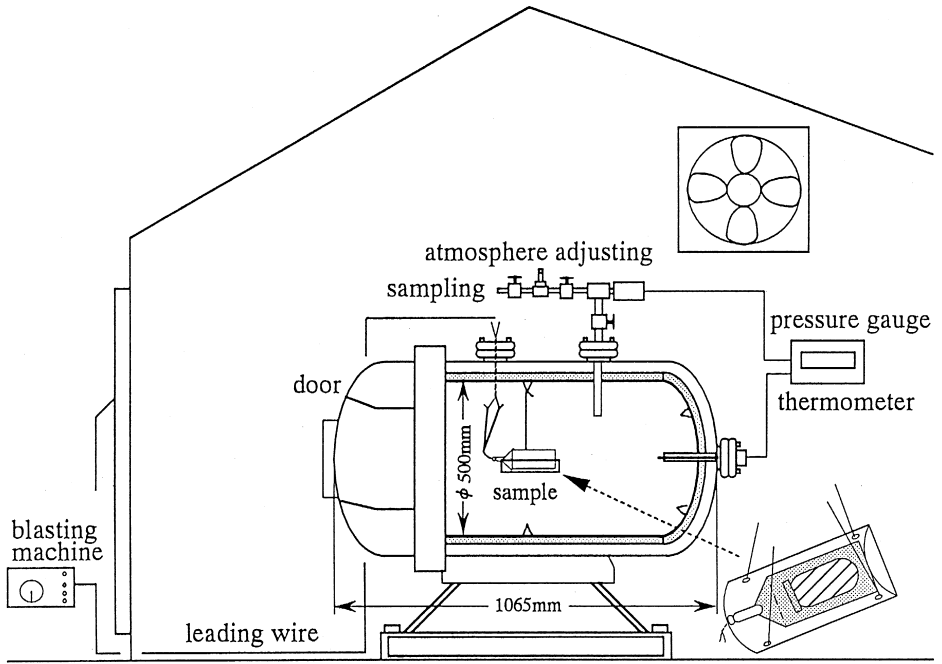


Fig. 1. Explosion experiment setup.

wrapping the bottle so that the entire bottle could be exploded, and the section to which the detonator to be inserted was conical-shaped at an angle of 90° so that detonation could efficiently take place. To shape the form of explosive out of a 50-mm diameter cylindrical ready-made explosive, cork borers and a specially processed conical shaper were used, and the same shaping process was followed.

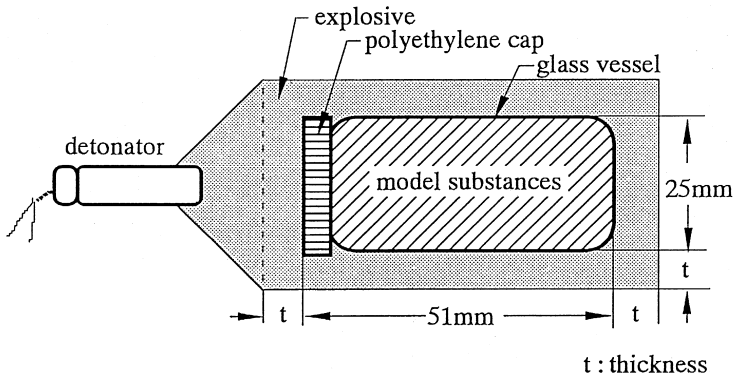


Fig. 2. Sample assembly.

In order to let the sample explode at the centre of the explosion chamber, a semi-cylindrical glass plate was hung by copper wire to the centre of the chamber and the sample was placed on this glass plate as shown in Fig. 1.

2.3.2. Test conditions

The test conditions are shown in Table 1. All of the tests were conducted under normal atmospheric pressure, and apart from the blank test, the quantity of naphthalene, the model substance, was constantly kept at 10.000 g. Table 1a shows the test conditions when the quantity of explosive was changed to 38.9, 54.9 and 81.4 g under air atmosphere in order to evaluate effects of the quantity of explosive on the explosion decomposition of the model substance. Table 1b shows the test conditions when the state

Table 1
Test conditions for explosion experiments

(a) Effects of quantity of explosive

Run no.	Naphthalene weight (g)	Explosive		Atmosphere			Excess oxygen (mol%)
		Weight (g)	Thickness (mm)	<i>P</i> (kPa)	<i>T</i> (K)	O ₂ concentration (mol%)	
A1	10.000	38.9	3.5	101	297	20.9	63
A2	10.000	54.9	5.5	101	300	20.9	62
A3	10.000	81.4	7.5	101	297	20.9	63

(b) Effects of contact conditions of model substance with explosive

A1	10.000	38.9	3.5	101	297	20.9	63
B1 ^a	10.000	38.9	~ 7	101	299	20.9	62
A2	10.000	54.9	5.5	101	300	20.9	62
B2 ^a	10.000	54.9	~ 11	101	297	20.9	63

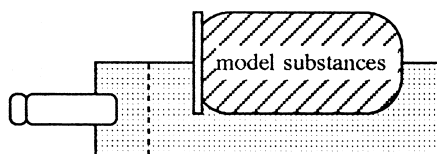
(c) Effects of atmosphere

C1	10.000	54.9	5.5	101	298	0.8	-94
C2	10.000	54.9	5.5	101	296	12.8	0
C3	10.000	54.9	5.5	101	300	20.9	62
C4	10.000	54.9	5.5	101	303	35.0	168

(d) Blank test of (a)

1	nothing	38.9	3.5	101	290	20.9	-
2	nothing	54.9	5.5	101	294	20.9	-
3	nothing	81.4	7.5	101	295	20.9	-

^aThe sample assembly for run numbers B1 and B2 is as follows (the cap of glass vessel is nothing).



of contact between the model substance and explosive was changed. Table 1c shows the test conditions when the oxygen concentration in the atmosphere inside the chamber was changed, and Table 1d shows the test conditions of the blank test where blank sampling bottles were used.

The explosive thickness in Table 1 was calculated from the diameters of two cork borers simultaneously used to shape the explosive, i.e., the outside diameter of the inner cork borer and the inside diameter of the outer cork borer. The excessive oxygen was defined by the Eq. (1).

$$\text{Excess oxygen (mol\%)} = [(A - B)/B] \quad (1)$$

where A is the number of oxygen atoms in the chamber before explosion and B is the number of oxygen atoms required for perfect combustion inside the chamber.

For calculating the excessive oxygen, oxygen in the atmosphere inside the chamber, the model substance naphthalene (10.000 g), polyethylene cap (0.850 g) of the sampling bottle, explosives contained in the detonator (primary explosive diazodinitrophenol 0.2 g and base charge penthrite 0.4 g) were taken into account, and it was assumed that carbon, hydrogen and nitrogen atoms ideally become carbon dioxide, water and nitrogen molecules, respectively. As the oxygen balance of the slurry explosive used was practically zero, the explosive itself was not included in the calculation of the excessive oxygen.

The oxygen concentration of the atmosphere was adjusted by means of discharging a predetermined quantity of air from the chamber after closing the door of the explosion chamber, and then introducing either oxygen or nitrogen. In the case of adjusting the atmosphere to nitrogen atmosphere, substitution with nitrogen was conducted for about 3 h.

2.3.3. Analysis

Sampling of the gaseous products was conducted approximately 30–50 min after the explosion when the gases in the chamber were thought to be evenly mixed through diffusion. After recording the temperature and pressure inside the chamber, gaseous products were fed into the Tedlar bags via the gas sampling pipe and were immediately analysed for carbon dioxide, carbon monoxide, C1–C5 hydrocarbons, volatile organic compounds and naphthalene vapour. Table 2 shows the analytical conditions of the gas chromatography.

After sampling of the gaseous products, the door of the explosion chamber was opened, and the explosion products adhering to the inner wall of the chamber were dried at room temperature. These products were scraped off by a brush and recovered after most of copper splinters of the detonator tube and suspending wire were picked out. The recovered solid residue was then ground into powder of 42 mesh or smaller with a mortar inside a dry ice box. A part of the powdery residue was dissolved in acetone and the naphthalene concentration of this solution was analysed by a gas chromatography to calculate the amount of naphthalene in the residue. For estimating the recovery ratio of solid residue, the amount of aluminium, which came from the explosive, in the residue was measured using atomic absorption analysis.

Table 2
Conditions for gas chromatography analysis

Species	Gas chromatography	Detector	Column
CO	Shimadzu Model GC8A	TCD	3 mm ID × 3 m Molecular Sieve 13X, 80/100 mesh 50°C, He 60 ml/min
CO ₂	Shimadzu Model GC8A	TCD	3 mm ID × 3 m Porapak Q, 80/100 mesh 50°C, He 41 ml/min
C1–C5 hydrocarbons	Shimadzu Model GC14A	FID	0.32 mm ID × 50 m fused silica PLOT Al ₂ O ₃ /KCl 50°C (2 min) → 195°C, 3°C/min, He 42 cm/s
Other volatile organic components	Shimadzu GCMS-5000	–	0.32 mm ID × 30 m DB-624 50°C (3 min) → 258°C, 10°C/min, He 56 cm/s
Naphthalene	Shimadzu GCMS-5000	–	0.32 mm ID × 30 m DB-5.625 50°C (3 min) → 250°C, 15°C/min, He 58 cm/s

2.4. Measurement of detonation velocity

In order to investigate the state of explosion, detonation velocity was measured by an independent set of tests in an explosion pit. Empty sampling bottles were used, but the assembly of the sample and quantity of the explosive employed were as same as those shown in Fig. 2 and Table 1d.

The ion gaps method [19], which are stipulated by the Japan Explosives Society Standards for measurement of detonation velocity, was selected. The test apparatus is illustrated in Fig. 3. Six sets of ion gaps made of enamel-coated copper wire (0.2 mm in diameter) were fixed to an acrylic ruler at a measuring interval of 11 mm, and then connected to an oscilloscope (Hewlett-Packard 54520A) via a hand-made pulse generator. After inserting these ion gaps into the explosive around the sampling bottle, the explosive was initiated, and the generated pulse waveforms were recorded by the oscilloscope.

3. Results and discussion

3.1. Effect of explosive quantity on propagation of detonation

The measurement results of detonation velocity are shown in Fig. 4 and Table 3. Fig. 4 shows the pulse waveform of Run no. 1 and the arrival times of the detonation wave at each ion gap are indicated by the pulses. The pulse waveforms of Run nos. 2 and 3 were similar to that of Run no. 1. Table 3 shows the propagation times of the detonation wave between the ion gaps (time intervals between the rising points of the pulses).

As the ion gaps were set up at interval of 11 mm, the average detonation velocity between the ion gaps could be determined using the time intervals between the rising

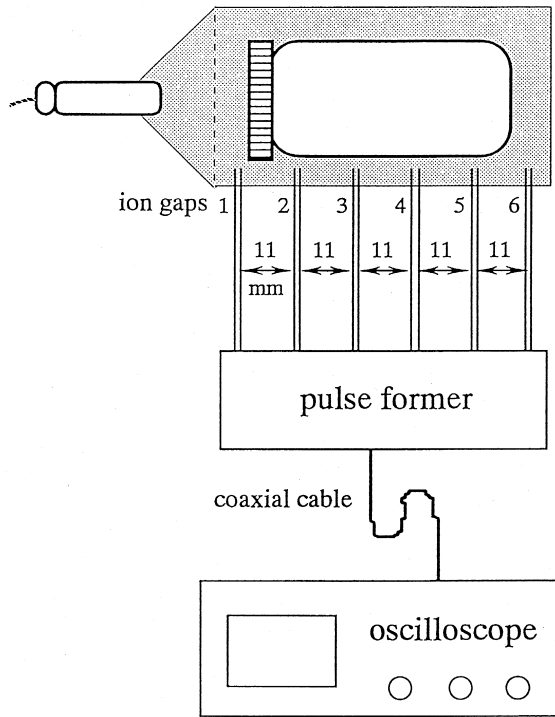


Fig. 3. Experimental setup for measurement of detonation velocity.

points of the pulse shown in Table 3, and the calculation results are shown in Fig. 5. It is indicated from Fig. 5 that the detonation velocity of the explosive around the sampling

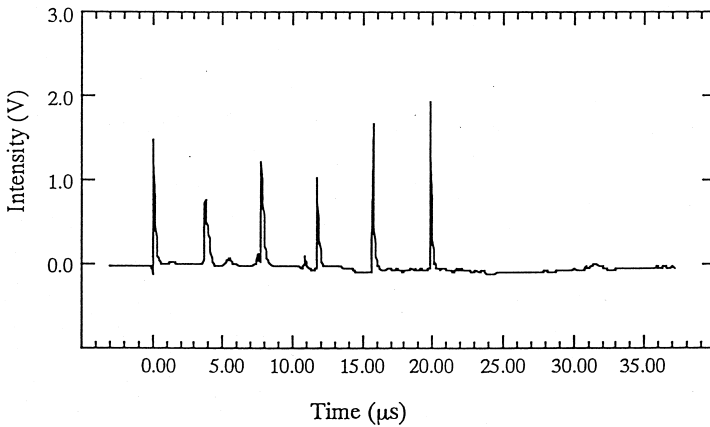


Fig. 4. Pulse waveform of Run no. 1.

Table 3
Time between ion gaps (μs)

Run no.	Explosive weight (g)	Ion gaps				
		1 → 2	2 → 3	3 → 4	4 → 5	5 → 6
1	38.9	3.66	4.06	3.96	3.99	4.12
2	54.9	3.15	3.39	3.51	3.38	3.25
3	81.4	3.01	3.15	2.90	2.98	3.11

bottle is about 2.5–3.0, 3.0–3.5 and 3.5–4.0 km/s for quantity of explosive of 38.9, 54.9 and 81.4 g, respectively.

It is generally understood that the propagation velocity of deflagration is several hundred meters per second at its fastest while the propagation velocity of detonation is larger than 2 km/s. Consequently, it is clear that the explosive reached the state of detonation at explosion for each quantity of explosive. In the case of Run no. 1 where a small quantity of explosive was used, it was predicted that detonation may be discontinued because of the thin explosive around the sampling bottle. The pulse waveform shown in Fig. 4 proves that detonation is propagated without discontinuation even if the quantity of explosive is 38.9 g.

In order to obtain information about the load on the model substance at explosion, the detonation pressure on the sampling bottle was estimated based on following equation [20].

$$P_{\lambda} = (1/4)\rho_0 D^2 \quad (2)$$

where, P_{λ} is the detonation pressure (GPa), ρ_0 is the density of the explosive (g/cm^3) and D is the detonation velocity (km/s).

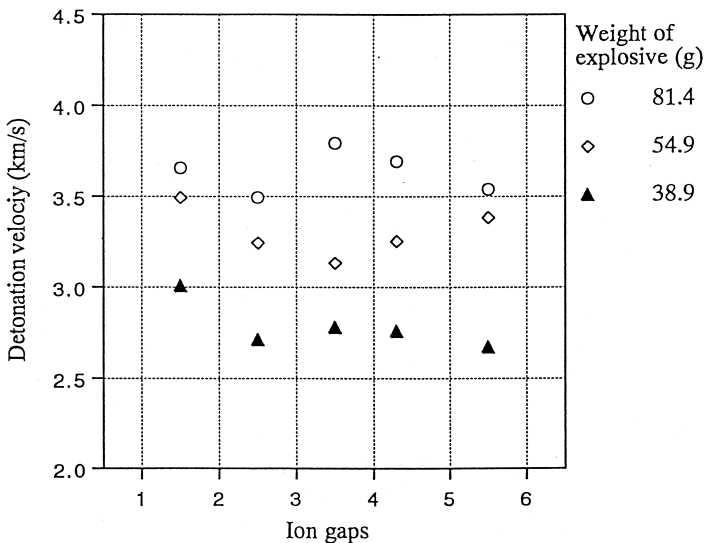


Fig. 5. Detonation velocity of the slurry explosive.

Table 4
Gaseous products from the explosion experiments (N.D.: not detected)

Run no.	Concentration of gaseous products											Sampling		
	CO (mol%)	CO ₂ (mol%)	CH ₄ (ppm)	C ₂ H ₂ (ppm)	C ₂ H ₄ (ppm)	C ₂ H ₆ (ppm)	C ₃ H ₆ (ppm)	C ₃ H ₈ (ppm)	C ₄ H ₈ (ppm)	C ₆ H ₆ (ppm)	C ₇ H ₈ (ppm)	C ₁₀ H ₈ (ppm)	Temperature (K)	Pressure (kPa)
1	0.51	1.61	187	51	93	3	8	N.D.	3	*	1	N.D.	292	107.3
2	0.41	2.44	37	19	57	*	7	1	4	1	3	N.D.	296	108.7
3	0.12	3.82	7	4	19	*	3	N.D.	2	1	5	N.D.	298	113.3
A1	0.21	10.48	43	19	36	N.D.	6	*	4	1	1	3	302	109.1
A2	0.23	11.62	44	24	26	*	4	*	3	6	4	38	309	109.9
A3	0.24	11.99	44	20	29	*	5	*	4	2	4	5	306	117.2
B1	0.13	10.03	13	16	9	N.D.	1	N.D.	1	*	1	11	304	108.4
B2	0.11	10.88	12	13	10	N.D.	2	*	1	1	2	10	302	109.6
C1	0.63	1.56	429	111	119	23	13	4	3	29	7	98	300	113.3
C2	1.24	9.34	215	102	82	3	7	*	2	29	3	75	301	112.0
C3	0.23	11.62	44	24	26	*	4	*	3	6	4	38	309	109.9
C4	0.09	11.91	34	7	23	2	5	*	3	4	6	17	308	109.2

* < 1 ppm.

The calculation results show that the detonation pressure were 2.3–2.8, 3.0–3.8 and 3.8–4.5 GPa for explosive quantities of 38.9, 54.9 and 81.4 g, respectively. The time duration of the detonation pressure were approximately 20, 17 and 15 μs , respectively, in terms of the detonation propagation time between the first and last ion gaps.

The nominal detonation velocity of the slurry explosive used is 5.3 km/s. Considering that this is the ideal detonation velocity, an increase of the explosive quantity should make the explosive pressure reach its maximum pressure of 8.8 GPa based on Eq. (2). Accordingly, the pressure on the model substance in the present tests is thought to be approximately half of the theoretical maximum pressure generated by the explosive. This would be a useful reference for the practical application of the explosion treatment or for the use of other kinds of explosives.

In the present tests, the minimum quantity of explosive used was 38.9 g because of the size of sampling bottle and the dimensions of the cork borers used to shape the explosive. If a less quantity of explosive had been used, shaping of the explosive could have proved difficult due to the requirement for a thinner explosive layer around the sampling bottle. Moreover, the detonation process could have been discontinued due to such thin explosive.

3.2. Products of explosive reaction

In order to evaluate the decomposability of the model substance naphthalene, the carbon-containing constituents of the gaseous products, and residual naphthalene vapour were analysed. The analysis results, together with the temperature and pressure at the time of sampling, are shown in Table 4. In regard to organic products Table 4 lists seven different constituents of lower hydrocarbons, as well as benzene and toluene as volatile organic constituents. Higher molecular products which were difficult to identify were detected from Run no. C1. Some other constituents were also found in some tests, but their identification were not carried out on the grounds that their concentrations were judged to be less than 1 ppm based on their respective peak area ratios.

Table 4 shows that carbon dioxide, carbon monoxide, methane, ethylene, acetylene are the dominant carbon-containing constituents among the gaseous products. Table 5 shows the calculation results of the carbon content when the carbon-containing constituents of gaseous products are classified into three groups, i.e. (i) CO and CO₂, (ii) C1–C4 hydrocarbons and (iii) benzene and toluene. From Table 5, the ratios of carbon contained in CO and CO₂ in the total carbon of gaseous products are 94.8 wt.% for Run no. C1 and 97.6–99.9 wt.% for other tests. Meanwhile, the ratio of carbon contained in C1–C4 hydrocarbons in the total carbon of organic constituents are 60–98 wt.%. These tendency are similar to that of gaseous products resulting from the incineration of hazardous waste [21].

Fig. 6 plots the excessive oxygen along the horizontal axis, and carbon contents of CO₂, CO, C1–C4 hydrocarbons, benzene and toluene in the total carbon of gaseous products along the vertical axis. Fig. 6 shows that with increase of the excessive oxygen, the ratio of CO₂ increases and gradually approaches 100 mol%, on the contrary the ratio of CO, C1–C4 hydrocarbons, benzene and toluene decreases. Such phenomena indicate that an increase of the excessive oxygen facilitates the production of CO₂ while suppressing the production of CO and organic constituents.

Table 5
Quantity of carbon contained in the gaseous products

Run no.	Weight of carbon (g)			
	In CO and CO ₂	In C1–C4 hydrocarbons	In benzene and toluene	Total
1	2.26	0.055	0.001	2.32
2	3.04	0.024	0.003	3.06
3	4.35	0.008	0.005	4.36
A1	11.21	0.020	0.001	11.23
A2	12.24	0.017	0.007	12.27
A3	13.61	0.019	0.004	13.63
B1	10.52	0.007	0.001	10.53
B2	11.58	0.007	0.002	11.59
C1	2.41	0.109	0.024	2.54
C2	11.44	0.067	0.021	11.53
C3	12.24	0.017	0.007	12.27
C4	12.36	0.013	0.007	12.38

The solid residue inside the chamber consisted mainly of glass constituents and splinters of the detonator tube and the suspending wire. Out of the residue of Run no. C1, incompletely combusted soot and fine silvery powder which was believed to be aluminium were observed. For Run nos. C1–C4 in which different excessive oxygen

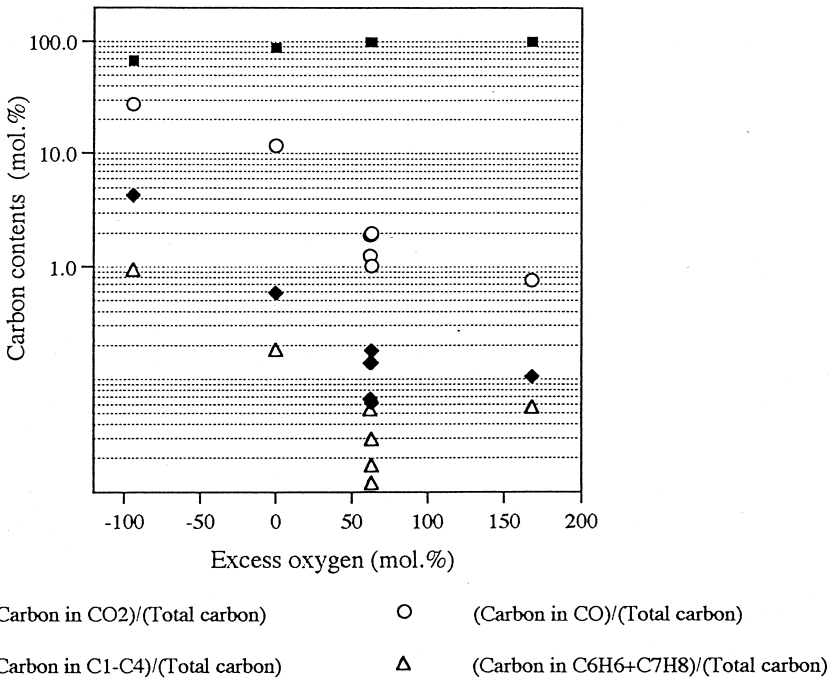


Fig. 6. Relationship between carbon contents and excess oxygen.

Table 6
Analysis result of explosion residue

Run no.	Residue (g)	Aluminium (g)	Naphthalene (mg)
C1	44.9	2.5	1892
C2	35.9	2.1	< 1
C3	40.2	2.4	< 1
C4	40.0	2.6	< 1

was applied, naphthalene and explosive-originating aluminium in the recovered solid residue were analysed and the analysis results are shown in Table 6. The amounts of detected aluminium were 2.1–2.6 g and, based on the quantity of explosive used and its aluminium content, the recovery ratio of aluminium was found to be approximately 70–90 wt.%. As for naphthalene, the amount detected was 1892 mg for Run no. C1 in which excessive oxygen was negative, and less than 1 mg for Run nos. C2–C4 in which excessive oxygen was zero or positive.

Comparing the naphthalene vapour pressure, calculated from the naphthalene concentration of the gaseous products at the time of sampling (Table 4), with the naphthalene's saturated vapour pressure at the same temperature, the presence of residual solid naphthalene in case of Run nos. C1 and C2 was suggested. Possible reasons why the presence of solid naphthalene was not confirmed in Run no. C2 are considered to be the adhesion of small quantity of undecomposed naphthalene on the inner wall of the chamber, as well as their scatter to the air during recovery operation.

3.3. Quantitative evaluation method of decomposability under the explosion treatment

In order to evaluate the decomposability of chemicals under the explosion treatment, as well as application extent of the explosion treatment, it is necessary to calculate decomposition ratio of chemicals. Assuming that after explosion treatment of a model substance in an explosion chamber, the decomposed model substance generates new products and the undecomposed part remains in the chamber, the decomposition ratio can be calculated by the following equation based on the mass of the residual model substance.

$$\begin{aligned} & \text{Decomposition ratio (wt.\%)} \\ &= \frac{\text{Mass of model substance (g)} - \text{Mass of residual model substance (g)}}{\text{Mass of model substance (g)}} \times 100 \end{aligned} \quad (3)$$

If the decomposition ratio is to be calculated based on the decomposition products after explosion, the following equation may be applied on condition that model substance is an organic compound.

$$\begin{aligned} & \text{Decomposition ratio (wt.\%)} \\ &= \frac{\text{In products, carbon content originating from model substance (g)}}{\text{Carbon content of model substance (g)}} \times 100 \end{aligned} \quad (4)$$

Here, the authors define the gasification ratio as follows.

$$\text{Gasification ratio (wt.\%)} = \frac{\text{In gaseous products, carbon content originating from model substance (g)}}{\text{Carbon content of model substance (g)}} \times 100 \quad (5)$$

Eqs. (4) and (5) indicate that the gasification ratio is identical to the decomposition ratio if all carbon-containing products of model substance by the explosion treatment are gaseous constituents.

Using Eq. (3), the decomposition ratio of naphthalene in Run nos. C1–C4 was estimated from the residual model substance. In the case of Run no. C1, the decomposition ratio was calculated using a recovery ratio of residual solid naphthalene of 70 wt.% which was the recovery ratio of explosive-originating aluminium in the solid residue. In the case of Run nos. C2–C4, as the amount of naphthalene in the solid residue was less than 1 mg, only the residual naphthalene vapour was considered for the estimation of decomposition ratio. On the other hand, the gasification ratio of each test was calculated by Eq. (5) using the amount of model substance naphthalene, and the carbon content of CO₂, CO, C1–C4 hydrocarbons, benzene and toluene shown in Table 5. To determine the carbon content originating from the model substance, those carbon which originated from the explosive, detonator and cap of the sampling bottle was calculated by the blank test, and then subtracted from the total carbon content. Table 7 shows the calculation results of both estimated decomposition ratio and gasification ratio.

In Run no. C1, the excessive oxygen was –94 mol% and the estimated decomposition ratio was 71.9 wt.%. An previous study by the authors mentioned that the difference between the decomposition ratio and gasification ratio is fairly large in a system where excessive oxygen is negative [11]. In Run no. C1, as only small amounts of CO and CO₂ were produced, making the carbon content (2.54 g) of the gaseous products lower than the carbon content (3.06 g) in the corresponding blank test (Run no. 2), the calculated gasification ratio showed a negative value. Consequently, it can be said that evaluation of the decomposition ratio based on the gasification ratio is difficult when excessive oxygen is negative.

Table 7
Estimated decomposition ratio and gasification ratio

Run no.	Explosion conditions			Residual naphthalene		Estimated decomposition ratio (wt.%)	Gasification ratio (wt.%)
	Naphthalene (g)	Explosive (g)	Excess oxygen (mol%)	As vapour (mg)	In solid residue (mg)		
A1	10.000	38.9	63	–	–	–	95.1
A2	10.000	54.9	62	–	–	–	98.2
A3	10.000	81.4	63	–	–	–	98.9
B1	10.000	38.9	62	–	–	–	95.4
B2	10.000	54.9	63	–	–	–	98.8
C1	10.000	54.9	–94	112	1892	71.9	–
C2	10.000	54.9	0	85	< 1	99.2	90.3
C3	10.000	54.9	62	41	< 1	99.6	98.2
C4	10.000	54.9	168	18	< 1	99.8	99.4

In Run no. C2 where excessive oxygen was zero, the difference between the estimated decomposition ratio and gasification ratio was 8.9 wt.%. Analysis of the gaseous products shows that the concentration of hydrogen of Run no. C2 was 11 times higher than that of the other tests where excessive oxygen is 62 mol% or higher, which suggest the production of those such as solid carbon which cannot be detected by gas chromatography. This in turn implies that the test condition of excessive oxygen of 0 mol% is insufficient for evaluating the decomposition ratio based on the gasification ratio. On the other hand, as described earlier, although there is a possibility of residual solid naphthalene in the chamber at the time of gas sampling in the case of Run no. C2, no naphthalene was detected in the solid residue. This implies that accurate quantification of the residual model substance is difficult when explosion treatments are conducted in a large explosion chamber.

Run nos. C3 and C4 were conducted under the air atmosphere and the atmosphere with a higher oxygen concentration. Their excessive oxygen was 62 and 168 mol%, and the difference between estimated decomposition ratio and gasification ratio reduced to 1.4 and 0.4 wt.%. Based on their gasification ratio (98.2 and 99.4 wt.%), the amount of naphthalene remained in the chamber was calculated to be 180 mg for Run no. C3 and 60 mg for Run no. C4. If assuming that the naphthalene vapour in the chamber at the time of gas sampling was in the state of saturation, the amount of existing naphthalene is calculated to be 177 mg for Run no. C3 and 155 mg for Run no. C4 from the equilibrium vapour pressure of naphthalene. In view of these figures, it is inferred that residual naphthalene in the chamber existed in the form of nearly saturated vapour in Run no. C3 and non-saturated vapour in Run no. C4. In these tests, the Tedlar bags were used to sample the gaseous products. Given the adsorption of naphthalene vapour to the Tedlar bags, the scale of the tests and the accuracy of the measuring system, etc. into consideration, it can be said that the gasification ratio and estimated decomposition ratio are fairly identical in the case of Run nos. C3 and C4. Consequently, the decomposition ratio of the model substance can be evaluated on the basis of the gasification ratio provided that excessive oxygen is not less than 62 mol%.

The above examination of a quantitative evaluation method for the decomposability of chemicals by explosion treatment confirms that the decomposition ratio can be estimated based on the gasification ratio provided that excessive oxygen is not less than 62 mol%, and such estimation is difficult if the excessive oxygen is 0 mol% or less. On the other hand, it is indicated that the method of evaluating the decomposition ratio by analysing the residual model substance is technically difficult when large scale explosion chamber is used, and the amount of residual model substance is small. In conclusion, when the excessive oxygen is 62 mol% or higher, which is an advantageous condition for the progress of explosive reaction, evaluation based on the gasification ratio can be considered a basic method of effectively evaluating the explosion decomposability of organic chemicals.

3.4. Factors effecting on decomposition under explosion treatment

3.4.1. Quantity of explosive

In order to determine the quantity of explosive to be used as a one of the basic condition for explosion treatment test, the relationship between the quantity of explosive

and the decomposition ratio of naphthalene was examined under the condition of air atmosphere. Fig. 7 plots the quantity of explosive (38.9, 54.9 and 81.4 g) along the horizontal axis, and the decomposition ratio based on the gasification ratio along the vertical axis. A tendency that the decomposition ratio of naphthalene increases in accordance with the quantity of explosive could be observed. This tendency does not constitute a straight line on the graph as the increase of the decomposition ratio slows down when the quantity of explosive exceeds approximately 54.9 g.

With the increase of the quantity of explosive used, the detonation pressure on the naphthalene at explosion increases, at the meantime, the generated calorific value increases also. While it is an interesting theme that the increase of decomposition ratio was caused mainly by whether heat or mechanochemical effect, the test results did not provide a clear answer.

In consideration of the fact that the use of 54.9 g of explosive with 10 g of naphthalene achieve a naphthalene decomposition ratio of 98.2 wt.% and that naphthalene is one of the most difficult organic chemical compounds to decompose, the authors think that the quantity of explosive used as basic test condition should be restricted to about 55 g.

3.4.2. Atmosphere

In the test system used this time, the excessive oxygen was determined by the amount of oxygen in the atmosphere inside the chamber and the mass of the model substance. In deciding the test conditions, the quantity of naphthalene, i.e. model substance, was set at 10 g in consideration of that the decomposition ratio could be evaluated based on the gasification ratio provided that the excessive oxygen, determined by the amount of oxygen contained in the normal pressure air atmosphere in the chamber, was around 60 mol%. The test results confirmed that the decomposition ratio can be evaluated using the gasification ratio under normal air pressure atmosphere as described earlier.

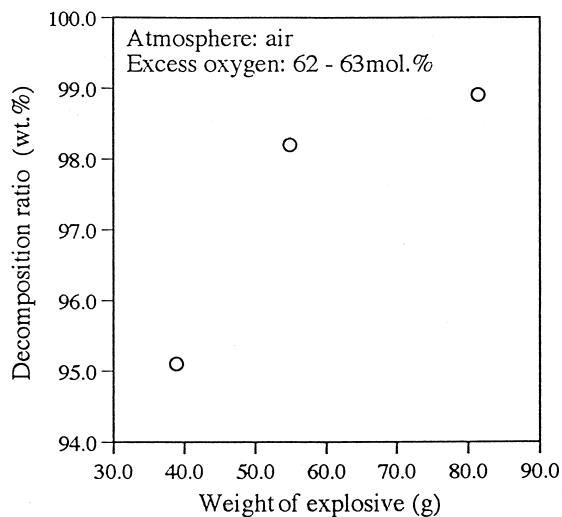


Fig. 7. Relationship between decomposition ratio and quantity of explosive.

Fig. 8 shows the correlation between the oxygen concentration in the atmosphere inside the chamber and the decomposition ratio of naphthalene when the quantity of explosive was 54.9 g. While the decomposition ratio of naphthalene under air atmosphere (oxygen concentration 20.9 mol%) was 98.2 wt.%, increasing of oxygen concentration of the atmosphere inside the chamber up to 35.0 mol% by inflowing of pure oxygen into the chamber, the decomposition ratio of naphthalene increased to 99.4 wt.%. This results can be attributed to the acceleration of the exothermic oxidation reaction between naphthalene as well as organic matters originating from decomposed naphthalene and oxygen due to an increased oxygen concentration in the atmosphere, and also to the acceleration of the oxidizing decomposition of naphthalene due to an increased temperature in the system. It may, therefore, be possible to make the decomposition ratio of naphthalene approach 100 wt.% with a further increase of the oxygen concentration.

Considering the facts that the decomposition ratio can be evaluated based on the gasification ratio under the condition of normal pressure air atmosphere and that the decomposition ratio of naphthalene under such condition reaches 98.2 wt.%, normal pressure air atmosphere is deemed to be appropriate as the basic atmosphere condition.

3.4.3. Contact conditions of model substance with explosive

In regard to the contact form of model substance with explosive, the assembly of the explosive wrapping the entire sampling bottle was selected as the basic assembly as shown in Fig. 9a. In order to evaluate the effects of contact conditions of model substance with explosive on the decomposition ratio of the model substance, Run nos. B1 and B2 were conducted in which only half of the sampling bottle was wrapped by the explosives as shown in Fig. 9b, while the same quantity of explosive and the same

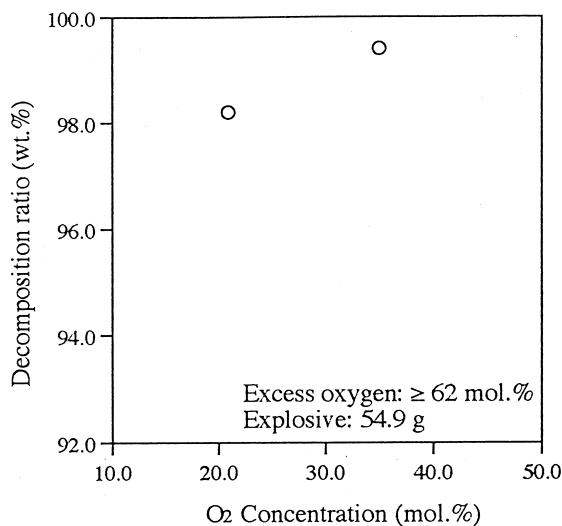


Fig. 8. Relationship between decomposition ratio and O₂ concentration of the atmosphere.

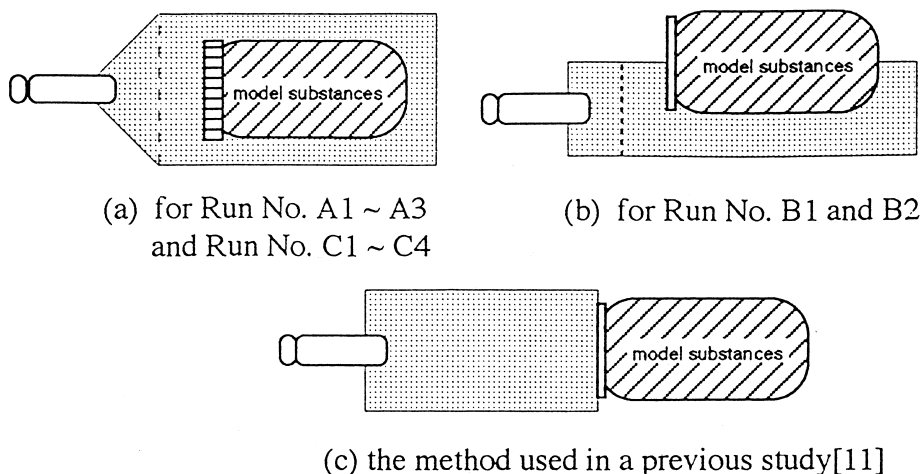


Fig. 9. Contact conditions of model substance with explosive.

atmosphere were used as those for Run nos. A1 and A2. Considering that the cap of the sampling bottle may be blown away in the case of the half-wrapped bottle, Run nos. B1 and B2 were conducted without the cap. So for calculating the gasification ratio of Run nos. B1 and B2, the mass of carbon contained in cap (0.728 g) was subtracted from the carbon content of the gaseous products of the blank test (Run nos. 1 and 2).

As shown in Table 7, decomposition ratio of Run nos. B1 and B2 were 95.4 and 98.8 wt.%, respectively, while that of Run nos. A1 and A2 were 95.1 and 98.2 wt.%, respectively. Unlike the pre-test prediction, the change of the contact form of the model substance with the explosive did not lower the decomposition ratio. In a previous paper [11], it was mentioned that when the model substance was placed next to the explosive as shown in Fig. 9c, some model substance scattered at the explosion, and adhered to the low temperature inner wall of the chamber and remained there without undergoing any reaction. In these tests, decreases of the decomposition ratio were not found. Possible reasons were thought to be that the degree of scattering of the model substance is reduced in the case of the sampling bottle being half-wrapped by the explosive compared to the juxtaposition of the model substance with the explosive, and that slurry explosive has a high explosion calorific value (5058 kJ/kg [22]), while AgN_3 used in the previous study has a low explosion calorific value (1916 kJ/kg [23]).

4. Conclusions

In this paper, a basic explosion treatment test method, which would comprise the basis to investigate the application extent of the explosion treatment of chemicals and the problems associated with explosion treatment, is examined.

First, the basic explosive, the scale of the explosion chamber and the assembly of the sample were decided based on the knowledge obtained from our earlier studies. Then, detonation velocity measurement was conducted, and the relationship between the

quantity of explosive and the state of detonation propagation was obtained. A quantitative method for evaluating the decomposability of organic chemicals under explosion treatment was investigated. The results indicate that evaluating the explosion decomposability of organic chemicals from the gasification ratio could be used as a basic method provided that the excessive oxygen is approximately 62 mol% or higher, which is an advantageous condition for the progressive explosion reaction. Furthermore, examinations of the possible effects of the quantity of explosive and conditions of atmosphere on the explosion decomposition of the model substance were conducted, and the basic test conditions regarding the quantity of explosive and condition of atmosphere were decided.

In conclusion, the basic explosion treatment test method described below is considered to be appropriate for organic chemicals. (1) Volume of the explosion chamber is about 200 l. (2) Atmosphere inside the explosion chamber is normal pressure air. (3) Assembly of sample is as shown in Fig. 2, and installation of sample in explosion chamber is as shown in Fig. 1. (4) Quantity of slurry explosive is about 55 g. (5) Deciding the quantity of the selected test sample that will satisfy the condition that the excess oxygen is not less than 62%. (7) Calculating gasification ratio based on quantitative analysis of CO, CO₂, C1–C5 hydrocarbons and volatile organic compounds of gaseous products. (8) Evaluating decomposition ratio based on the gasification ratio.

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References

- [1] S. Takei, H. Ouchi, M. Itoh, F. Yoshizawa, M. Tamura, T. Yoshida, *Journal of Japan Society for Safety Engineering* 22 (1983) 292.
- [2] K. Shirasuka, E. Shouto, H. Takatsuki, T. Takahashi, H. Taniguchi, S. Hayano, Annual report, Nissan Science Foundation 8 (1985) 361.
- [3] H. Li, M. Arai, M. Tamura, Y. Suzuki, *Journal of Japan Society for Safety Engineering* 35 (1996) 158.
- [4] Y. Suzuki, *Journal of Medical Wastes Research Association, Japan* 10 (1997) 13.
- [5] Manufacturing Chemists' Association, *Laboratory Waste Disposal Manual*, 2nd edn., Manufacturing Chemists' Association, Washington, DC, 1969, p. 148.
- [6] H.J. Sanders, *Chemical and Engineering News* 64 (5) (1986) 21.
- [7] B.C. McKusick, *Journal of Chemical Education* 63 (1986) A128.
- [8] M. Hori, J. Yang, *Journal of Japan Society for Safety Engineering* 33 (1994) 183.
- [9] H. Li, N. Kikuchi, M. Itoh, M. Arai, M. Tamura, T. Matsunaga, T. Matsuzawa, *Proceedings of the Japan Explosives Society, 1994 Spring Meeting*, Japan Explosives Society, Tokyo, Japan, 1994, p. 89.
- [10] H. Li, M. Arai, M. Tamura, T. Matsunaga, M. Iida, *Journal of the Japan Explosives Society* 57 (1996) 271.
- [11] H. Li, M. Arai, M. Tamura, M. Iida, T. Matsunaga, *Journal of the Japan Explosives Society* 58 (1997) 211.

- [12] S. Takei, K. Muranaga, A. Aoki, H. Ouchi, M. Tamura, T. Yoshida, *Journal of Japan Society for Safety Engineering* 23 (1984) 35.
- [13] T. Koshigawa, A. Miyake, T. Ogawa, T. Matsunaga, M. Iida, Y. Hanai, *Proceedings of the Japan Explosives Society, 1994 Autumn Meeting, Japan Explosives Society, Tokyo, Japan, 1994*, p. 33.
- [14] T. Katsuragi, A. Miyake, T. Ogawa, T. Uchida, *Proceedings of the Japan Explosives Society, 1994 Autumn Meeting, Japan Explosives Society, Tokyo, Japan, 1994*, p. 27.
- [15] T. Katsuragi, A. Miyake, T. Ogawa, T. Matsunaga, M. Iida, Y. Hanai, *Proceedings of the Japan Society for Safety Engineering, 28th Meeting, Japan Society for Safety Engineering, Yokohama, Japan, 1995*, p. 87.
- [16] K. Shibasaki, A. Miyake, T. Ogawa, K. Miyamoto, T. Matsunaga, M. Iida, *Proceedings of the Japan Explosives Society, 1997 Autumn Meeting, Japan Explosives Society, Tokyo, Japan, 1997*, p. 37.
- [17] C.C. Lee, G.L. Huffman, S.M. Sasseville, *Hazardous Waste and Hazardous Materials* 7 (1990) 385.
- [18] P.H. Taylor, B. Dellinger, C.C. Lee, *Environmental Science and Technology* 24 (1990) 316.
- [19] K. Tanaka, *Journal of the Industrial Explosives Society, Japan* 29 (1968) 441.
- [20] N.F. Scilly, *Journal of Loss Prevention in the Process Industries* 8 (1995) 265.
- [21] C.R. Dempsey, E.T. Oppelt, *Air and Waste* 43 (1993) 25.
- [22] T. Urbanski, *Chemistry and Technology of Explosives, Vol. 4*, Pergamon, Oxford, 1988, p. 550.
- [23] I. Fukuyama, T. Ogawa, A. Miyake, *Propellants, Explosives, Pyrotechnics* 11 (1986) 140.