Explosion Properties of Highly Concentrated Ozone Gas

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Abstract

Explosive self-decomposition characteristics of gaseous ozone with a concentration up to almost 100 vol% were quantitatively investigated using a closed system with an electric spark device. The lower self-decomposition (explosion) limit for ozone diluted by oxygen at room temperature and atmospheric pressure was 10-11 vol%, and so ozone with a concentration of more than 10-11 vol% will lead to an explosive chain decomposition reaction leading to complete conversion to oxygen in a vessel. The lower explosion limit shifts to higher concentration value with the decrease of the pressure. The limit value was about 80 vol% under a reduced pressure of 10 Torr. We also confirmed that the explosion trigger energy value (minimum ignition energy) was strongly dependent on ozone concentration and pressure. For example, the value for 15 vol% ozone under the pressure of 76 Torr was not more than 1/20 (about 200 mJ) of that at atmospheric pressure, and the value for 13 vol% ozone (about 580 mJ) was approximately 30 times higher than that of 20 vol% (about 20 mJ) under the same pressure of 76 Torr. Moreover, the physical characteristics of the trigger energy source (spark gap, electrode tip angle, etc.) leading to the decomposition (explosion) of ozone were investigated under various conditions.

1. Introduction

The strong oxidation capacity and sterilizing properties of ozone are very promising, and ozone is now widely applicable to various kinds of industrial field, such as water treatment. Gaseous ozone of low concentration below 10 vol% can be produced by a commercial ozone generator. Because of the strong oxidation capacity, the demands for more highly concentrated ozone are expanding and much wider application is expected.

Since the commercial ozone generators do not produce highly concentrated ozone (more than 10 vol%), it is necessary to find ways to condense ozone. The authors investigated a new technique to obtain highly concentrated ozone. Selective adsorption onto adsorbents (Koike et al., 2000), selective dissolution in solvents (Brabets et al., 1988) and distillation (Berkley et al., 1989) are proposed to condense the ozone from the ozone/oxygen mixture gas produced by the ozone generator. Ozone is an endothermic compound and has self-decomposing property. We should understand that concentrated gaseous ozone easily leads to explosive decomposition if a trigger is applied. Therefore, special care should be taken in handling concentrated ozone. Although there are some reports on ozone decomposition characteristics (e.g. Cook et al., 1956, Streng et al., 1956), the results are mostly in low-concentrated area of ozone and they are not in good agreement each other. Moreover, no systematic studies on ozone explosion properties have been carried out so far.

Our results on explosion hazard of high-concentration ozone gas in a closed system are to be introduced in this paper.

2. Experimental

Figure 1 shows the schematic flow diagram for concentrated ozone production. Oxygen gas of 99.99 vol% purity was fed to an ozone generator at 1.2 L/min and 0.05 MPa, and an ozone-oxygen gas mixture was produced with about 7 vol% ozone concentration. The mixture was then introduced to the ozone adsorption column loaded with the specially treated adsorbent, where ozone in the ozone-oxygen mixture would be separated from oxygen. The adsorbent has excellent compatibility with polar molecules, such as ozone. The column was maintained at -78 dgree C with dry-ice and ethyl alcohol during the ozone adsorption process. After the adsorption reached to the saturated state, the supply of the mixture gas was stopped and the dry-ice bath was removed. Then the temperature of the column was gradually raised to room temperature. With an increase of temperature, the ozone-enriched gas was desorbed from the adsorbent and was stored in the ozone storage vessel. The exhaust gas from the system, containing ozone, was vented through an ozone destruction line equipped with several kinds of catalysts, which can decompose ozone below the threshold-limit value.

Figure 2 shows the outline of the experimental setup for the investigation on ozone explosion characteristics. The explosion chamber used in our experiments is a cylindrical high-pressure resistant vessel constructed of 316L stainless steel with 90 mm in inside diameter and 160 mm long. Before carrying out a series of experiments, the inner surface of the explosion chamber was passivated sufficiently by the technique proposed by Koike et al. (1998), in order to prevent supplied ozone from decomposing imprudently. Ozone gas was supplied to the explosion chamber from the ozone storage vessel and diluted by pure oxygen. The ozone concentration in ozone-oxygen mixture was determined by precise measurement of pressure increase at the same temperature before and after compulsory explosion procedure. The trigger applied for explosion was a d. c. electric spark generated between tungsten electrodes. The electric spark was prepared and regulated by a specially designed trigger energy generator. The trigger energy was supplied from a power supply which can be charged up to 1200 V. The power supply generates a single pulse. The discharge current was controlled through resistors ranging resistance from 50 ohm to 1000 ohm. The voltage and current during discharge were monitored by an oscilloscope, and the trigger energy was finally calculated by following Eq. (1):

$$E = V \times I \times t \qquad (1)$$

where E, V, I and t denote the trigger energy, discharge voltage, discharge current and the duration of discharge, respectively. As an example, waveforms (voltage and current) of the electrical discharge are shown in Fig. 3.

3. Results and discussion

3.1 Explosion limit of ozone in oxygen

Figure 4 shows lower explosion limit (total pressure) as a function of ozone concentration under atmospheric pressure or less at room temperature. The lower self-decomposition (explosion) limit for ozone diluted by oxygen at room temperature and atmospheric pressure was 10-11 vol%, while there was no upper limit like the case of an explosion of acetylene. Ozone with a concentration of more than 10-11 vol% could cause an explosive chain decomposition reaction leading to complete conversion to oxygen in a vessel. The lower explosion limit (concentration) of ozone tends to rise with the decrease of pressure as combustible gases. However, this is not clear in the range from 800 Torr to 100 Torr. The explosion limit sharply increases at the pressure of 100 Torr or less. For example, the lower explosion limits at 600 Torr, 200 Torr, 80 Torr and 20 Torr are estimated to be 12 vol%, 12.5 vol%, 15 vol% and 30 vol%, respectively. These data suggest that if the ozone concentration is higher, greater attention is required for safe handling. The raise of lower explosion limit concentration with the decrease of pressure results from mean free path. The probability of collision of molecules each other is reversely proportion to mean free path.

Lower explosion limit in the range of low pressure is introdeced in Fig. 5. Ozone with the concentrations of 60 vol% or more is likely to explode even at 10 Torr. Minimum explosion pressures of hydrogen and methane in air are reported to be 11.5 Torr and 30 Torr, respectively. Compared with hydrogen and methane, ozone can be considered to have low minimum explosion pressure.

3.2 Minimum trigger energy for ozone explosion

Minimum trigger energies for ozone explosion were investigated under various pressure and concentration. Figure 6 indicates that as the ozone concentration is lowered, minimum trigger energy required for explosion becomes larger. Ozone with the concentrations of 10 vol% or less under atmospheric pressure would not explode even if a gigantic energy, such as 1 J, was given. Minimum trigger energy was greatly influenced by pressure and ozone concentration. In the case of 15 vol% of ozone, no explosions occurred at 76 Torr as long as energy of 400 mJ or less was supplied, while ozone exploded easily at 760 Torr even if only 20 mJ of trigger energy was supplied. Moreover, the value for 13 vol% ozone (about 580 mJ) was approximately 30 times higher than that of 20 vol% (about 20 mJ) under the same pressure of 76 Torr. A chain reaction is believed to be proceeded more easily with pressure. Increasing pressure is equivalent to increasing number of collision of ozone molecules.

3.3 Influence of tip angle, spark gap of discharge electrodes and spark duration on ozone explosion

As shown so far, ozone explosion is influenced by the trigger energy. The generation of the trigger also depends on the electrical discharge conditions and the discharge is influenced by electrode system. We investigated influence of tip angle of one pair of electrodes and of the electrode gap. Figure 7 shows the minimum trigger energy as a function of electrode tip angle at the ozone concentration of 12.4 vol% and 14.3 vol% ozone at 200 Torr. The spark gap was 1.5 mm. There are no effects of tip angle on the trigger energy for ozone explosion. The minimum trigger energies for 12.4 vol% and 14.3 vol% of ozone were estimated to be 83 mJ and 5 mJ, respectively. There is 16 times difference between two ignition energies in changing ozone concentration only 2 vol%

point. It can be seen that the trigger energy strongly depends on the ozone concentration.

Figure 8 shows the influence of spark gap on the minimum trigger energy for 12.4 vol% and 14.3 vol% ozone concentration at 200 Torr. The tip angle used was 60 degree. It is shown that the minimum ignition energy was strongly dependent on spark gap. Required trigger energy became smaller with the increase of spark gap. No discharge could be produced when the spark gap was more than 3 mm. The smaller the spark gap is, the larger the heat transfer of exothermic ozone decomposition reaction to the discharge electrodes becomes.

Spark duration influence on ozone explosion was also investigated because the duration is directly related to the total heat energy. Ignition energy is expressed as the product of voltage, current and duration of discharge, as shown in Eq. (1). Therefore, we can get the same ignition energy by choosing the three parameters independently. Figure 9 illustrated the result of the effects of spark duration on the minimum ignition energy. It was found that ozone explosion was greatly influenced by spark duration.

4. Conclusion

As a result of our explosion experiments using electrical discharge, lower explosion limit of ozone diluted oxygen was about 10 vol%. The lower explosion limit shifted to higher concentration with the decrease of pressure. Specially, the tendency was conspicuous when the pressure was less than 100 Torr. The minimum trigger energy was strongly dependent on initial pressure. For example, the trigger energy of 15 vol% ozone at 76 Torr was estimated to be 400 mJ, while that at 760 Torr was estimated to be 20 mJ. A little change of ozone concentration also resulted in large difference of minimum trigger energy. There was 16 times difference of ignition energy between 12.4 vol% and 14.3 vol% ozone at 200 torr. Tip angle of discharge electrode didn't influence ozone explosion. However, the longer the spark gap or spark duration was, the smaller minimum ignition energy of ozone became.

Acknowledgement

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Figure caption

Fig. 1 Schematic flow diagram for high-concentration ozone production

Fig. 2 Apparatus for ozone explosion study

Fig. 3 An example of waveform observed by an oscilloscope during discharge

Fig. 4 Pressure dependence on lower explosion limit of ozone

Fig. 5 Lower explosion limit in the range of low pressure

Fig. 6 Relation between minimum trigger energy and ozone concentration

Fig. 7 Effect of ozone concentration and tip angle of discharge electrodes on minimum trigger energy

Fig. 8 Influence of spark gap of discharge electrode on minimum trigger energy

Fig. 9 Spark duration dependence on minimum trigger energy of ozone with a concentration of 14.3 vol%

Fig. 1

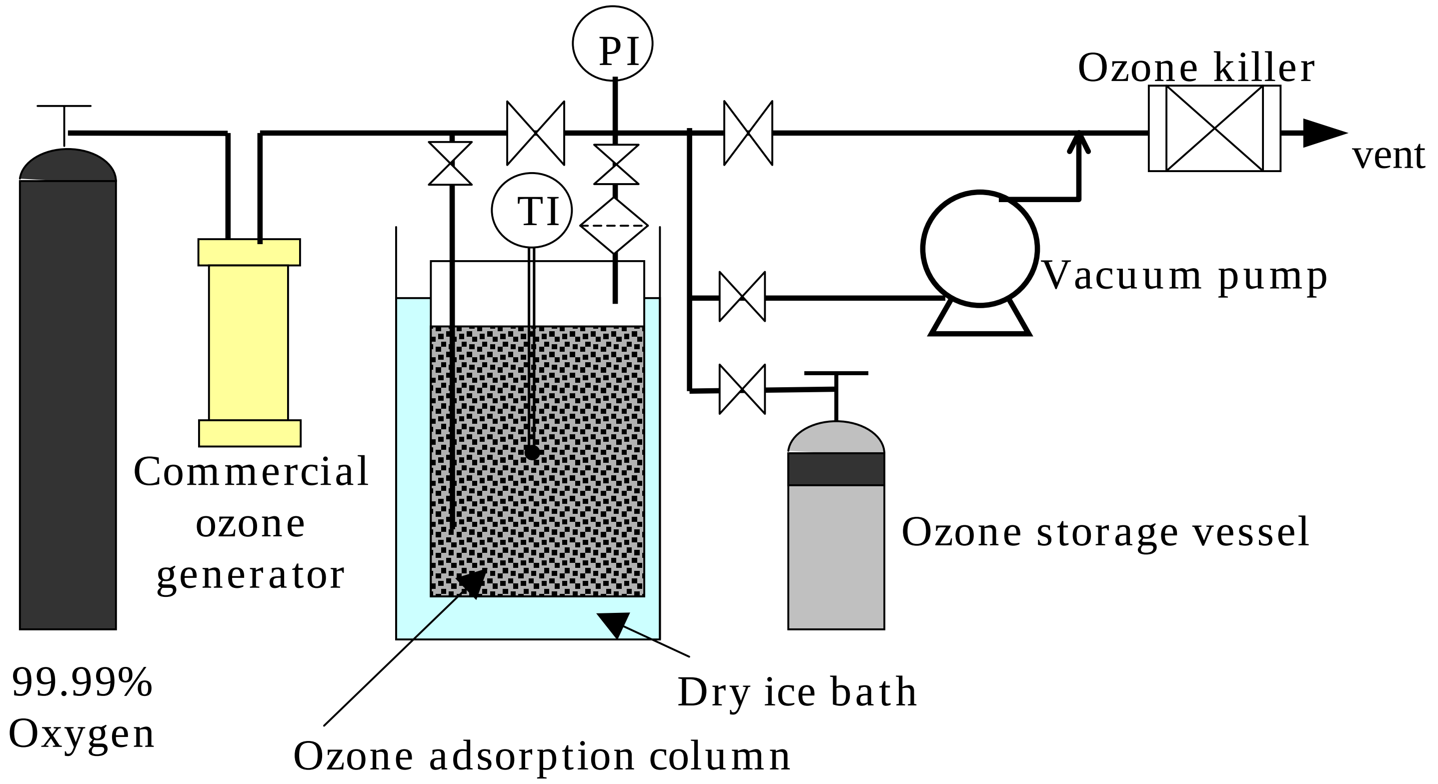

PI
Ozone killer
vent
TI
Vacuum pump
Commercial ozone generator
Ozone storage vessel
99.99% Oxygen
Dry ice bath
Ozone adsorption column

Fig. 2

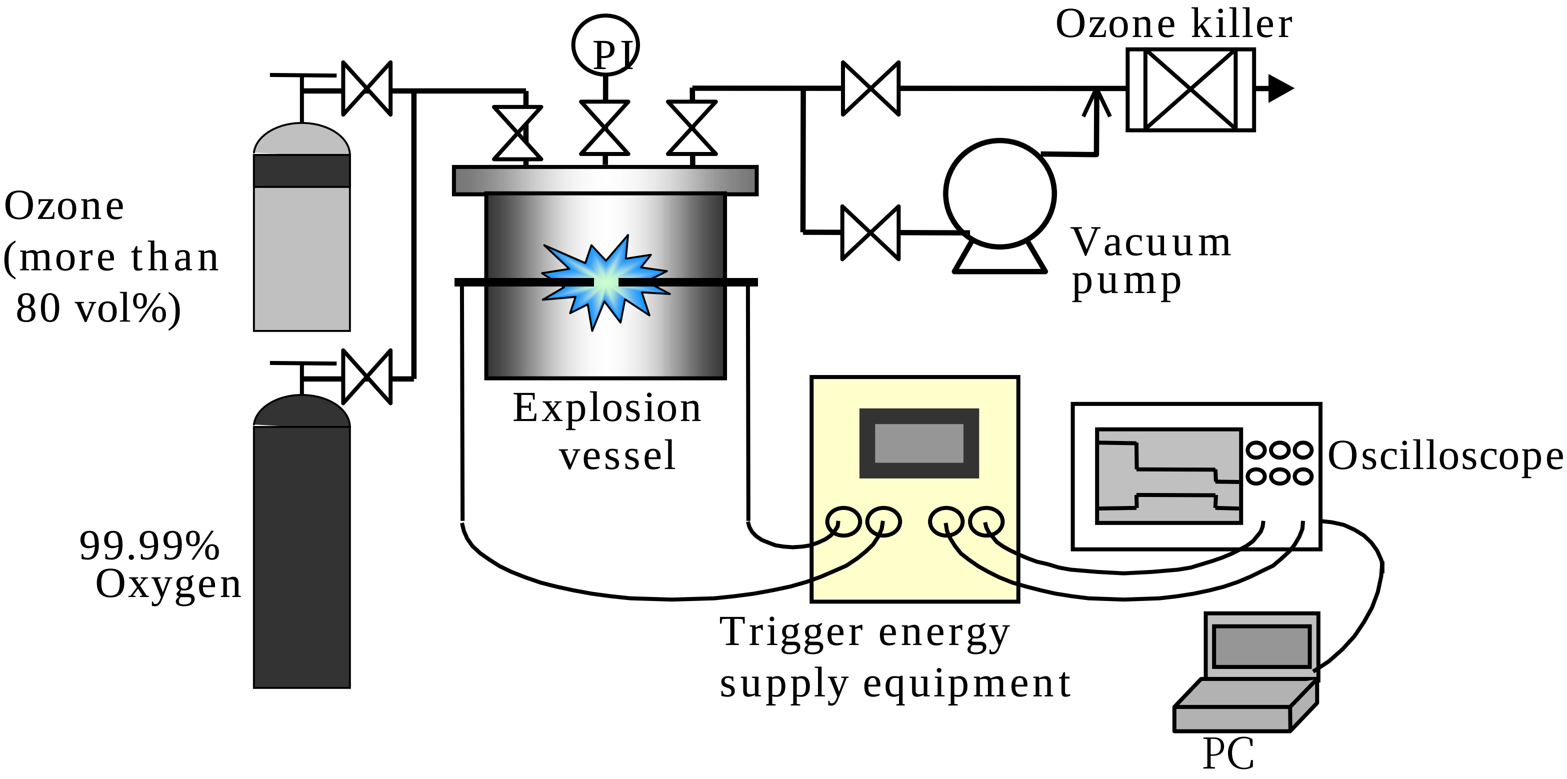
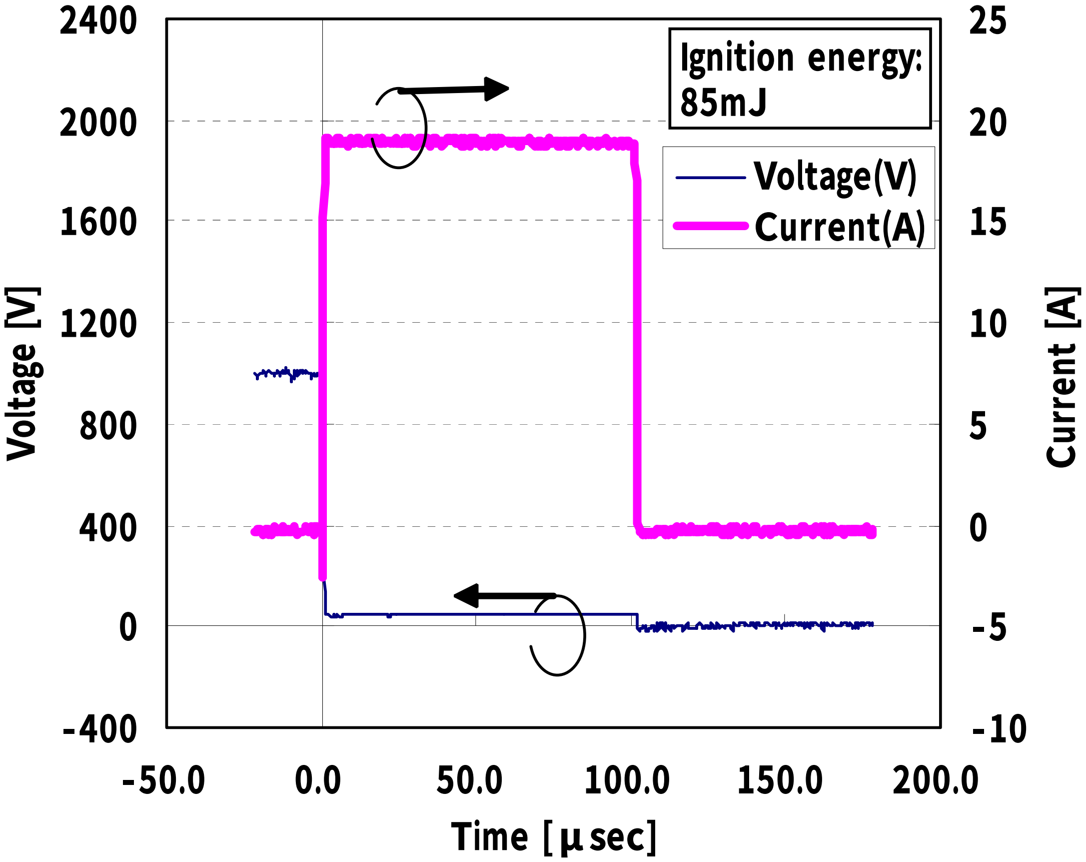
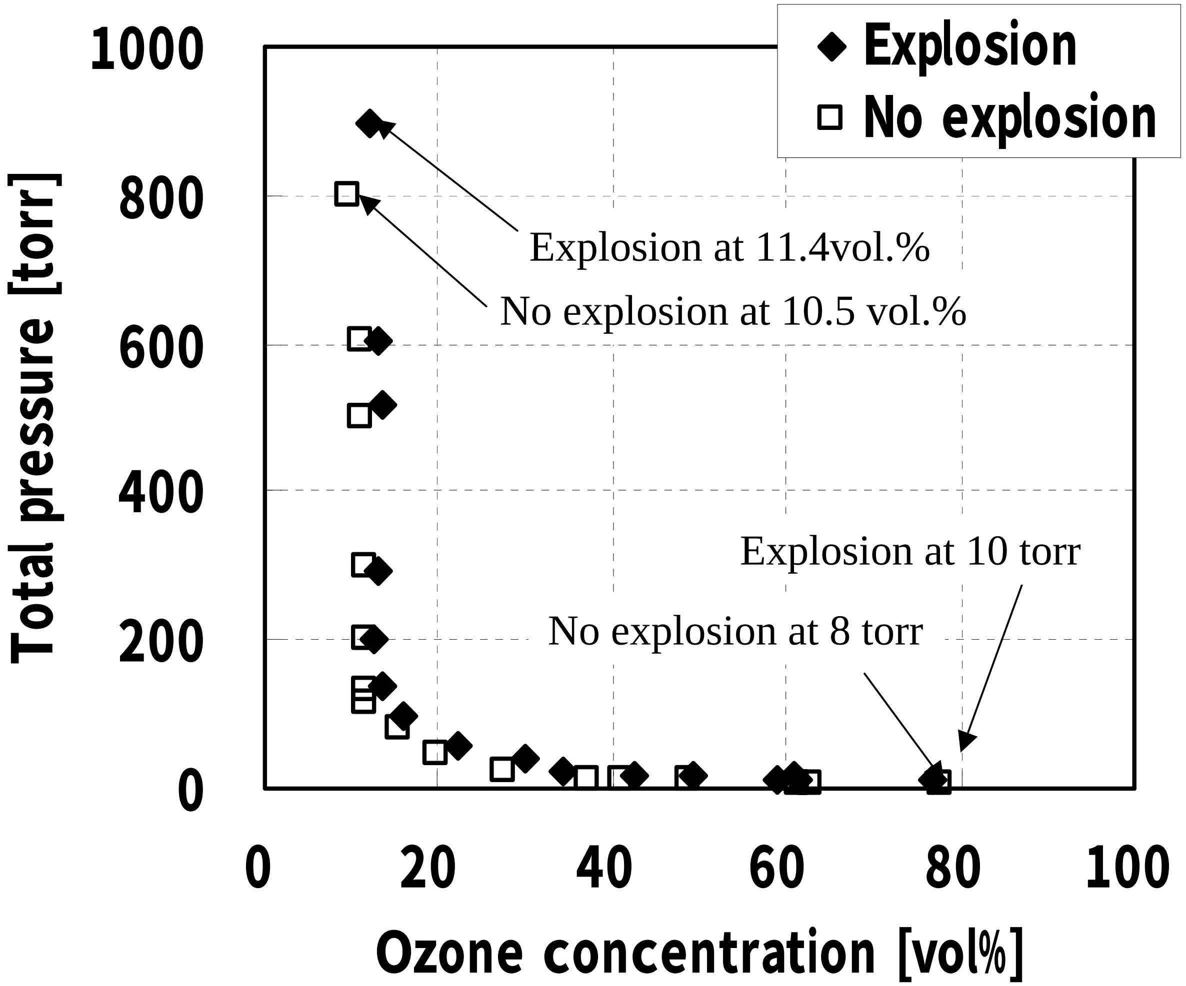

Ozone killer
PI
Ozone
(more than
80 vol%)
Vacuum
pump
Explosion
vessel
Oscilloscope
99.99%
Oxygen
Trigger energy
supply equipment
PC

Fig. 3



Ignition energy: 85mJ
Voltage(V)
Current(A)
2400
2000
1600
1200
800
400
0
-400
Voltage [V]
25
20
15
10
5
0
-5
-10
Current [A]
-50.0
0.0
50.0
100.0
150.0
200.0
Time [μsec]

Fig. 4



◆ Explosion
☐ No explosion
Explosion at 11.4vol.%
No explosion at 10.5 vol.%
Explosion at 10 torr
No explosion at 8 torr
Total pressure [torr]
0
200
400
600
800
1000
Ozone concentration [vol%]
0
20
40
60
80
100

Fig. 5

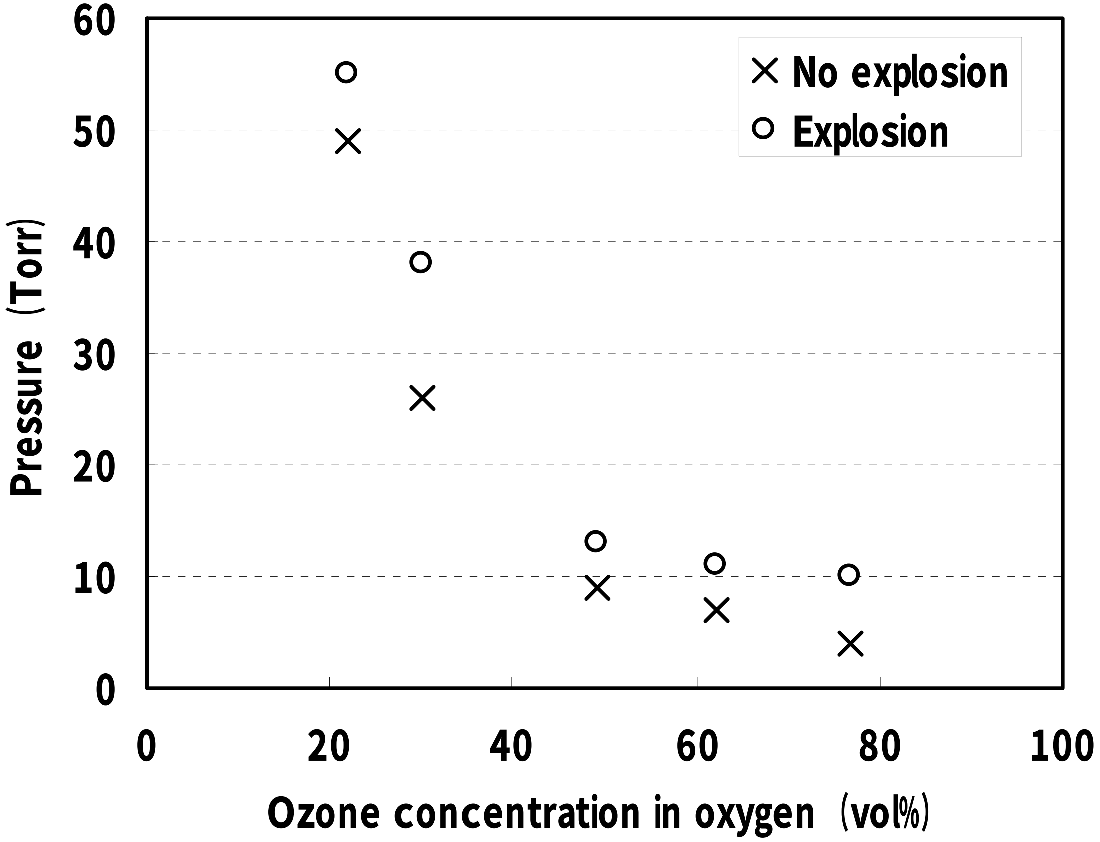

60
50
40
30
20
10
0
Pressure (Torr)
0
20
40
60
80
100
Ozone concentration in oxygen (vol%)
× No explosion
○ Explosion

Fig. 6

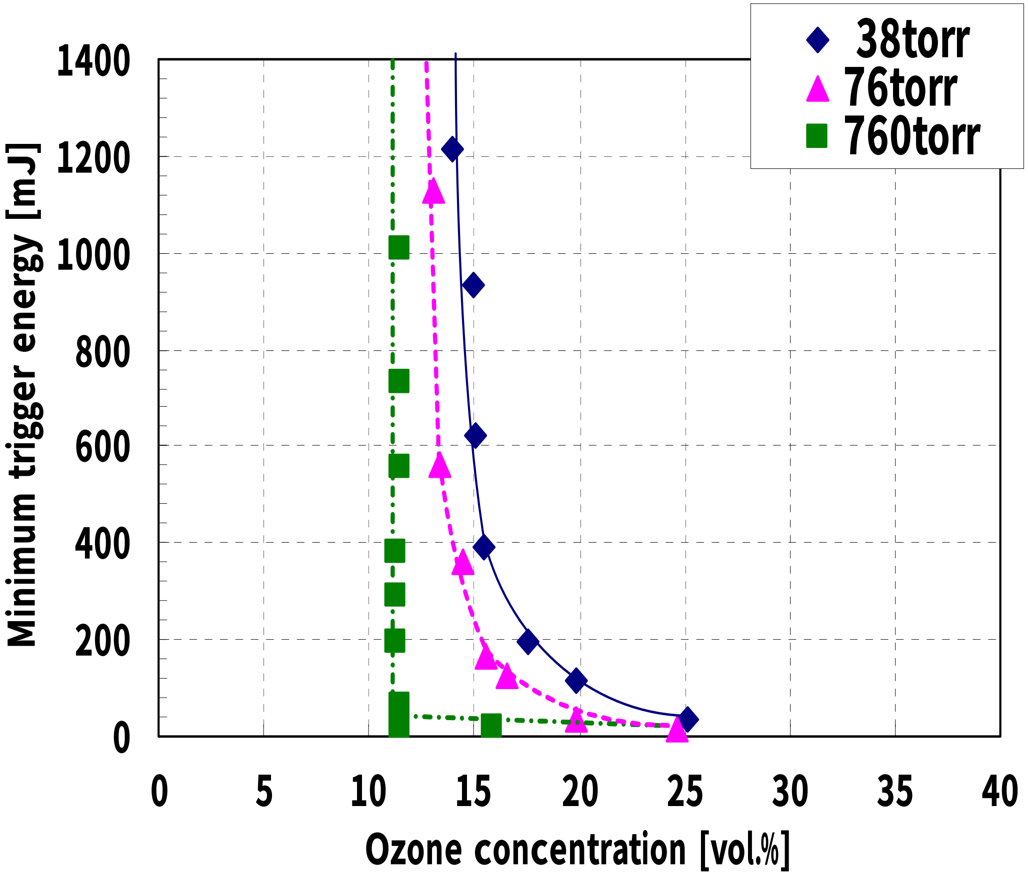
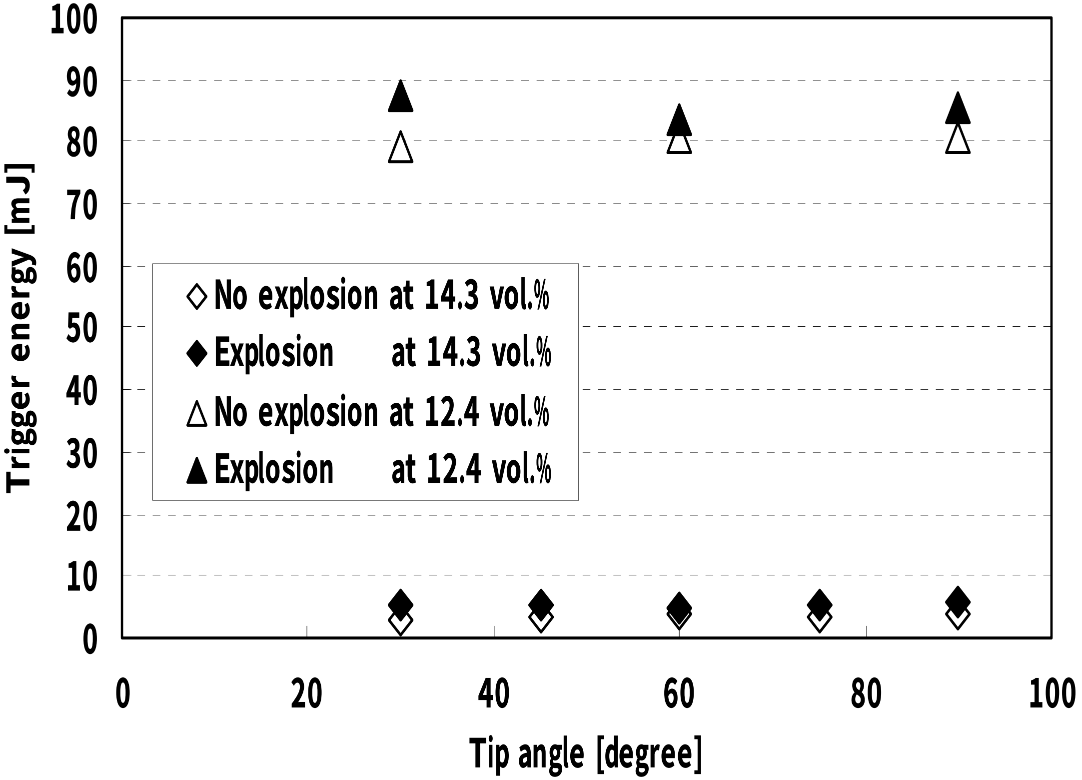

◆ 38torr
▲ 76torr
■ 760torr
Minimum trigger energy [mJ]
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
40
Ozone concentration [vol.%]

Fig. 7



100
90
80
70
60
50
40
30
20
10
0
Trigger energy [mJ]
0
20
40
60
80
100
Tip angle [degree]
◇ No explosion at 14.3 vol.%
◆ Explosion at 14.3 vol.%
△ No explosion at 12.4 vol.%
▲ Explosion at 12.4 vol.%

Fig. 8

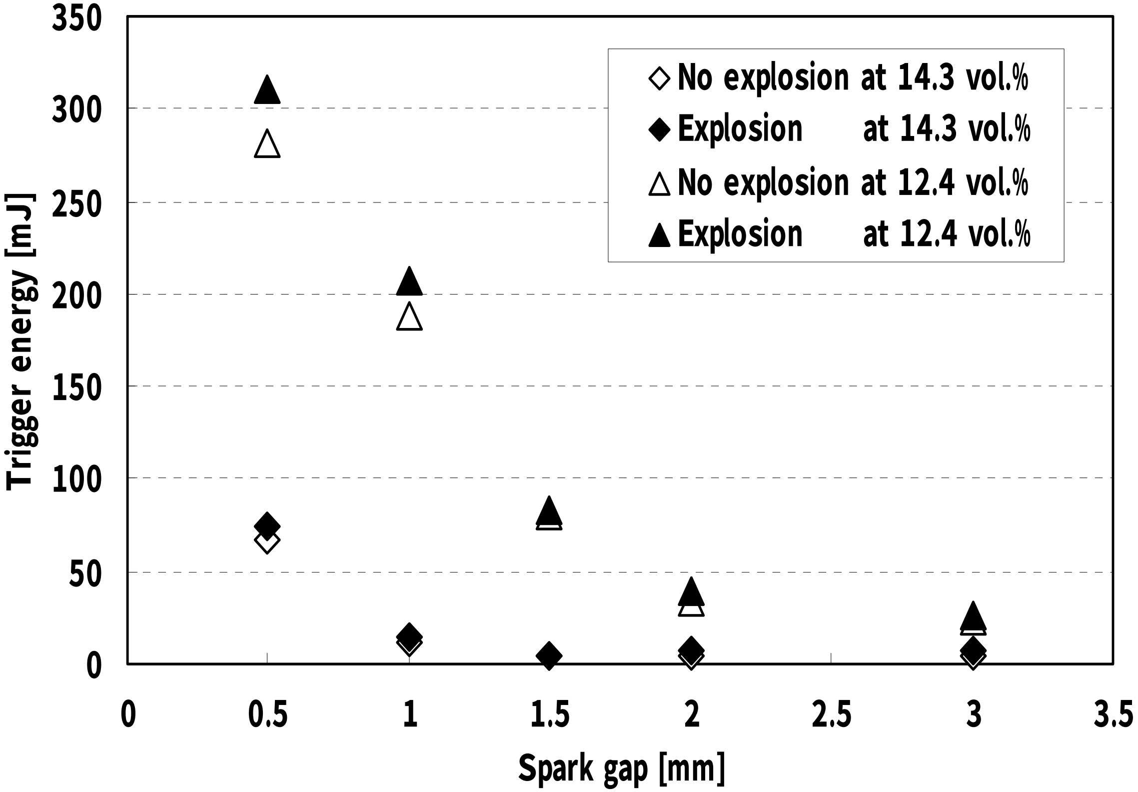
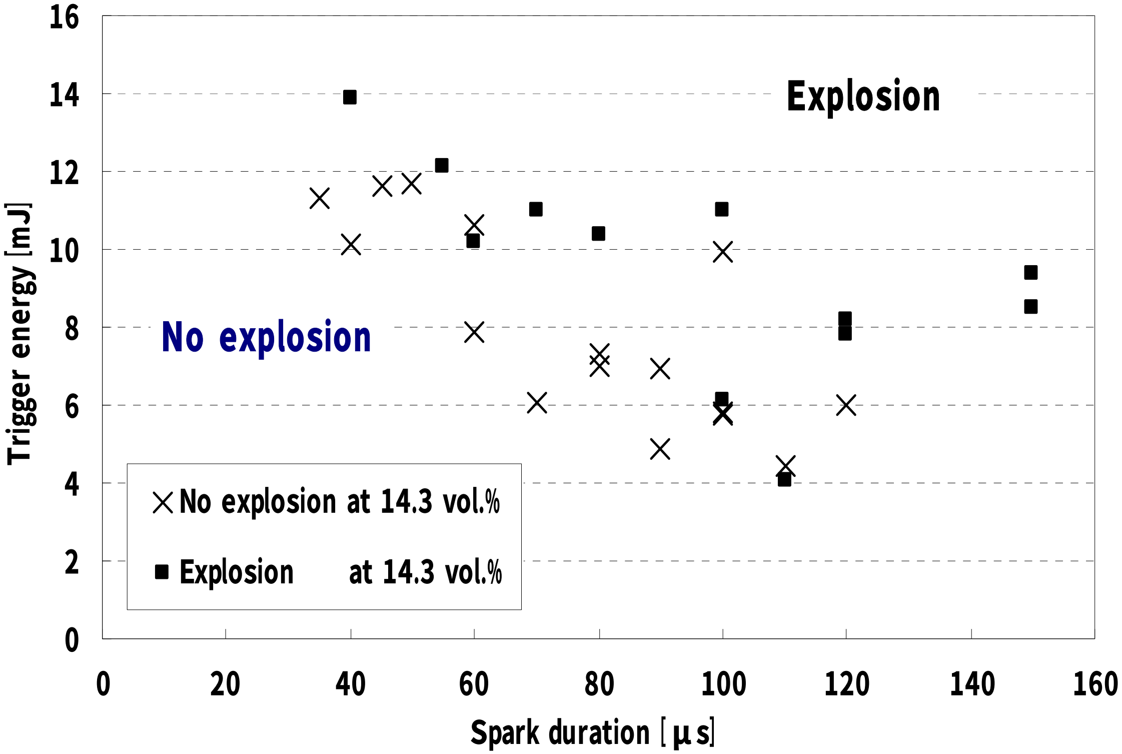

350
300
250
200
150
100
50
0
Trigger energy [mJ]
0
0.5
1
1.5
2
2.5
3
3.5
Spark gap [mm]
◇ No explosion at 14.3 vol.%
◆ Explosion at 14.3 vol.%
△ No explosion at 12.4 vol.%
▲ Explosion at 12.4 vol.%

Fig. 9



Explosion
No explosion
× No explosion at 14.3 vol.%
■ Explosion at 14.3 vol.%
Trigger energy [mJ]
Spark duration [μs]
0
2
4
6
8
10
12
14
16
0
20
40
60
80
100
120
140
160