Abstract: The ozone is very well known as the most useful oxidant for wide industrial field due to its strong oxidizing power and non-formation of undesirable by-product. Nowadays, industrial ozone generation has been improved to fulfill higher ozone generating efficiencies, and higher ozone concentrations. To reach the improvement of the ozone production, a superposition of different type discharges is applied to same reaction space (or volume) to increase energy density at same space. To improve the low efficiency of dc discharge and narrow gap of surface discharge, a investigation was focused to the superposition with a dc streamer (corona) and a surface (ac) discharge. This paper describes the ozone generation characteristics of the superimposed discharge.

1. Introduction

Ozone, historically mainly used for the treatment of drinking water, is one of the strongest oxidizing and bleaching agents and it has definite advantages over other commercial oxidants, namely, no undesirable by-products or residues are formed. Since the on-site production of the ozone requires only air and electricity no transport of potentially dangerous chemicals is involved in the ozone applications. These are the main reasons why the ozone is increasingly used for many kinds of oxidizing processes. The ozone also attacks the respiratory tract. The safe concentration is considered to be about 0.1 ppm, a value that is today occasionally surpassed in extreme smog situations.

Some chemical reactions can result in the formation of ozone. UV-radiation can also be employed to produce small amounts ozone. Larger quantities of ozone, however, are exclusively produced using electrical discharges. With growing interest in the improvement of the ozone production in the industrial fields, many types of ozonizer using the electrical discharges have been proposed for the higher efficiency and the higher performance at atmospheric pressure. Among them, the ozonizer using superimposed discharges has been investigated as an alternative to the silent discharge ozone generators.\(^\text{[1]}\) For example, the superposition of the silent and the surface discharge, and the superposition of ultra violet ray and the surface discharge, etc were proposed. Especially, the superposition of the dc and the surface (ac) discharge has been investigated since they do not require a dielectric barrier between metal electrodes in the dc discharge. Also, it has been investigated to improve the low efficiency of the dc discharge and narrow gap of the surface discharge. Because
the superposition of different type discharges is applied to same reaction space (or volume), the synergetic (or superposition) effects are caused by the increased energy density at the same space.

2. Experimental Setup

The oxygen feed gas flows through a 5 mm gap between a tungsten wire of 0.1 mm diameter and a plate electrode. This gap is larger than the optimum gap (as known 1-3 mm) of silent discharge. A high dc voltage for the dc discharge is applied to the wire electrode. The plate electrode for the surface discharge is composed of single ruthenium oxide (RuO) strip of 2 mm width on the top ceramic (alumina : Al₂O₃) surface and two ones of 1 mm width on the bottom surface. A high ac voltage for the surface discharge is applied to the plate electrode as shown in Fig.1. Applied voltages were 3 to 6.6 kVrms (ac) in the surface discharge, 8.2 kV (dc) in a weak positive dc streamer, and minus 6 to minus 7.2 kV (dc) in negative dc corona discharges.

![Figure 1. Schematic Diagram of Superposition Type Ozonizer and Measuring System](image)

Including these electrodes, the main reactor was made from acryl to observe discharge aspects by naked eyes. The internal dimension of reactor was 129 x 19 x 20 mm (Length x Width x Height). The internal volume was 0.05 liter. The residual times of oxygen molecule in the reactor are 3.2, and 1.5 seconds for the flow rate of 1.0, 1.5, and 2.0 L/min., respectively.

EG-2001 ozone monitor of Ebara Company measured ozone concentrations. This monitor measures the concentrations using the ultraviolet absorption properties by the ozone. In this method, the ultraviolet of 253.7 mm wavelengths is used. This wavelength is close to the maximum absorption by the ozone and is easily obtained using low-pressure mercury lamps.

Flow regulator ranging from 1 L/min. to 2 L/min. controlled a gas flow rate to survey the effects of flow rates.

The internal temperature of ozonizer was recorded by the thermo-couple function of HR 2300 hybrid recorder of Yokogawa. Almel and chromel of ceramic clad wires with 0.1 mm diameter were used for thermocouple.

A TDS 380 P oscilloscope of Tektronix and 2011 DC milli-ampere meter of Yokogawa measured the dc discharge power. When we put the applied the ac voltage V on the x-axis and the voltage
U (as a measure of the charge Q) on the y-axis of an oscilloscope in the x-y mode, we get a closed curve. The area inside the closed curve is proportional to the energy dissipated in the surface discharge during one cycle. Thus ac discharge power can be measured using the inside area of closed curve so called V-Q Lissajous figure.

3. Experimental Results

To investigate the ozone generation characteristics of superimposed discharge, the ozone concentration and the discharge power with time were measured for each discharge, respectively—surface discharge, dc discharges, and superimposed discharge.

The ozone concentrations were measured every 30 second until 10 minutes. Two or three times measurements at least were carried out to confirm reproducibility. Among them, the measured data which variations with time were less than 7% except the case of negative dc corona discharge were selected for analysis. The absolute values of the variation were 1 to 24 ppm through all of flow rates. Measured data at 10 minute were used to compare each other.

The ozone concentration by the surface discharge was very stable and high at low discharge power region (below 700 mW/ (L/min.)) and the efficiency was relatively higher than those of other discharges. Although stable weak positive dc streamer discharge occurred between the wire and the plate electrode, there was no ozone generation. In the case of negative dc corona discharge, the ozone generation was not stable compared to the surface discharge and the efficiency was very low due to irregular corona discharge occurrence.

Maximum ozone concentration and efficiency were appeared under the superimposed discharge with the weak positive dc streamer and the surface discharge. The comparison results of ozone concentration, efficiency, and gas temperature for each discharge were depicted as follows.

A. Ozone Concentration

The ozone concentrations with power density (ratio of discharge power to gas flow rate) for each discharge were shown in Fig.2. In this figure, the ozone concentration tendency (curve) of the superimposed discharge with the weak positive dc streamer and surface discharge showed the largest concentration below 700 mW/ (L/min.). Except the superimposed discharge with negative dc and the surface discharge, the ozone concentrations of each discharge were measured with the variation of the applied ac voltages under a fixed dc voltage. Under the weak positive dc streamer discharge, the ozone concentration was 0 ppm.

The maximum ozone concentration in the superposition of the weak positive dc streamer and the surface discharge was 675 ppm at 1.0 L/min., 469 ppm at 1.5 L/min. and 385 ppm at 2.0 L/min., respectively. It is clear that the superposition of the weak positive dc streamer corona and surface discharge is more productive to the ozone generation than the superposition of the negative dc corona and the surface discharge in relatively low discharge power density region. Figure 2, thus, showed the polarity effects of applied voltage. It could be guessed that this fact was caused by the
large discharge volume of streamer discharge than the one of corona discharge.

And the ozone concentration of the superimposed discharge in Fig.3 was greater than the concentration sum obtained with the surface discharge and with the weak positive dc streamer discharge at flow rate of 1.5 L /min. Thus these differences between the measured and the sum-synergetic effects-can be defined as the superposition effects.

The superposition effects with other flow rate are shown in Fig.4. This figure showed that the superposition effects were saturated around 300 mW. The maximum difference was 250 ppm at 335 mW under 1.0 L /min. This showed that superimposed discharge was more effective on ozone generation in the low discharge power region than high discharge power region.

The discharge power of the superimposed discharge used to the confirmation of superposition effects was the sum of the discharge power with individual discharges-dc and surface discharge. Thus the real value of superimposed discharge power needs confirmation by measurement in later.
B. Efficiency

The efficiencies with the (discharge) power density for each discharge were shown in Fig.5. Although the efficiency of surface discharge increased with the power density, the efficiency of the superimposed discharge decreased with the power density. And the difference between the efficiency curves of the superimposed and the surface discharge decreased with the power density. These facts showed that superposition effect was more enhanced in the low power density region than the high power density region as like the case of concentration. The maximum efficiency with the power density was 235.6 g/ kWh at the flow rate of 1.5 L /min. This value is almost same as the general level of the silent discharge.\[^{13}\]

Figure 5. Comparison of Efficiencies with Power Density for Each Discharge

In the case of the superimposed discharge, the efficiency of superposition with the weak positive dc streamer and surface discharge was larger than that of superposition with negative dc weak corona and surface discharge below 700 mW/ (L /min.) as shown in Fig. 5. The efficiency of the superimposed discharge with the surface and the negative dc corona discharge was located between
the efficiencies of the surface discharge and the negative dc corona discharge. From these results, the superimposed discharge with the weak positive dc streamer and surface discharge was more effective on ozone generation than the superimposed discharge with negative dc corona and surface discharge, too.

C. Gas Temperature

The gas temperatures around gas outlet were measured to check the temperature variation of internal gas in the reactor. The gas temperatures with the (discharge) power density for each discharge were compared to each other as shown in Fig.6. In this figure, the gas temperature of the superimposed discharge was rapidly increased with the power density in relatively low discharge power density range. The maximum temperature of the superimposed discharge with the weak positive dc streamer and surface discharge was 40.4°C at around 730 mW when flow rate was 2 L/min. The background temperature was 25.4°C. The gas temperature of the surface discharge showed the lowest variation. This fact showed that the ozone generation by the surface discharge could be carried out under low temperature variation. The variation of gas temperature of the superimposed discharge with negative dc corona and surface discharge was larger than those of the other discharges and has not constant tendency with the power density.

![Figure 6. Comparison of Internal Gas Temperatures for Each Discharge](image)

And the increment of the gas temperature of the superimposed discharge with the weak positive dc streamer and the surface discharge -15°C - was larger than that of the superposition discharge with negative dc corona and surface discharge in relatively low power density range. The large discharge volume can explain this phenomenon, I think.

D. Waveform of Discharge Current

To investigate the occurrence condition of the superimposed discharge in simple, I examined the waveforms of discharge current for each discharge. In the case of surface discharge, the discharge current occurred during only two-quarter cycles of the applied voltage as like silent discharge as shown in Fig.7(a). But the discharge current in the negative dc corona discharge occurred only
one time during about two cycles of applied voltage as shown in figure 7(b). The discharge current of the superimposed discharge with negative dc corona and surface discharge occurred during one cycle of applied voltage as shown in Fig.7(c). It can be considered from figure 7(c) that the additional discharge currents of the superimposed discharge occurred during another two-quarter cycles of applied voltage compared to the discharge current waveform of surface discharge cause the superposition effects.

4. Conclusions

From the above investigation results for some parameter related superposition of the dc and the surface discharge, it was found the polarity effects of applied voltage and flow rate effects for ozone generation and efficiency at the superimposed discharge. The investigated experimental results of the superimposed discharge can be, thus, summarized as follows:

1) The superimposed discharge with the weak positive dc streamer and the surface discharge showed better enhancement for the ozone generation and the efficiency than does the superimposed discharge with the negative dc corona and the surface discharge below 700 mW/(L/min.). It can be guessed that this phenomenon was caused by large active volume. And superposition effects on ozone generation were saturated around 300 mW.

2) The maximum efficiency was occurred under the superimposed discharge with the positive dc streamer and the surface discharge. The value was 235.6 g/kWh that was almost twice of the efficiency of the individual surface discharge and is almost same as the general level of silent discharge at 1.5 L/min.

3) Flow rate of 1.5 L/min. was effective on the ozone concentration and the efficiency for each discharge.

4) The superimposed discharge showed rapid increment of gas temperature from 25.4 to 40.4°C below 700 mW/(L/min.). The ozone generation by the surface discharge was carried out under low gas temperature variation.
Although the discharge current of surface discharge occurred during only two-quarter cycle of applied voltage, the discharge current of the superimposed discharge occurred during one cycle of applied voltage. It can be considered that the additional discharge currents of the superimposed discharge occurred during another two-quarter cycle cause the superposition effects.

References

