Generation of ozone by pulsed corona discharge over water surface in hybrid gas-liquid electrical discharge reactor

P. Lukes¹, M. Clupek¹, V. Babicky¹, V. Janda², P. Sunka¹
¹Institute of Plasma Physics, Academy of Sciences of the Czech Republic, v.v.i.
Za Slovankou 3, Prague 182 00, Czech Republic
²Department of Water Technology and Environmental Engineering, Institute of Chemical Technology, Technicka 5, Prague 160 28, Czech Republic

Production of ozone generated by the gas phase pulse positive corona discharge above water was investigated for different discharge gap spacing (2.5-10 mm), applied input power (2-45 W), and gas composition (oxygen mixtures with argon or nitrogen). Ozone concentration increased with increasing power input and with increasing discharge gap. The production of ozone was significantly affected by the presence of water vapor formed through the vaporization of water at the gas-liquid interface by the action of the gas phase discharge. The highest energy efficiency for ozone production was obtained using high voltage pulses of approximately 150 ns duration in Ar/O₂ mixtures with the maximum efficiency of 23 g/kWh for 40% argon content.

Introduction

Advanced oxidation water treatment processes that utilize highly reactive radicals such as the hydroxyl radical are of increasing interest for the degradation of organic compounds in contaminated and polluted waters. Various combinations of ozone, hydrogen peroxide, and UV light have been studied as means to produce hydroxyl radicals in water and to effectively degrade many organic compounds. Ozone has typically been produced by electric discharge plasma reactors placed upstream of the water treatment process, and the gas phase ozone thus produced has been sparged into the liquid alone or in combinations with the addition of hydrogen peroxide and UV light. In attempts to bring the ozone generation step closer to the ozone utilization step and to develop plasma reactors that may be suitable for direct water treatment a number of different types of plasma reactors utilizing electrical discharges have been studied. For example, AC, DC or pulsed electrical discharges have been generated in a variety of electrode geometries either directly in the liquid phase or in the gas phase in close proximity to the liquid surface. Electrical discharges generated directly in the liquid were demonstrated to initiate a variety of physical and chemical effects in water including the high electric field, intense ultraviolet radiation, overpressure shock waves and, of particular importance, formation of various reactive chemical species such as radicals (H·, O·, OH·) and molecular species (H₂O₂, H₂, O₂, O₃). Production of these chemical species has also been reported for electrical discharges generated above the liquid water surface. These reactive species and physical conditions in turn have been shown to be effective at degrading a variety of organic compounds and in the destruction and inactivation of microorganisms in water [1].

Hybrid electrical discharge reactors utilize both the gas phase non-thermal plasma formed above the water surface and direct liquid phase corona-like discharge in the water. The main advantage of these reactors is the production of the same chemical species and physical factors as initiated by the individual gas and liquid phase discharges. Previous experiments have demonstrated the formation of ozone in the gas phase and H₂O₂ and OH radicals in the liquid phase in these reactors [2,3]. The combined action of these reactive species, as well as possible reaction processes occurring at the gas-liquid interface, can lead to enhancement of the overall efficiency of the electrical discharge process for the removal of pollutants from water [4,5]. In order to optimize the power delivered into the two discharges generated in the gas and the liquid phases and to effectively tune the power supply to the hybrid discharge reactor we have constructed a gas-liquid discharge reactor with separately charged electrodes in the gas and liquid phase discharges. In the present work, the formation of ozone by the gas phase discharge over the water surface in this hybrid discharge reactor was investigated. The effects of discharge gap spacing, electrical power applied to the reactor and gas phase composition (oxygen and O₂/Ar, O₂/N₂ mixtures) on ozone production was determined.
Experimental

The discharge reactor is a closed box with Plexiglass walls with outer dimensions of 200×200×200 mm. It consists of two separately charged high voltage electrodes; one placed in the water and one placed in the gas phase above the water. Electrodes are separated by a circular perforated plate made from stainless steel connected with the electrically grounded stainless steel tube of the inner diameter of 160 mm. The high voltage needle electrode in the liquid is made from a mechanically sharpened tungsten wire placed along the axis of the stainless steel tubular ground electrode. The gas phase high voltage electrode is made from RVC disk (diameter 50 mm × thickness 10 mm), which is attached to a stainless steel holder connected to the pulsed high voltage. The distance between the RVC electrode and the ground stainless steel plate submerged in the water is fixed at 40 mm. The gas phase discharge gap between the RVC electrode and the water surface is varied through adjustment of the volume of the aqueous solution used in the reactor. The separate charging of the liquid phase needle electrode and the gas phase RVC electrode is provided by two pulse power supplies that allow for independent control of the gas and liquid phase discharges including separate variation of the input power, voltage, and pulse repetition rate for each phase. Each of them consists of high voltage 0-50 kV DC source, rotating double spark gap giving the maximum pulse repetition frequency of 100 Hz and storage capacitor with variable capacity in the range of 0.2-10 nF.

Results and discussion

Effect of discharge gap spacing on ozone formation

Figure 1 shows the dependence of (a) ozone concentration and (b) ozone production efficiency on the applied power input for different discharge gap spaces between the high voltage RVC electrode and the water surface measured in oxygen. The power input was varied from 11 to 45 W using different applied voltages of positive polarity from 15 to 30 kV at a constant pulse repetition frequency of 50 Hz. The discharge gap space was varied from 2.5 to 10 mm at each applied power input. Reported ozone concentrations are steady state values of the volume fractions of ozone in the output gas, in terms of parts per million (ppmv).

![Figure 1](image_url)

**Figure 1.** (a) Ozone concentration and (b) ozone production efficiency measured in oxygen as a function of applied power input for different discharge gap spacing. Gas flow rate 2.5 l/min, C=2 nF, discharge gap spacing: ●, 2.5 mm; □, 5 mm; ▲, 7.5 mm; ■, 10 mm.

It is apparent that for the same power input the ozone concentration and production efficiency increased with the increasing gap spacing. However, when the same discharge gap was used, the ozone concentration increased with increasing power input, opposite to the effect observed for ozone energy yield. For a fixed discharge gap spacing d it can be expected that a higher power input results in a larger average electric field \(E=U/d\), and higher average power density in the discharge \(P/Sd\). Increasing the electric field implies increasing \(E/N\) and higher mean electron energy in the discharge. Therefore, with a higher power input a larger amount of atomic
oxygen can be formed through electron impact dissociation of oxygen, which results in a larger generation of ozone. At the same time, however, a decrease of ozone energy yield with higher applied power input indicates that increases in power density in the discharge can lead to higher power consumption by heat dissipation and subsequently to a larger thermal decomposition of ozone in the discharge [6,7].

In addition to the effects of gap spacing on electric field and power density in the discharge, larger discharge gap leads to the formation of a significantly different kind of discharge. In small gaps ($\leq 5$ mm) very thin glow-like corona discharge filaments, which homogenously filled the discharge gap above the water surface, were formed during each pulse. With larger discharge gaps smaller numbers of brighter tuft-like corona discharge filaments were formed in each pulse, and in the discharge gap of 10 mm only single bright discharge channels were formed per each pulse. Therefore, as the number of plasma channels decreases with increasing discharge gap, the volume of plasma decreases and the charge transferred in each plasma channel increases for the same applied voltage. This implies higher electron mean energy and gas temperature in the discharge, which could explain the increase of ozone production rate with decreasing energy efficiency observed with larger discharge gap spaces.

Consequently, a detrimental effect of water vapor on ozone formation by the gas phase discharge generated above the water should be also taken into account. Since plasma channels formed in the gas are in direct contact with the water surface, the solution can be locally heated and vaporized by the action of the discharge. Typically, the concentrations of water measured in the output gas were $1.5\div2.0$ vol.% compared to less than $0.1$ vol.% in the inlet gas but even higher concentrations can be expected in the region of the gas phase discharge above the water surface. Thus, the water vapor can absorb a substantial part of electronic energy of the discharge that could otherwise be used in the ozone formation process. $H$ and $OH$ radicals can be formed from water vapor and, consequently, cause reactions that destroy ozone molecules. In addition, $O$ atoms formed through electron dissociation of oxygen can combine with water molecules and their products, preventing ozone formation [8].

**Effect of gas composition on ozone formation**

Figure 2a shows the effects of gas composition on ozone production measured in $N_2/O_2$ and $Ar/O_2$ mixtures for different oxygen content. The same total gas flow rate of 2.5 l/min, power input of 20 W ($U=20$ kV, $f=50$ Hz, $E_p=0.4$ J/pulse) and discharge gap spacing of 5 mm were used in each case. It is apparent that the presence of argon and nitrogen in the mixtures with oxygen had different effects on the production of ozone. Figure 2a indicates an improved ozone production in the presence of argon in $Ar/O_2$ mixtures. On the other hand, in $N_2/O_2$ mixtures ozone production was considerably suppressed by the presence of nitrogen.

**Figure 2.** Ozone concentration measured in $Ar/O_2$ and $N_2/O_2$ mixtures as a function of oxygen concentration. Gas flow rate 2.5 l/min, discharge gap spacing 5 mm. (a) $U=20$ kV, $C=2$ nF, $P=20$ W; (b) $U=30$ kV, $C=0.2$ nF, $P=4.5$ W.
It is known that both nitrogen and argon can have catalytic effects on the production of ozone [6-10]. In the case of nitrogen such an effect is caused by the reactions of nitrogen atoms and electronically excited nitrogen molecules \( \text{N}_2(A^3\Sigma_u^+) \) and \( \text{N}_2(B^3\Pi_g) \) with oxygen, which can produce additional oxygen atoms for generation of ozone. However, at higher specific energy densities in the discharge such a positive effect of nitrogen can be counteracted by quenching of oxygen atoms and destruction of ozone by the relatively high concentrations of nitrogen atoms and nitrogen oxides. In Ar/O\(_2\) mixtures these side reactions cannot occur since argon as monoatomic and chemically inert gas cannot serve as a chemical quencher of atomic oxygen and its catalytic effect is mostly due to the involvement of argon as the third collision partner in the ozone formation. Therefore, significantly reduced production of ozone in the N\(_2\)/O\(_2\) mixtures shown in Figure 2a can be explained by the inhibition effect of N atoms and NO\(_x\) caused most likely by the excessive energy density in the discharge.

To decrease both the magnitude and pulse duration of the power delivered into the discharge the charging capacity of 0.2 nF was used instead of 2.0 nF. This resulted in the formation of voltage and current pulses with oscillatory characteristics and with a pulse duration of approximately 150 ns FWHM compared to typical values of about 500 ns FWHM of voltage and current pulses generated using storage capacitor of 2.0 nF. Comparison of the trends in ozone formation in figures 2a and 2b indicates significant improvement in the ozone production efficiency using smaller charging capacitance, especially in N\(_2\)/O\(_2\) mixtures, although the total amount of ozone formation was smaller than for the 2 nF case. Moreover, in Ar/O\(_2\) mixtures ozone was formed in larger amounts than obtained in pure oxygen. Figure 2b shows that the production of ozone in Ar/O\(_2\) mixtures with argon content in the range of 10-70% was significantly enhanced with the maximum amount of ozone production occurring with 40% argon. This corresponded to the maximum ozone production efficiency of 23 g/kWh.

Conclusions

In summary, although the efficiency of ozone production was significantly enhanced using high voltage of shorter pulse width, the obtained ozone yields (~10-20 g/kWh) are still much lower than yields reported for ozone production using corona discharges in dry oxygen or air (~50-150 g/kWh) [10-13]. It is apparent that water vapor formed through the vaporization of water surface by the gas phase discharge is one of the most important reasons of this state. However, the formation of OH radicals in water vapor or at gas-liquid phase interface is also desired since they significantly contribute in degradation of organic compounds dissolved in water [4,5]. Thus, a compromise between production of ozone in high concentrations and with high energy efficiency, and production of OH radicals by the gas phase discharge generated above aqueous solution has to be considered in further development of hybrid gas-liquid discharge reactors. It should be also emphasized that rather than development of a new type of ozone generator the final objective is the most efficient utilization of chemically active species (O\(_3\), OH· and O radicals, and other species) formed by the gas phase discharge in the removal of pollutants from water.

Acknowledgement

This work was supported by the Academy of Sciences of the Czech Republic (No. K2043105).

References