OZONE FORMATION IN AN ELECTRIC DISCHARGE A FERROELECTRIC SURFACE[1)]

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An electric discharge has been generated in a gas layer between two electrodes made of a dielectric (ferroelectric of dielectric permittivity as high as 12000). The influence of the discharge power and the oxygen flow on the concentration of the ozone formed as well as the efficiency of the ozone production have been studied for the reactor construction. The comparison of the process efficiency per volume unit shows the advantage of the more efficient and compact new type of the plasma reactor in comparison with the conventional laboratory ozonizer.

I. INTRODUCTION

Ozone is one of the strongest oxidative agents, whose use does not leave any impurities. Ozone is used for water purification both from organic and inorganic contaminations as well as for disinfection, flue gases utilization and in chemical industry in ozonolysis reactions [1].

The main source of ozone in industry is the electric discharge. The main drawback of this method is, in spite of many studies, a too high energy consumption. Hence, numerous investigations are carried out all the world over concerning the ozone synthesis in an electrical discharge. Those studies are related not only to the development of the theoretical principles of the process but also to the construction of new reactors and methods of carrying out the process itself [2—5].

Such studies are under way in Poland, too. Special attention is devoted to the use of materials and construction available in Poland. One of the new sources of ozone is the electric discharge at the ferroelectric surface. The discharge takes place in a gas layer between two dielectric plates. The dielectric is ferroelectric. The discharge characteristics depend at the ferroelectric properties, mainly on dielectric permitivity and its temperature dependence [6]. The use of two dielec-

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tric plates is reasonable because the ozone concentration and the charge density attain maximum values near the dielectric layers.

The aim of this paper is a tentative characteristic of this ozone source in a small laboratory reactor supplied with oxygen.

II. EXPERIMENTAL

Experiments were performed in the reactor described earlier [7, 8]. It basically consists of the system: metallic electrode — ferroelectric sample — gas layer — ferroelectric sample — metallic electrode. An A.C. discharge (50 Hz) was generated in the gas layer between the plates. Ceramic consisting predominantly of barium titanate was used as the ferroelectric. Its relative dielectric permittivity was 12000 and the Curie point 309 K. The experiments were carried out under the pressure of 112 kPa in a flowing system. The reagent was oxygen containing no more than 0.5 vol. % of nitrogen. The oxygen was purified and dried passing through columns with silica gel, KOH and P_2O_5 prior to its introduction into the reactor. The ozone formed was analysed by a modified iodometric method.

The values of the oxygen flow rate as well as the ozone concentration were given according to the temperature of 293.2 K and the pressure of 103.3 kPa.

The electric discharge proceeds in the gas volume given by the constant distance between the ferroelectric samples and the surface of the metallic electrode. Thus, the volume of the discharge zone and the residence time of the reactants in the discharge can be calculated [7, 8]. The residence time is obviously proportional to the reciprocal flow rate.

III. RESULTS AND DISCUSSION

The dependence between the ozone concentration and the oxygen flow rate is characteristic of ozonators. The ozone concentration decreases rapidly with an increasing oxygen flow rate. Thus, the longer the residence time of gases in the discharge zone is, the higher is the ozone concentration in the off-gases. An increase of the discharge power increases the ozone concentration up to a certain value (Fig. 1, 2). A further power increase causes a small drop in the ozone concentration for a given flow rate. The highest ozone concentration is 39.1×10^{-5} mol/dm^3 (19 mg/dm^3) for an oxygen flow rate equal to 1.56 dm^3/h and a power equal to 2.44 VA.

The important parameters characterizing the process are: the ozone production which defines the amount of ozone formed during one hour of the process and the energy yield of the process defining the amount of ozone formed during one hour of the reaction course per one kilowatt of the discharge power.

The rise in the discharge power causes an increase of the ozone production and a decrease in the energy yield of the process (Fig. 3, 4). Independently of the reagent flow rate favourable conditions for the process occur for powers within the range of 1.0—1.5 VA, because the production value increases no more and the energy yield does not drop too much.

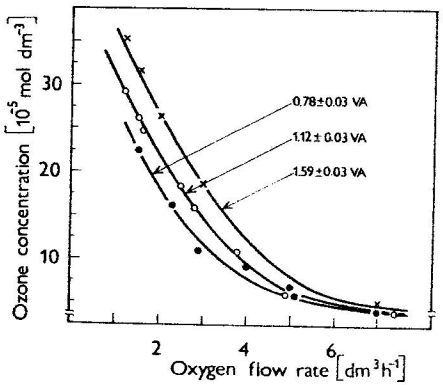

Fig. 1. Effect of oxygen flow rate on ozone concentration (constant power discharge).

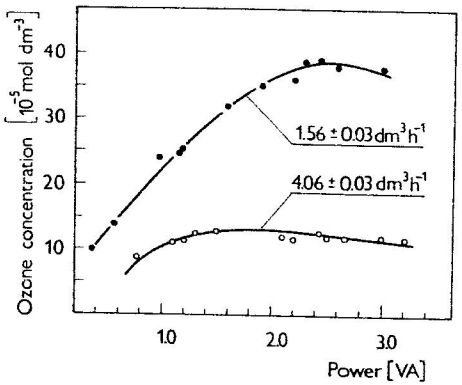

Fig. 2. Effect of power on ozone concentration (constant flow rate of oxygen).

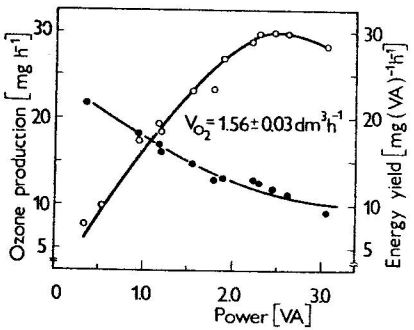

Fig. 3. Effect of power on ozone production and energy yield at an oxygen flow rate equal to (1.56 ± 0.03) dm^3 h^{-1}.

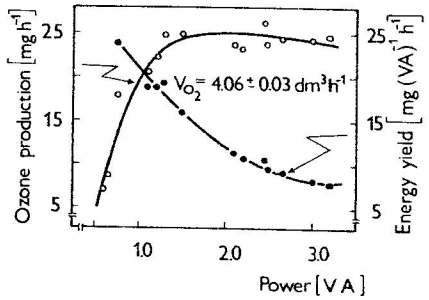

Fig. 4. Effect of power on ozone production and energy yield at an oxygen flow rate equal to (4.06 ± 0.03) dm^3 h^{-1}.

Both the production and the energy yield of the process increase with increasing residence time up to 0.1 s and then decrease in spite of the fact that the ozone concentration increases systematically (Fig. 5). Such a dependence for ozonators is not typical. Usually these two parameters decrease with increasing residence time in the discharge zone.

This phenomenon may be caused either by an error in determining low ozone concentrations or by the characteristics of the process itself for the given experimental conditions. The results of experiments presented in the paper of Opalinska et al. [9] were obtained by the determination of the ozone concentration by the measurement of the absorbance at the wavelength of 254 nm. The experiments were carried out in the same reactor. An analogous dependence of the production and the energy yield on residence time as that described in this paper, has been found. It may be concluded, therefore, that this dependence results from the specificity of the chemical process itself, which is carried out in the reactor of a given design.

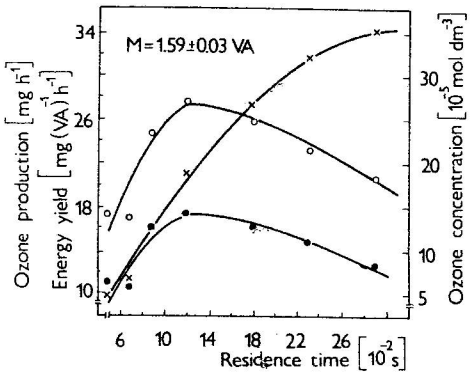

Fig. 5. Effect of residence time on ozone production (○), energy yield (●) and ozone concentration (×). Power discharge equal to (1.59 ± 0.03) VA.

Regarding the gas flow and the power applied, the residence time of gases seems to be too short. Thus, the chemical process has not attained its maximum yield and an adequately high ozone concentration. Concerning the chemical effect of the process, the gas — dynamic conditions are decisive in comparison with the power applied. The fact that the production and the energy yield for the times corresponding to the oxygen flow 5 and 7 dm³/h are practically the same, speaks in favour of the above argumentation (see Fig. 5). The same is true in the case of the ozone concentration which is almost not influenced by power (see Fig. 1). The oscilloscopic patterns of charge and voltage fluctuations in times prove that the discharge is generated only once during one half of the period. For the residence time equal to 0.05; 0.07; 0.12 and 0.19 s, the generated discharge was 5; 7; 11 and 18 times, respectively. The amount of gas flowing within this time through the discharge is the same and the oxygen flow rate is equal to 7.0; 5.0; 3.0 and 2.0 dm³/h, respectively. The number of the discharges increases too slowly in relation to the velocity of the gas flowing through the discharge, for the process parameters to be improved. This can be achieved by the reactor's scaling-up and increase of current frequency supplying the system.

The highest ozone production amounted to 27.7 mg/h; while the corresponding energy yield is 17.5 mg/(VA) for the ozone concentration equal to 19.1×10^{-5} mol/dm³ (9.2 mg/dm³), the oxygen flow rate 3.03 dm³/h, and the power 1.59 VA (Fig. 6).

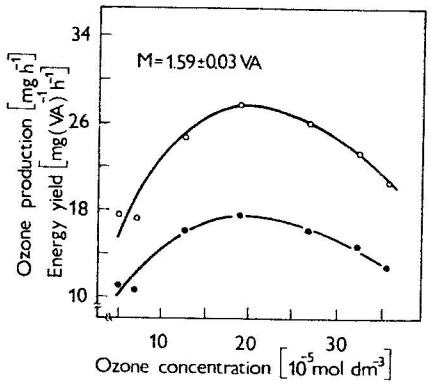

Fig. 6. Relation between ozone production (○), energy yield (●) and ozone concentration. Power discharge equal to (1.59 ± 0.03) VA.

The real power supplied to the reactor was determined by measuring the surface area of the Lissajous figures. The real power amounts to 70% of the apparent power. In that case the energy efficiency is equal to 25 mg/(Wh) for the power of 1.11 W.

The discharge zone in the described reactor is very small (9×10^{-2} cm³), which makes a comparison of these results with those characteristic of typical laboratory ozonators (with the discharge zone 150—200 cm³) difficult. It seems reasonable, therefore, to compare the parameters characterizing the proofs in relation to 1 cm³ of volume of the discharge zone. For tubular ozonators the reported energy yield amounts to 110—170 mg/(Wh) [1]. Thus, assuming the mean volume of the discharge zone equal to 175 cm³, an efficiency of 0.6—1.0 mg/(W/h) per 1 cm³ of the volume would be achieved, whereas for the reactor described in this paper this value equals 271 mg/(Wh).

In paper [1] the ozone production of 12.7 g/h was reported. Thus, the ozone production per a discharge zone unit is 73 mg/h, whereas for the presented reactor 310 mg/h.

A comparison of the results shows that the discharge on the ferroelectric surface is characterized by a high energy density, which for the example under discussion is equal to 12 W/cm³.

IV. CONCLUSIONS

1. In the range of the process parameters applied to a constant reactor construction, the maximum ozone production was 27.7 mg/h and the corresponding

energy yield 25 mg/(Wh). These values have been obtained for the ozone concentration equal to 9.2 mg/dm^3 the oxygen flow rate 3.03 dm^3/h, and the power 1.11 W.

2. The ozone production related to 1 cm^3 of the discharge zone was 310 mg/h and the energy efficiency 271 mg/(Wh). This proves a high energy density in the electric discharge on the ferroelectric surface.
3. A comparison of the results with those obtained for typical laboratory ozonators justifies further studies of the improvment of the system used, e.g. an enlargement of the ferroelectric sample surfaces and an increase of the supplied current frequency. This will allow the energy parameters of the process to be improved for oxygen flow rates lower than 3.0 dm^3/h.

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REFERENCES

[1] Horath, M., Bilitzky, L., Huttner, J.: *Ozone*, Académiai Kiadó, Budapest 1985.
[2] Eliasson, M., Hirth, M., Kogelschatz, U.: J. Phys. D.: Appl. Phys. *20* (1987), 1421.
[3] Rutscher, A., Wagner, H.-E.: Beitr. Plasmaphys. *25* (1985), 315.
[4] Masuda, S., Akutsu, K., Kuroda, M.: *8th Intern. Symp. Plasma Chem.*, Tokyo 1987, p. 816.
[5] Yambe, C., Hayashi, M., Tachioka, Y., Hori, K.: *8th Intern. Symp. Plasma Chem.*, Tokyo 1987, p. 742.
[6] Janus, H., Opalińska, T.: *7th Intern. Symp. Plasma Chem.*, Eindhoven 1985, p. 905.
[7] Szymański, A., Opalińska, T.: Acta Phys. Slov., *35* (1985), 363.
[8] Opalińska, T., Szymański, A.: *8th Intern. Symp. Plasma Chem.*, Tokyo 1987, p. 811.
[9] Opalińska, T., Szymański, A., Sabadil, H., Wagner, H.-E.: *Beitr. Plasmaphys.*, in press.

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ЭЛЕКТРОСИНТЕЗ ОЗОНА НА СЕГНЕТОЭЛЕКТРИЧЕСКОЙ КЕРАМИКЕ

Изучен синтез озона из кислорода в электрическом разряде между двумя диэлектрическими электродами. В качестве диэлектрика использовалась сегнетоэлектрическая керамика (12000).

В этом реакторе исследовалось влияние мощности разряда и объемной скорости поток кислорода на энергетическую эффективность процесса электросинтеза озона.

Сравнение эффективностей процесса для обычного лабораторного озонатора и описанного в работе реактора показало определенные преимущества последнего: компактность высокий удельный энерговклад и высокая энергетическая эффективность процесса по отношению к 1 см^3 зоны разряда.