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Macrokinetic study on ozone boundary concentration. Effect of temperature

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ABSTRACT

The process of ozone production in pure oxygen using the tubular, high voltage pulse supplied ozonizer was studied. The unusual methodology of conducting kinetics measurements of the ozone synthesis process was presented. It was shown how the process rate changes along the discharge gap. The effect of power density and gas residence time in the discharge gap on the process rate was analysed. The temperature influence on the course of the process, particularly on the ozone boundary concentration and ozone decomposition rate constant, was discussed.

1. Introduction

The use of ozone and the methods of its generation are of great interest for many years [1–8]. This results mostly from the desire to obtain high ozone concentration with employing the feasibly high energy efficiency of the process. A significant progress in this area has been achieved due to applying pulse suppliers [9–13] and new types of discharge systems [14–19], among others. An ozone generation process is also a matter of quite a number of model studies [20–25], because it is the simplest reaction system obtained under low temperature plasma conditions. Kinetics of this process arouses a particular interest [26–30].

The kinetics of chemical processes is inextricably linked to the temperature, at which they are carried out. The chemical processes progress in homogenous conditions very rarely. Especially high heterogeneity of thermal conditions in the reaction space is present in the processes led in a dielectric barrier discharge (DBD), what results from its nature [31]. A dielectric barrier discharge is generated in a gas flowing through a narrow gap, created between electrodes of a significant surface area, separated with the use of a solid dielectric. The role of the dielectric (barrier) is to scatter the total electric charge flowing through the gap, into series of fine and numerous microdischarge channels, which cover the entire gap. The microdischarge channels [32] are formed periodically during the flow of electrons and periodically disappear. They constitute only the small part of the total discharge gap volume and create the irregular net of active areas, in which the chemical reactions occur. Therefore, the gas composition and temperature within the microdischarge channels is completely different from its surrounding (see: Fig. 1). The temperature and the concentrations of the reagents in the microdischarge channels depend on the energies of the flowing electrons, local current densities in the gap (electrons concentration), the gas temperature in the moment of the microdischarge formation, the initial concentration and time. The microdischarge channels are surrounded with the gas, which temperature and composition is the same as it was within the microdischarge channels before the electrons flow. The lifetime of the microdischarges is very short. After tens of microseconds since the beginning of the electrons flow [33] the gas in the microdischarges channels reaches the state of conversion. Due to the occurrence of the local concentration and temperature gradients between the active and passive areas the processes of diffusion and mixing begin. They effect in averaging concentrations and temperature values. As a result the average gas temperature T_g in the gap increases in relation to the inlet gas temperature T_{g0}.

When ozone is synthesised from the pure oxygen, the most important reactions occurring in the microdischarge channels are:

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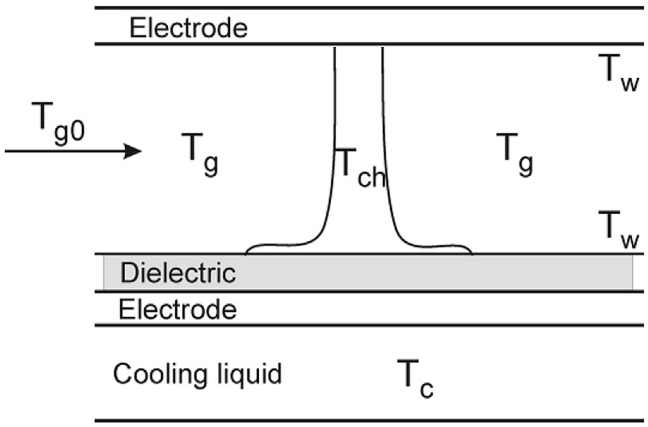

Fig. 1. Temperatures in the gap; T_{g0} – inlet gas temperature, T_{ch} – gas temperature in the microdischarge channel, T_g – temperature of the gas, T_c – cooling liquid temperature, T_w – temperature of the electrodes walls.

$$O_2 + e \rightarrow O + O + e \quad k1 = f(E/n) \tag{1}$$

$$O + O_2 + M \rightarrow O_3^* + M \rightarrow O_3 + M \quad k_2 = 6.4 \cdot 10^{-35} \cdot \exp(663/T_{ch}) \tag{2}$$

$$O_3^* + O \rightarrow O_2 + O_2 \quad k_3 = 8 \cdot 10^{-12} \cdot \exp(-507/T_{ch}) \tag{3}$$

$$O_3 + O \rightarrow O_2 + O_2 \quad k_4 = 1.8 \cdot 10^{-11} \cdot \exp(-2300/T_{ch}) \tag{4}$$

$$O + O + M \rightarrow O_2 + M \quad k_5 = 1.3 \cdot 10^{-32} (300/T_{ch}) \cdot \exp(-170/T_{ch}) \tag{5}$$

They form the well-known mechanism of ozone synthesis [31], in which the competing groups of reactions: in favour of ozone synthesis (1–2) or in favour of its decomposition (1, 3–4) can be distinguished. The rate of these reactions is affected by the reduced electric field E/n or the gas temperature T_{ch} in the microdischarge channel. The rate constant values [29,34,35] are expressed in cm^3/s for two-body collision and in cm^6/s for three-body collision.

In the depicted process mechanism, the key role plays the reaction of molecular oxygen dissociation (reaction (1)), which occurs due to the energy delivered by the high-energy electrons ($\geq$6 eV). Ozone is formed in the reaction between atomic and molecular oxygen (reaction (2)). In this reaction, the immediate energetic stabilisation of the formed O_3^* molecule, by divesting the energy excess, is extremely important. That energy is captured by the molecule M (M = O, O_2, O_3 or electrodes walls) and goes to the reaction system in the form of a heat. When the concentration of atomic oxygen in the microdischarge channels is high, the formation of energy-stable ozone molecules may be limited trough the occurrence of the reaction (3). A part of oxygen atoms can be consumed in the reactions (4) and (5). However, in the reaction (4) oxygen atoms participate in ozone decomposition. Ozone can also be decomposed by electrons, especially when their (both ozone and electrons) concentrations are high:

$$O_3 + e \rightarrow O + O_2 + e \quad k_6 = f(E/n) \tag{6}$$

Since in the expected reaction (2) only the small part of the created atomic oxygen is consumed, the energy delivered for the reaction (1) occurrence is lost to a significant degree (is turned into heat transferred to the reaction system, more precisely). The mechanism of the heat emission and corresponding effects of temperature changes in the microdischarge channel and then in the discharge gap were analysed in detail in Ref. [36] among others. As it was stated previously, the reactions (1)–(6) occur in the limited volume occupied by the microdischarge channels (isolated from the rest of the gas in the gap), what in natural way causes the short, but intense, gas temperature increase in these channels and the local temporary pressure increase also. The presence of temperature and pressure gradients leads to the heat release outside the channels and causes the mixing of the heated gas with the cold one. As a result of processes of mass and heat exchange occurring simultaneously, the ozone concentrations evens and the gas temperature stabilises in the gap.

1.1. The ozone boundary concentration. The average gas temperature in the gap

In the majority of experiments described in the literature, an ozone concentration is measured only at the ozonizer outlet, hence after the termination of chemical and physical transformation cycles occurring in the discharge gap. These concentrations, obtained for different discharge powers and gas flow rates, are usually correlated with the specific energy. The specific energy, P/V, is a useful equivalent process parameter, which characterizes conditions in an ozonizer taking into account both streams brought to it (the energy stream, i.e. power and reactant stream, i.e. gas flow rate V). The relation between the obtained ozone concentration c_{O3} and the specific energy is expressed by the exponential Vasil'ev-Kobosev-Eremin (VKE) formula [37]:

$$c_{O_3} = c_{O_3}^* \left[1 - \exp\left(- k_d \left(\frac{P}{V} \right) \right) \right] \tag{7}$$

in which the c^*_{O3} is the ozone boundary concentration, and the k_d is the macroscopic constant rate of ozone decomposition.

However, the P/V ratio is not a fully unequivocal parameter, because both P and V are the independent process parameters itself. Both of them affect the gas temperature in the gap. Depending on the way of changing the P/V value, the $c_{O3}(P/V)$ characteristics of slightly different nature are obtained [38,39]. If the changed parameter is the power, then its increase (for V = const) causes in sequence: the increase, the reaching of the maximum and then the decrease of ozone concentration (see: Fig. 2a, dashed lines). On the other hand, if the increase of the specific energy is obtained by decreasing the gas flow rate (for P = const) the maximum ozone concentration does not appear and the obtained $c_{O3}(P/V)$ dependencies are exponential, that is consistent with the VKE formula. These dependencies may even suggest that the increase of power clearly adversely affects the ozone concentration. However, if the ozone concentration is depicted as the function of residence time τ, then the effect of the power becomes easier to be properly interpreted (Fig. 2b).

Fig. 2b depicts the effect of residence time on the ozone concentration for the increasing powers (P_1, P_2, and P_3). As can be easily noticed, for the low powers the ozone concentration tends to the boundary value of c^*_{O3}, while for the highest power the concentration is noticeably lower. All of the $c_{O3}(\tau)$ dependencies are exponential and all of them tend asymptotically to a certain concentration boundary value. However, if the power is too high the asymptote is placed lower. It is undoubtedly related to the conditions occurring in the discharge gap when the power is increased.

It is commonly believed that the observed ozone concentration decrease is the result of the ozone decomposition caused by the increase of gas temperature in the gap. However, in the light of the process mechanism presented previously and the mechanism of