acta physica slovaca vol. 56 No. 2, 109 – 113 **April 2006**

NON-THERMAL PLASMA AT ATMOSPHERIC PRESSURE FOR OZONE GENERATION AND VOLATILE ORGANIC COMPOUNDS DECOMPOSITION[1]

S. Pekárek[2], J. Khun
Czech Technical University, FEE, Technická 2, 166 27 Prague 6, Czech Republic

Received 6 December 2005, in final form 7 February 2006, accepted 21 February 2006

The non-thermal plasma technologies based on electrical discharges play an important role in ecological applications. The classical corona discharge is however relatively low power discharge. With the aim to extend its current-voltage range we studied hollow needle-to-plate DC corona discharge enhanced by the flow of a gas through the needle electrode. With this type of the discharge we performed an extensive study of ozone generation and volatile organic compounds (VOCs) decomposition. We found that supply of air through the needle substantially increases current-voltage range of the discharge in comparison with classical pin-to-plate corona discharge. Consequently the ozone generation as well as toluene decomposition efficiency was increased.

PACS: 52.80.Hc, 82.33.Xj

1 Introduction

Non-thermal plasma is usually referred to as plasma in which the temperature of electrons is higher than the temperature of ions. The key advantage of the non-thermal plasma application for ozone generation and VOC decomposition is the "directed" energy consumption. In this case the energy delivered to the discharge is predominantly used for the generation of highly energetic electrons and only little energy is lost in the heating of the volume of a gas. Consequently the technologies based on the non-thermal plasma can be highly effective in promoting oxidation, enhancing molecular dissociation or producing free radicals to stimulate plasmachemical reactions, which can be used for ozone generation or decomposition of volatile organic compounds.

Non-thermal plasma is generated by electrical discharges most frequently by a corona discharge. The corona is generated by a strong electric field and at least one of the electrodes is a thin wire, a needle or has a sharp edge. The other electrode is most frequently a plate or a cylinder. Due to the fact that corona discharge is relatively low power electrical discharge for practical application it is necessary to enhance the discharge power. To do this and at the same time to prevent discharge transition to a spark two ways are used:

1. Pulse voltage is applied on the electrodes.

[1]Presented at 15-th Conference of Czech and Slovak Physicist, Košice, Slovakia, September 5–8, 2005
[2]E-mail address: pekarek@fel.cvut.cz

2. Application of the gas flow.

There are several types of electrode configurations of the gas flow stabilized discharge. One of these involves crenellated pins to plate electrode configuration with the flow of a gas medium around the pins [1].

We have however suggested a new approach to the discharge stabilization, which involves supply of the gas through the needle [2]. The advantage of this arrangement is that all the gas passes through the discharge region and therefore is affected by plasmachemical processes.

We have studied application of the gas flow enhanced hollow needle-to-plate DC corona discharge for ozone generation and VOC decomposition.

2 Ozone generation

Ozone is a powerful disinfecting and oxidizing agent, which is used in a wide range of applications such as water treatment applications, treatment of municipal and waste water, food processing, fire restoration, restoration of buildings after floods etc.

Ozone generation by electrical discharge in air is rather complicated because of the destruction processes due to the existence of nitrogen oxides [3]. Reaction rates of ozone creation and destruction processes depend on different parameters — for example on electric parameters of the discharge, temperature etc.

One of the most easily discharge controlled parameter is discharge voltage, which determines the electric field, energy distribution of electrons and consequently dissociation rates coefficients of $\mathrm{O_2}$ and $\mathrm{N_2}$ by electron impact reactions. These coefficients are usually treated as functions of reduced electric field, which is defined as a ratio of electric field strength per unit gas density (E/n). As an example the reduced electric field about 100 Td is equivalent to an electric field approximately 25 kV/cm at atmospheric pressure and at temperature 300 K. According to [4] the optimum reduced electric field for ozone formation from air is about 200 Td.

Another important parameter, which influences ozone production, is a gas temperature. Speaking generally increasing gas temperature substantially reduces ozone generation processes. Thus, for example the main ozone formation reaction dominant at atmospheric pressure is reaction

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M}, \tag{1}$$

where M represents molecular oxygen or nitrogen. In this case the reaction rate dependence on the gas temperature T_g is given by following equation

$$k = 2.5 \times 10^{-35} \exp\left(970/T_\mathrm{g}\right) \qquad (\mathrm{cm^6 \cdot mol^{-2} \cdot s^{-1}; K}). \tag{2}$$

From this expression it is seen that reaction rate of ozone generation decreases with increasing gas temperature.

Contrary to ozone, $\mathrm{NO_x}$ formation is favoured by heat and linked with the discharge path temperature. Thus for example the reaction

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2} \tag{3}$$

is significantly enhanced by increasing the gas temperature

$$k = 1.5 \times 10^{-12} \exp\left(-1300/T_\mathrm{g}\right) \qquad (\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}; K}). \tag{4}$$

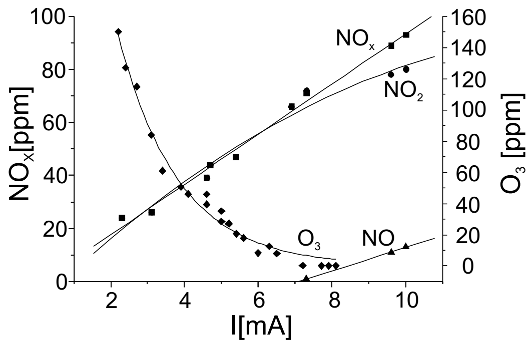

Fig. 1. Ozone and nitrogen oxides concentration for the discharge with needle negative (Q = 5 slm).

From Fig. 1 [3] it is seen that ozone generation from air could not be separated from the production of nitrogen oxides. This causes unpleasant effect called discharge poisoning — that is the production of nitrogen oxides prevails over the production of ozone, so that finally no ozone is produced. These results were obtained for a single hollow needle-to-plate discharge, with the supply of air through the needle electrode [3].

In this experiment the distance between the tip of the needle and the plane electrode was $d = 3.2$ mm. Airflow rate through the needle was adjusted to 14 slm. Concentration of ozone was measured by the absorption of the 254 nm U.V. spectral line with ozone monitor ML9811 (Monitor Laboratories, measuring range 0.01 – 20 ppm) or with API 450 ozone monitor (Advanced Pollution Instrumentation, measuring range 1 – 1000 ppm).

Simultaneously with ozone were measured concentrations of nitrogen monoxide NO and nitrogen dioxide $\mathrm{NO_2}$ by flue gas analyzer GA-60 (Madur Electronics).

In general it can be said the usage of hollow needle-to-plate electrode configuration with the supply of air through the needle increases current-voltage range of the discharge [5] in comparison with classical pin-to-plate corona. Consequently the number of electrons is increased and plasmachemical reactions are enhanced.

3 Decomposition of volatile organic compounds — VOCs

Various technologies such as thermal incineration, catalytic oxidation, adsorption, biofiltration, membrane separation or UV-oxidation have been tested for VOCs decomposition. These conventional techniques require relatively high capital costs and hence are inefficient for low VOC concentrations. They are also often burdened by secondary waste. In the latter case, the environmental problem is shifted from the gaseous phase to a solid or liquid phase. Furthermore these processes can be sensitive to poisoning and deactivation.

Contrary to these conventional techniques the non-thermal plasma technologies can be highly effective because of the directed energy consumption. Speaking generally the mechanism of VOC decomposition by non-thermal plasma processes can be summarized as follows:

1. Direct electron impact dissociation and dissociative ionization of VOC and air molecules.

2. Ionization-dissociative recombination two-stage processes for radical formation and indirect VOC destruction.

3. Electron attachment — positive-negative ion two stage recombination processes for radical formation and indirect VOC destruction.

4. Ion-molecule reactions for radical formation.

5. Radical oxidation and reduction processes for VOC destruction.

6. Heterogeneous aerosol surface reactions and ion-induced aerosol formation for VOC conversion.

Depending on the type of VOCs and plasmachemical reactor used, the relative importance of each of above processes differs.

We tested decomposition of toluene, hydrocarbons contained in a gasoline and n-heptane in the mixture with air by needle-to-plate and multi-needle-to-plate electrical discharge [6,7]. Thus in [7] it was found that the toluene decomposition efficiency was increased by 20 % when the mixture of air and toluene was flowing through the needles in comparison with the situation when it was flowing around and partially through the needles. In addition it was observed that decomposition efficiency exhibits strong polarity effects and it depends on energy density delivered to the discharge. In this experiment the electrode system of the reactor channel consisted of 15 hollow stainless needles, which were used as a cathode. The needles were situated perpendicularly against the metallic plate, which was used as an anode. The distance between the tips of the needles and the plate electrode was 3.9 mm. Identification and quantification of volatile hydrocarbons was performed after their backward desorption by chromatographic analysis-capillary gas chromatography with mass spectrometric (GC-MS) or flame ionization (GCFID) detection. Determination of aldehydes, in the form of their hydrazon derivatives, was realized using high-resolution liquid chromatography (RP-HPLC) with UV detection.

Except of above-mentioned plasmachemical reactors there exist also so-called hybrid plasmachemical systems for VOCs decomposition. These systems consist of the combination of electrical discharge and catalyst or adsorbent.

We found that combination of the non-thermal plasma produced by hollow needle-to-plate electrical discharge with TiO_2 photocatalyst increases n-heptane decomposition efficiency and it is possible to operate the discharge at lower power conditions for the same decomposition efficiency as without the photocatalyst [8]. This result can be explained by combined effect of plasmachemical reactions and photocatalytic action of TiO_2, which is induced by UV radiation produced in the discharge.

4 Conclusions

Non-thermal plasma produced by electrical discharges seems to be efficient for certain applications such as ozone generation or VOC decomposition.

In the field of ozone generation our research is oriented to new approaches leading to higher attainable ozone concentrations and lower energy consumption.

We also studied decomposition of different types of VOC by hollow needle-to-plate discharge and by the discharge combined with a photocatalyst.

Acknowledgement: This work is supported by the Research Project of the Czech Technical University in Prague No. 6840770016.

References

[1] Yu. Akishev et al.: *Journal of Physics D, Appl. Physics* **34** (2001) pp. 2875–2882

[2] S. Pekárek et al.: *Plasma Sources Science and Technology* **8** (1999) pp. 513–518

[3] S. Pekárek and J. Rosenkranz: *Ozone Science & Eng.* **24** (2002) pp. 221–226

[4] U. Kogelschatz et al.: *J. Phys IV France* **7** Colloque C4: 47–63, Suppl. Journ de Physique III (1997)

[5] S. Pekárek and J. Khun: *Proceedings of the XV^{th} International Conference on Gas Discharges and their Applications, Volume 1*, Toulouse, France, September 5–10, 2004, pp. 509–512

[6] S. Pekárek, M. Pospíšil: *Czechoslovak Journal of Physics* **52** (2002) pp. 762–768

[7] S. Pekárek et al.: *Journal of Physics D, Appl. Physics* **34** (2001) L117–121

[8] S. Pekárek et al.: *Proc. of 17^{th} Int. Symp. on Plasma Chemistry CD–ROM*, Toronto, 2005, ID 234