IJPGC2003-40149

POSSIBILITIES OF FORMALDEHYDE REMOVAL BY DISCHARGE PLASMA

Karol Hensel, Joanna Pawłat, Kazunori Takashima and Akira Mizuno

Toyohashi University of Technology
Department of Ecological Engineering
Tempaku-cho, 441-8580 Toyohashi, Japan

Saga University
School of Science and Engineering
Honjo-machi, 840-8502 Saga, Japan

IJPGC2003-40149

POSSIBILITIES OF FORMALDEHYDE REMOVAL BY DISCHARGE PLASMA

Karol Hensel / Toyohashi University of Technology,
Department of Ecological Engineering,
Tempaku-cho, 441-8580 Toyohashi, Japan
Tel: (0532)-47-0111, ext. 7212, Fax: (0532)-44-6929
khensel@mail.eco.tut.ac.jp

Joanna Pawlat / Saga University,
Faculty of Electrical and Electronic Engineering,
School of Science and Engineering,
1 Honjo-machi, 840-8502 Saga, Japan
Tel: (0952)-28-8642, Fax: (0952)-28-8651

Kazunori Takashima / Toyohashi University of
Technology, Department of Ecological Engineering,
Tempaku-cho, 441-8580 Toyohashi, Japan
Tel: (0532)-47-0111, ext. 7212, Fax: (0532)-44-6929

Akira Mizuno / Toyohashi University of Technology,
Department of Ecological Engineering,
Tempaku-cho, 441-8580 Toyohashi, Japan
Tel: (0532)-47-0111, ext. 7212, Fax: (0532)-44-6929

ABSTRACT
Removal of formaldehyde by streamer corona discharge was studied experimentally. It was shown the removal efficiency as well as the by-products of the chemical process in the non-thermal plasma of the discharge depend on the initial concentration, gas flow rate, carrier gas, discharge polarity and discharge mode. A combined effect of plasma and catalytic pellets of various materials placed in the discharge reactor was investigated too.

INTRODUCTION
Volatile organic compounds (VOC) are considered as toxic air pollutants generated in urban and industrial areas. Their control in the atmosphere is a major environmental problem and many researchers have focused on their decomposition. A promising method to control VOCs is the use of non-thermal plasma. The plasma is highly effective producing free radicals, enhancing molecular dissociation and promoting oxidation. Moreover, the combination of non-thermal plasma with catalyst is an attractive method for enhancing the efficiency of VOC destruction.

Formaldehyde is one of the most common VOCs. It is a flammable, colorless gas with a pungent, suffocating odor. Formaldehyde is used mainly for the production of urea-formaldehyde resins, phenol-formaldehyde resins and plastics. It also has miscellaneous uses in agriculture, cosmetics, paper and textile industries and is also used in human medicine. Formaldehyde is released by gas cookers and is found in tobacco smoke. It is also used in building materials such as plywood, chipboard and paneling. Emissions from gasoline powered motor vehicles are a source of formaldehyde in dry air too [1].

Numerous adverse health problems have been ascribed to formaldehyde exposure, ranging from well documented effects such as eye, nose and throat irritation, to more controversial claims including asthma, cancer, chronic respiratory diseases and neuropsychological problems. Although evidence of cancer formation is unequivocal, the extrapolation of these results to humans has been controversial.

The aim of the research was to investigate the possibility of formaldehyde reduction from dry air and nitrogen using DC streamer corona discharge and to evaluate efficiency of its treatment in different conditions. Pellets of various catalytic materials were used to affect the decomposition and their effect was partially investigated too. Although the chemical reactions and process, mainly the one affected by presence of catalyst, are complicated, several experimental results are presented.

NOMENCLATURE
Formaldehyde, Corona Discharge, Catalytic Material, IR Spectrometry

EXPERIMENTAL APARATUS
The used experimental reactor is depicted in the fig. 1. Discharge reactor of multi-point-to-mesh geometry was used and set inside Pyrex glass tube 35 mm diameter. The distance between electrodes was set to 16 mm. The tube was closed with silicon stoppers at the both ends. DC high voltage power supply was used to generate streamer corona discharge. Discharge current and voltage were measured by digital multi meter and high voltage probe (Tektronix P6015A) connected to oscilloscope (Tektronix TDS644A).

The formaldehyde vapors were produced by bubbling liquid solution of formaldehyde (Waco 064-00406) with dry air or nitrogen and their concentration varied between 100 - 1200
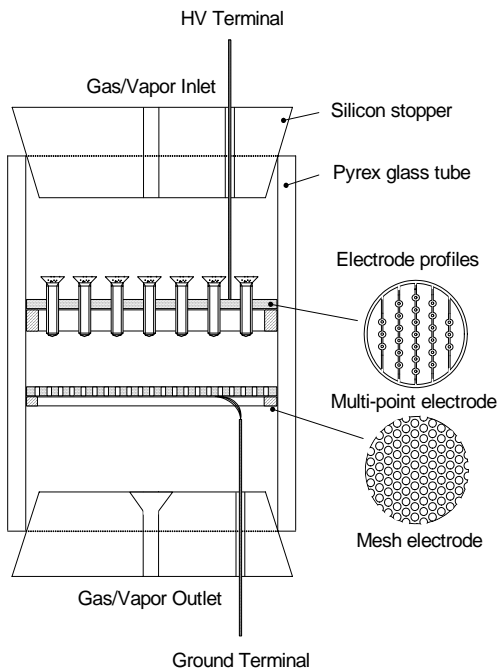
Figure 1: *Experimental reactor.*

ppm. The total gas flow rate was 0.25, 0.5 or 1.0 lpm and was controlled by mass flow meters. The experiment was carried out at the room temperature.

In the experiment, where catalyst was used to affect the removal of formaldehyde, an 8mm thick layer of pellets was placed on the mesh electrode .

The analysis of gas composition was performed by infrared (Bio-Rad FTS-3000), ultraviolet (Shimadzu UV-1200) spectrometry and gas analyzing tubes (Gastec).

EXPERIMENTAL RESULTS

Formaldehyde is an organic compound, which can be comfortably detected by infrared absorption spectrometry. Typical aldehydic absorption characteristics are stretching vibration of carbonyl group C=O in the region 1740-1720 cm^{-1}
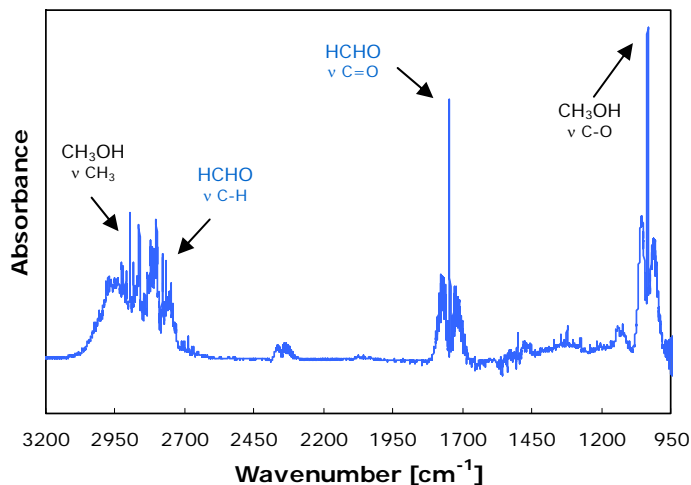

Figure 2: *IR spectrum of formaldehyde.*

and aldehydic C-H stretching vibration in the 2830-2695 cm^{-1} region (fig. 2). The formaldehyde solution used for the experiment contained 5% of methanol as a stabilizer. The infrared spectrometry is effective method for the quantitative and qualitative analysis of products of formaldehyde decomposition, which was utilized in the experiment.

DC streamer corona discharge of positive polarity was used primarily as a medium for formaldehyde treatment (fig. 3). Most of the experiments were performed in the dry air. For the comparison, however, also nitrogen mixtures, negative polarity, and other discharge modes were partially investigated too.

Figure 3: *DC streamer corona discharge.*

A specific input energy (SIE) was used to evaluate the efficiency of the process. It is defined as discharge energy dissipated per unit volume of the gas.

1. Chemical Processes and By-Products

Formaldehyde decomposition results mostly into formation of carbon oxide CO and formic acid HCOOH. The formation of CO occurs most probably by photolytic reactions HCHO + hν → HO$_2$ + CO or HCHO + hν → CO + H$_2$, by light produced by streamer discharge. In dry air, where oxygen is present, CO can also be formed by HCHO + hν → H + HCO followed by HCO + O$_2$ → CO + HO$_2$. Oxygen in the gas mixtures also supports formaldehyde oxidation to formic acid by oxygen radicals, produced through dissociation of molecular ozone by the discharge (HCHO + O → HCO + OH → HCOOH). Surprisingly, the reaction with ozone appeared not to be effective. Oxidation of formaldehyde mixed with the gas containing high concentration of ozone (up to 1000 ppm) was negligible. Due to the existing oxidation process the removal was slightly better in the mixtures with dry air as a carrier gas. The process of formaldehyde removal leads also to formation of many other minor products. Their presence and concentration was monitored by absorption spectrometry and will be discussed in the following sections.

2. Effect of Initial Concentration and Flow Rate

Removal efficiency of formaldehyde depended on its initial concentration. For smaller initial concentration, higher removal efficiency was achieved. As can be seen on fig. 4, removal efficiency of 60% was achieved in the case of initial 480 ppm compared with only 45% for 1220 ppm initial concentration in the same conditions (air, 300 J/l, 0.25 lpm). As expected, an increase of initial concentration of formaldehyde resulted in the increased formation of CO and HCOOH (latter
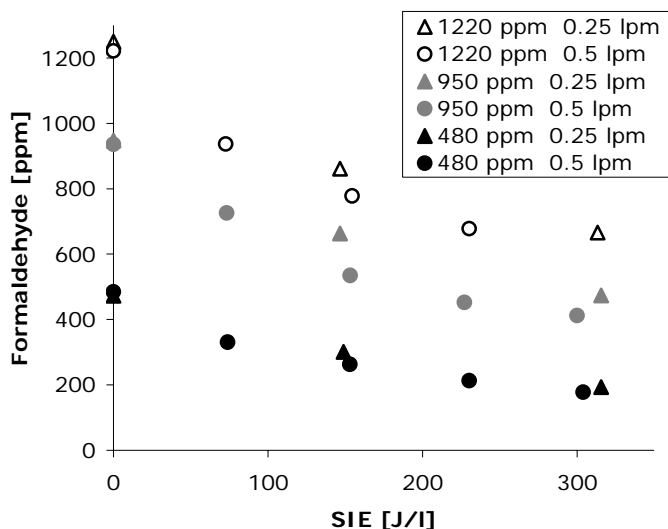
Figure 4: *Formaldehyde decomposition in dry air.*

in dry air mixtures only). For the results presented in the figure, with SIE 300 J/l concentration of HCOOH produced (in ppm) was approximately 13-17% of initial HCHO concentration. Similarly, concentration of CO (in ppm) was about 40-60% of initial concentration of formaldehyde, where relatively higher CO production was achieved with smaller initial concentration of HCHO. Part of CO produced may, however, be produced also by dissociation of CO_2 present in the system as impurity.

The removal of formaldehyde was also affected by gas flowrate. Increasing the flowrate from 0.25 lpm to 1.0 lpm at the constant SIE caused more formaldehyde was removed.

3. Effect of Carrier Gas

Comparing the removal efficiencies of formaldehyde in dry air and nitrogen (fig. 5) for the same SIE, the removal is better in dry air mixtures. It is because of mentioned oxidation processes caused by oxygen radicals. Regarding the formation of by-products, production of CO (2169 cm^{-1}) is higher in dry air. Similarly, formation of formic acid in the discharge was confirmed. Its concentration in nitrogen mixtures is, however,
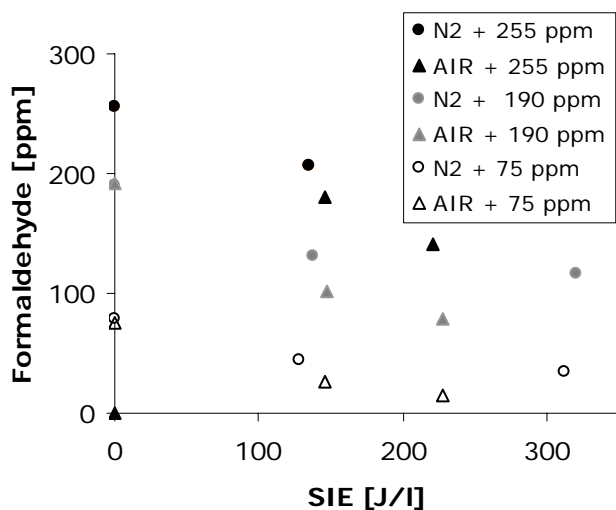

Figure 5: *Formaldehyde decomposition depending on the carrier gas, initial concentration and SIE.*

negligible. In the spectrum the absorption band at 1775 cm^{-1} belongs to stretching vibration of carbonyl group C=O, which appear next to the C=O group of formaldehyde (1745cm^{-1}) Vibration appearing at the 1105 cm^{-1} also belongs to the acid and corresponds to stretching vibration of C-O in COOH group.

During the discharge in dry air, ozone is produced. It happens via the reaction of oxygen molecules with oxygen radicals produced in the discharge. Although ozone does not much affect formaldehyde removal, the oxygen radicals do. For the same SIE and increasing initial concentration of formaldehyde, the amount of ozone produced by the discharge (1055 cm^{-1}) was found decreased, as can be seen in fig. 6. The reason is oxygen radicals are used rather for oxidation of formaldehyde than for ozone production. The reaction of formaldehyde with oxygen radicals HCHO + O → HCO + OH can either lead to formation of formic acid in the next step → HCOOH or result in the increase of CO concentration probably via HCHO + OH → HO$_2$ + CO, thanks to OH radicals produced in the previous step.
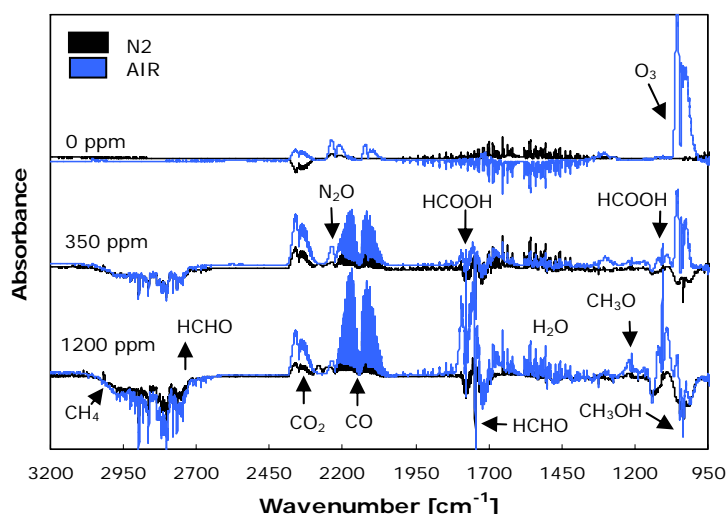

Figure 6: *Differential spectra of formaldehyde decomposition in dry air and nitrogen gas (300 J/l).*

Besides HCHO, CO and HCOOH, there are also other by-products which appeared in the absorption spectra. During the removal process several tenth of ppm of CO_2 (2360 cm^{-1}) is produced, as well as N_2O (2235 cm^{-1}). Methanol vapors contained in formaldehyde solution are removed by discharge too (region 3200-2900 cm^{-1}).

In addition, absorption band at 1210 cm^{-1} is assumed to belong to CH$_3$O* methoxy group resulting from removal of methanol vapors. Finally, absorption at 1755 cm^{-1} is believed to be CH$_3$OCO methyl formate and can be found only in dry air mixtures.

Although removal of formaldehyde in nitrogen mixtures is less effective, compared with dry air it produces less CO_2, NO_2 and N_2O. Also different to dry air mixture is appearance of a very small band at 3018 cm^{-1}, which can only be found in nitrogen mixtures and represents CH$_4$.

4. Effect of Discharge Mode

The discharge mode also affects the chemical process in the discharge. First, the efficiency of formaldehyde removal
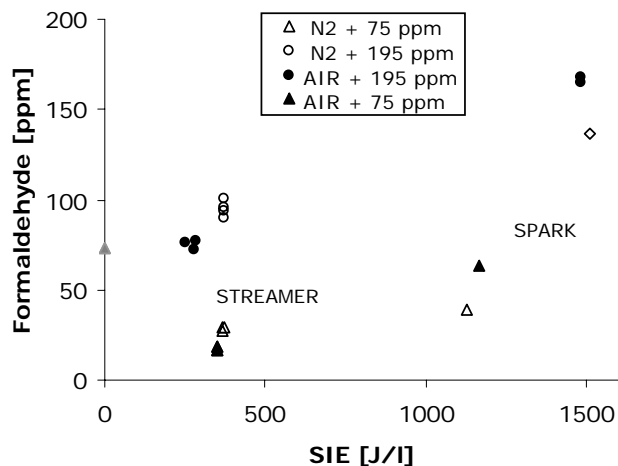
Figure 7: *Formaldehyde decomposition in dry air and nitrogen under streamer and spark discharges.*

rapidly decreases if the discharge transforms into spark as can be seen in fig. 7. While during the streamer discharge the efficiency of formaldehyde removal was better in dry air mixtures, spark formation gave opposite result. This is the result of formation of NO_X in dry air, which uses part of the discharge energy.

Comparing streamer mode of DC corona discharge with the spark discharge in dry air, several differences can be found also in the absorption spectra (fig. 8). During the spark the formation of HCOOH is negligible. Smaller removal of formaldehyde causes smaller production of CO and increase of CO_2 production. Formation of ozone is also suppressed by rising temperature, but also due to the formation of NO (1900 cm^{-1}) and its oxidation to NO_2 (1627, 2920 cm^{-1}) as well as oxidation of CO into CO_2.
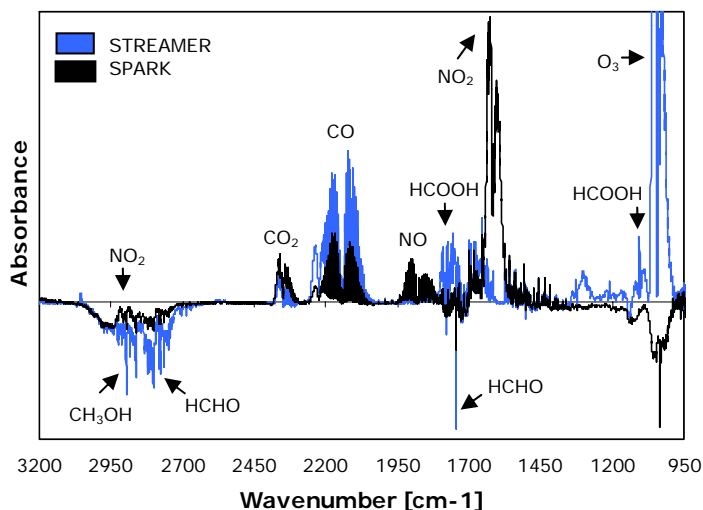

Figure 8: *Differential spectra of formaldehyde decomposition by streamer (300 J/l) and spark (1500 J/l) discharges in air.*

There are not many differences in the absorption spectra between dry air and nitrogen, concerning formaldehyde removal, if the discharge transform into spark. The main difference is probably enhanced productions of CO_2, NO and

NO_2 in dry air and on the other hand (similar to streamer discharge) production of CH_4 in nitrogen.

5. Effect of Discharge Polarity

The effect of discharge polarity was briefly examined too. Application of negative voltage to a multi-point electrode, however, produced a glow type corona discharge, which turned out not to be very effective for formaldehyde removal. To produce the similar amount of oxygen radicals/ozone necessary for oxidation of formaldehyde, power consumption extremely increases. However, achieving the same production of oxygen radicals/ozone in both polarities resulted in approximately the same amount of formaldehyde removed.

6. Effect of Catalyst

The effect of catalytic material present in the discharge volume have been investigated partially too. A layer of catalytic pellets (TiO_2, Pt/Al_2O_3 and other materials) with the thickness of 8mm was placed onto mesh electrode (fig. 9). Catalysts were expected to affect the formaldehyde decomposition, either due to their activation by discharge (TiO_2), usually resulting in improvement of oxidative removal of small amounts of VOCs, or by their abilities to adsorb various compounds to their surface.
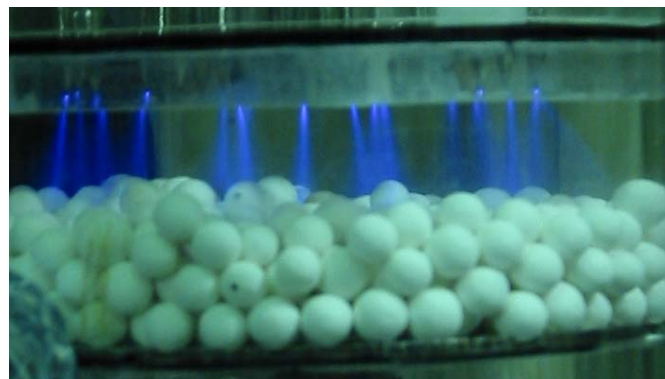

Figure 9: *Streamer corona discharge with TiO_2 catalyst placed on the grounded electrode.*

The presence of the catalytic material in the discharge reactor caused concentration of formaldehyde at the outlet of the reactor decreased, due to its adsorption to the surface of pellets. Thus prior to the every experiment a certain time was needed (several hours) until concentration of formaldehyde at the reactor outlet saturated. The outlet concentration either reached the level of input concentration (e.g. TiO_2) or saturated at the value down bellow the inlet concentration (e.g. Pt/Al_2O_3, here the output concentration did not exceed 20% of the input). The adsorption properties of catalytic material can be seen even without discharge, by changes of the absorption spectra of the gas composition at the outlet compared with the input gas composition (e.g. formic acid missing in the spectrum when TiO_2 is used, due to its adsorption to the surface [2]). Comparably less were affected the concentrations of other gas components, e.g. ozone or nitrogen oxides. Regarding concentration of ozone, minimal difference between inlet and outlet concentration was observed in the cases of TiO_2, γ-Al_2O_3, Pt/Al_2O_3 and NaY zeolite catalysts. On the other hand, an
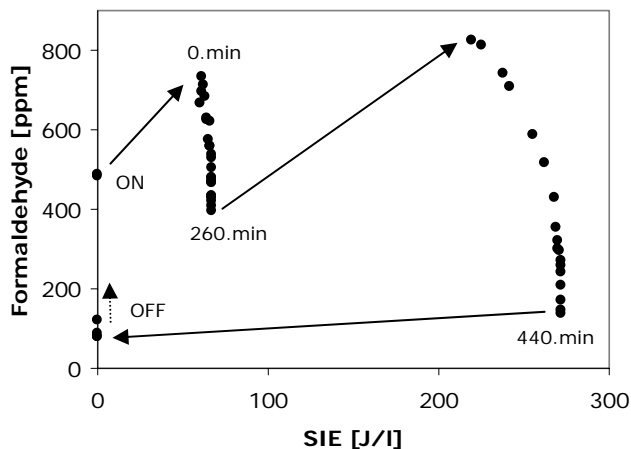
Figure 10: *Formaldehyde decomposition using TiO2 pellets in the discharge volume (480ppm in air).*

effective sorption of ozone was observed especially in the cases of zeolite molecular sieves 3A, 4A, 13X (Tosoh) and MnO_2.

Regarding the formaldehyde treatment using discharge in the reactor with catalytic pellets, the effect of TiO_2 pellets is reported here as an example. In the case of TiO_2 pellets and with 480 ppm of initial formaldehyde (fig. 10) an application of the discharge caused concentration of the formaldehyde behind the reactor suddenly increased exceeding the initial value. One of the reasons is that part of formaldehyde adsorbed by pellets was released from the surface. Within 260 minutes during which SIE of the discharge was kept constant (approx. 65 J/l) the concentration decreased a little bellow the input concentration. Increasing SIE further (220-272 J/l) and waiting for another 180 minutes, the amount of formaldehyde removed increased to 71% (272 J/l) and slowly saturated. Comparing the results in fig. 4 and fig.10, an increase in removal efficiency of formaldehyde can be seen. After switching the discharge off, the concentration of formaldehyde decreased a little further and then gradually started to recover toward the initial value.

The increase of the concentration of formaldehyde during the discharge with catalytic pellets can be explained either by desorption of formaldehyde molecules adsorbed before the discharge, caused by increased temperature in the reactor and streamer contact with pellets. The increase can also be explained by formation of formaldehyde from methanol $CH_3OH \rightarrow CH_3O$ (ad) $\rightarrow$ HCHO (g) + H (ad) at higher temperatures [3] or from adsorbed formic acid HCOOH (ad) $\rightarrow$ HCHO (g) + ½ O_2 and 2 HCOOH (ad) $\rightarrow$ HCHO (g) + CO_2 + H_2O [2].

To find out more about the effect of individual catalyst on both volume and surface chemistry, additional measurements must be performed during long time discharge operation. The analysis of the gas mixture must further be supplemented with the analysis of pellets surface.

CONCLUSIONS

The possibility of formaldehyde removal from the dry air and nitrogen was investigated. DC streamer corona discharge appeared to be effective method for its decomposition. For a given SIE, removal efficiency increased when initial concentration of formaldehyde was decreased and its gas flow increased. Removal was more effective in dry air mixtures, due to existing oxidation process resulting in the formation of HCOOH and CO. The efficiency is very low if the discharge transforms into the spark. In such case, removal in nitrogen mixtures is a little better, as in dry air formation of NO_X becomes important. No difference between used polarities concerning the oxidation of formaldehyde by oxygen radicals was observed. The only difference is higher power consumption in negative polarity caused by glow mode of corona discharge. A combination of plasma and catalyst to improve/affect the process of formaldehyde removal was investigated. Improvement was observed when TiO_2 pellets were used, although the presence of the catalyst especially due to their adsorbing abilities complicates the analysis.

REFERENCES
[1] http://www.nsc.org/library/chemical/formalde.htm
[2] Tanner R.E., 2002, Structure and Chemical Reactivity of Adsorbed Carboxylic Acids on Anatase TiO_2 (001), Surface Science **506**, 251-271.
[3] Wang, Q. and Madix, R.J., 2002, Partial Oxidation of Methanol to Formaldehyde on a Model Supported Monolayer Vanadia Catalysts: Vanadia on TiO_2, Surface Science **496**, 51-63.