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ABSTRACTS AND FULL-PAPERS CD

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Combination of Plasma and Catalyst for Removal of Formaldehyde

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Abstract

Removal of formaldehyde by streamer corona discharge was studied. Efficiency of the removal and by-products formation in the non-thermal plasma of the discharge depending on the initial concentration, gas flow rate, carrier gas and discharge polarity was evaluated. The combined effect of plasma and catalytic pellets of various materials placed in the discharge reactor was investigated via by-products formation. Adsorption abilities of catalyst pellets combined with discharge affected the chemical process and formed by-products. An improvement compared with using plasma or catalyst only was observed for TiO₂, γ -Al₂O₃ and 13X pellets at higher input energies and long operating times.

1. Introduction

Formaldehyde is one of the most common volatile organic compounds (VOC), used mainly for the production of urea-formaldehyde resins, phenol-formaldehyde resins, plastics and intermediates. It is also used in building materials such as plywood, chipboard and panelling, released by gas cookers, found in tobacco smoke and emissions from gasoline powered motor vehicles. Numerous adverse health problems have been ascribed to formaldehyde exposure, such as eye, nose and throat irritation, to more controversial claims including asthma, cancer, chronic respiratory diseases and neuropsychological problems [1].

A number of studies have been directed to formaldehyde removal, most of them related to its removal by adsorbents, e.g. activated carbon, ceramic porous materials and composite oxidized catalyst [2, 3]. Recently a promising method of non-thermal plasma is used to control VOCs. The plasma is highly effective producing active radicals, enhancing molecular dissociation and promoting oxidation. In addition, its combination with the catalyst was found to effect the formation of active radicals, control their distribution and therefore process of treatment [4, 5].

The authors performed the research to investigate the possibilities of formaldehyde reduction from dry air and nitrogen using DC streamer corona discharge. Evaluation of removal efficiency in different conditions was made. In addition, a combination of discharge plasma with catalyst was investigated too. Pellets of various catalytic materials were placed in the discharge reactor and their effect on the decomposition and by-products formation was studied.

2. Experimental Apparatus

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. A layer of 8mm thickness composed of catalytic pellets (average diameter 2-3 mm) was placed on the mesh electrode. The investigated materials were TiO₂, Pt/Al₂O₃, γ -Al₂O₃, zeolites 13X and LZ-Y54. The formaldehyde vapours were produced by bubbling 36% liquid solution of formaldehyde by dry air or nitrogen. The total gas flow rate 0.25, 0.5 or 1.0 l/min was controlled by mass flow meters. DC high voltage power supply was used to generate streamer corona discharge. Evaluation of efficiency of the removal

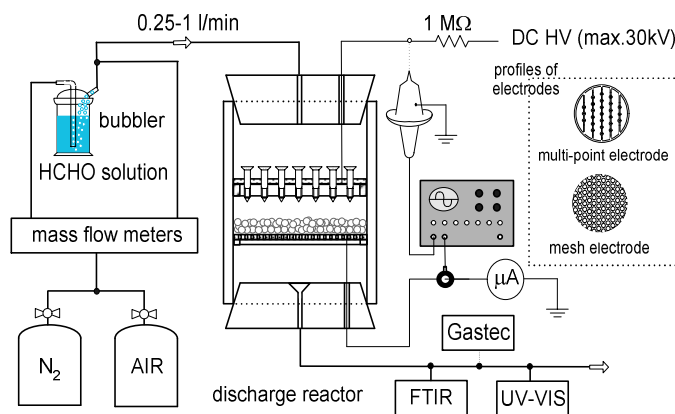


Figure 1: Experimental setup.

process the term of specific input energy (SIE), defined as discharge energy dissipated per unit volume of the gas, was used. The analysis of gas composition was performed using infrared spectrometry (Bio-Rad FTS-3000), ultraviolet spectrometry (Shimadzu UV-1200) and gas analyzing tubes (Gastec).

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

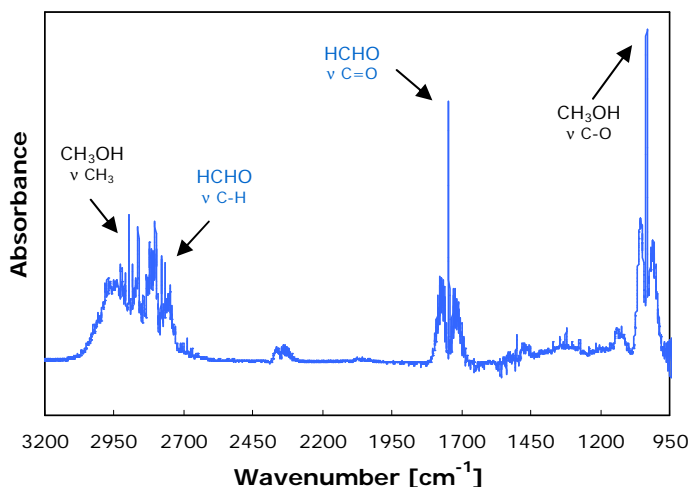


Figure 2: IR spectrum of used formaldehyde vapours.

3.1 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 ($\text{HCHO} + h\nu \rightarrow \text{HO}_2 + \text{CO}$ or $\text{HCHO} + h\nu \rightarrow \text{CO} + \text{H}_2$) by light produced by streamer discharge. In dry air, where oxygen is present, CO can also be formed by reaction ($\text{HCHO} + h\nu \rightarrow \text{H} + \text{HCO}$), followed by ($\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$). Oxygen in the gas mixtures also supports formaldehyde oxidation to formic acid by oxygen radicals, produced through dissociation of molecular ozone by the discharge ($\text{HCHO} + \text{O} \rightarrow \text{HCO} + \text{OH} \rightarrow \text{HCOOH}$). The reaction with ozone ($\text{HCHO} + \text{O}_3 \rightarrow \text{HCOOH} + \text{O}_2$) appeared not to be much effective. Oxidation of formaldehyde mixed with the gas containing high concentration of ozone (up to 1000 ppm) was negligible. Carbon oxide formed is expected to be further oxidized in carbon dioxide, either by ozone but rather OH radicals ($\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$, $\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$). Due to the existing oxidation process the removal is slightly better in dry air mixtures. The process of formaldehyde removal leads also to formation of many other minor products (e.g. CH_3O , CH_3OCO and CH_4).

3.2 Removal by Plasma

Removal efficiency of formaldehyde depended on its *initial concentration*. For smaller initial concentrations, higher removal efficiency was achieved. An increase of initial concentration of formaldehyde resulted in the increased formation of CO and HCOOH. Increasing SIE resulted in decrease of relative production of HCOOH and increase of relative production of CO. As follows from the carbon balance, part of CO is also produced from methanol contained in the formaldehyde solution. Increasing the *gas flow rate* from 0.25 to 1.0 l/min at the constant SIE caused more formaldehyde was removed with relatively smaller production of HCOOH and CO. As follows also from carbon balance, it can be explained by smaller decomposition of methanol at higher gas flow and better utilization of energy for HCHO removal. The effect of *discharge polarity* was examined too. Achieving the same production of oxygen radicals/ozone in both polarities (although at different SIE) resulted in approximately the same amount of formaldehyde removed.

Finally the removal efficiency of formaldehyde depends also on the *carrier gas*. At the same SIE, the removal is better in dry air mixtures, rather than nitrogen. It is because of existing oxidation processes driven by oxygen radicals. The reaction of formaldehyde with oxygen radicals can either lead to formation of HCOOH or production of CO. Generally, the production of CO is higher in dry air, while formation of formic acid was found negligible in nitrogen mixtures. Removal of formaldehyde in nitrogen mixtures is less effective, however, compared with dry air it produces less CO_2 , NO_2 and N_2O .

3.3 Removal by Plasma and Catalyst

The presence of catalyst pellets in the discharge volume has been investigated for effect on removal of formaldehyde and formed by-products. A layer of catalyst pellets with the thickness of 8 mm was placed

onto mesh electrode. Catalysts were expected to affect the formaldehyde decomposition, either due to their activation by discharge (TiO_2), and utilizing their oxidative properties ($\text{Pt}/\text{Al}_2\text{O}_3$) both resulting in improvement of oxidative removal of small amounts of VOCs and/or to their adsorption abilities (especially zeolites).

Effects of Catalyst

The effect of catalytic material without discharge was examined from differential spectra of gas composition at inlet and outlet of reactor. The presence of the catalytic material in the discharge reactor caused concentration of formaldehyde at the outlet of the reactor decreased, due to adsorption to the surface of pellets or oxidation properties. 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 almost reached the level of input concentration (e.g. TiO_2) or saturated at the value down below the inlet concentration, e.g. $\text{Pt}/\text{Al}_2\text{O}_3$ or zeolites (fig.3). Comparing the absorption spectra of the input and output gas composition, generally observed effect was specific removal of formaldehyde and methanol, without formation of by-products. Formation of CO , CO_2 and HCOOH was not observed. It can be explained by adsorption properties of the used pellets.

The effect of adsorption without by-products formation was the most evident in the cases of $\gamma\text{-Al}_2\text{O}_3$ and LZ-Y54. Using 13X, also the effective removal of water vapours was observed. Adsorption effect of TiO_2 pellets after was minimal among the used catalyst. The best result for formaldehyde removal was obtained using $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, which can be explained by both adsorption and effective oxidative removal of formaldehyde by catalyst. Different to all other catalysts, the removal here was accompanied by formation of CO_2 (2360 cm^{-1}) and CH_3OCO (1755 cm^{-1}).

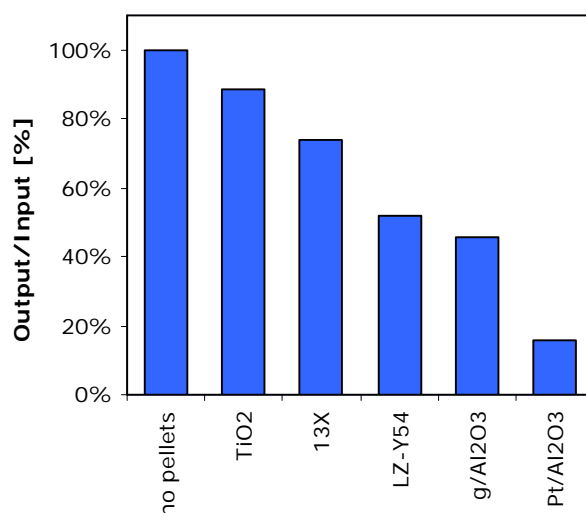


Figure 3: Formaldehyde removal by pellets without discharge (230 ppm in air; after 12-14 hours).

Effects of Discharge and Catalyst

The layer of catalyst pellets between electrodes resulted in smaller onset and operating voltage for a given current. The streamers generated by discharge with pellets had faster rise time and their distribution appeared to be more uniform. The discharge was more stable with minimum of random spark breakdowns (fig. 4).

Formaldehyde treatment using discharge with catalyst pellets and its development in time and depended on SIE in the case of TiO_2 pellets is reported here as an example (fig. 5). Concentration of formaldehyde was 200 ppm. An application of the discharge resulted in sudden increase of formaldehyde concentration (exceeding the initial value). Within 240 minutes during which SIE of the discharge was kept almost

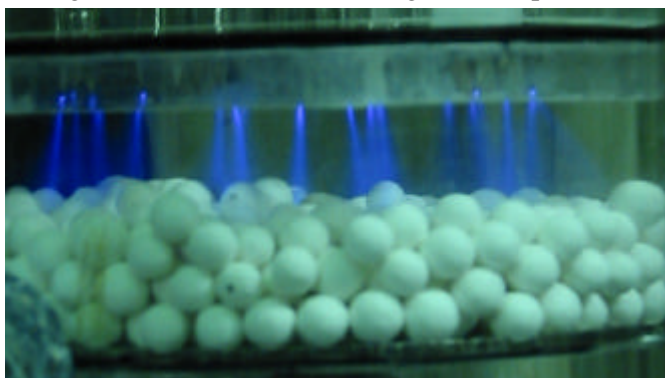


Figure 4: Streamer corona discharge with TiO_2 catalyst placed on the grounded electrode.

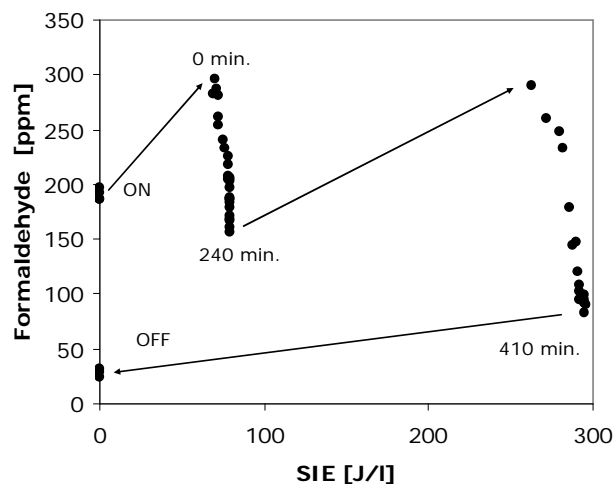


Figure 5: Formaldehyde decomposition using TiO_2 pellets in the discharge volume (200 ppm in air).

constant (approx. 75 J/l) the concentration decreased below the input concentration. Increasing SIE further (265-294 J/l) and waiting for additional 170 minutes, the amount of formaldehyde removed increased to 60% (294 J/l) slowly saturating in time. 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 result from *desorption* of formaldehyde molecules adsorbed before the discharge. It is suggested that desorption from the surface occurs during the contact of the streamers with the surface of pellets, which increase the local temperature. In a similar way a possibility of discharge formation between catalyst pellets must be considered as another source of formaldehyde increase. Assuming TiO₂ catalyst, the concentration of formaldehyde may also increase due to its formation from adsorbed molecules of methanol CH₃OH → CH₃O(ad) → HCHO(g) + H(ad) at higher temperatures [6], eventually formic acid HCOOH(ad) → HCHO(g) + ½O₂ and 2HCOOH(ad) → HCHO(g) + CO₂ + H₂O [7]. The effect of desorption is the most evident after the discharge application or during sudden increase of the discharge power. In such moment desorption effect prevails the removal caused by discharge for a limited period giving a negative result of the treatment. The negative result is however recovered during long operation times and using higher SIE and is also dependent on the used catalyst material.

Comparing the results of formaldehyde removal using *different catalysts*, the relative improvement of removal efficiency was observed especially at higher SIE (> 200 J/l). The effect of treatment time was important as the concentration of formaldehyde decreased slowly and at the constant SIE more than three hours were needed for data saturation. Tendency similar to that of TiO₂ was observed in the cases of 13X, LZ-Y54 and γ-Al₂O₃. Small SIE (less than 100 J/l) gave negative result of formaldehyde removal. However increasing SIE to 300 J/l the treatment efficiency was improved, while achieved efficiency was better than using either catalyst or plasma alone (e.g. TiO₂, 13X, γ-Al₂O₃). The case of Pt/Al₂O₃ appeared to be a little different compared with the other catalyst. Although similar to other catalyst, the discharge caused concentration of formaldehyde at the reactor output increased, however further increase of SIE had negative impact on the removal efficiency. Using discharge and catalyst affects also the type and amount of by-products formed both without and with discharge (fig. 6).

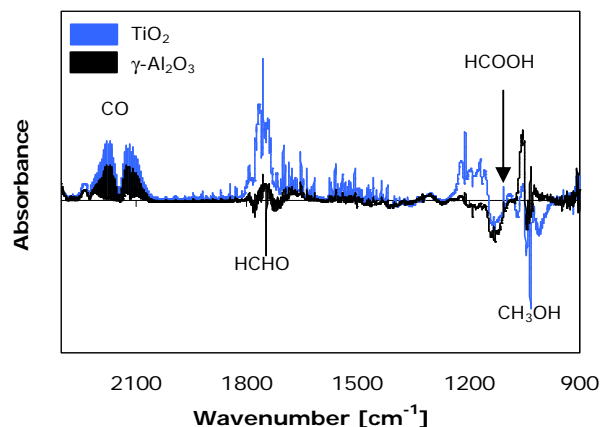


Figure 6: Part of differential spectra for discharge with TiO₂ and γ-Al₂O₃ catalyst (250 ppm HCHO, 250 J/l).

Conclusions

The possibility of formaldehyde removal by streamer corona from the dry air and nitrogen was investigated. For a given SIE, removal efficiency increased when initial concentration of formaldehyde and decreased with the gas flow rate. Removal was more effective in dry air mixtures, due to the existing oxidation process. A combination of plasma and catalyst was investigated and improvement was observed when TiO₂, γ-Al₂O₃ and 13X pellets were used at higher SIE. Presence of catalyst affected also formation of by-products

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