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High-molecular products analysis of VOC destruction in atmospheric pressure discharge

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Abstract. We investigate the issue of applicability of the solid phase microextraction (SPME) in the analysis of volatile organic compounds (VOCs) destruction products in the gliding arc discharge. Our research is focused on the measurements with the simple one stage gliding arc reactor, applied voltage was varied in the range of 3.5 – 4 kV. As a carrier gas, the dry air and its mixtures with nitrogen and oxygen, enriched by toluene, with flow rate of 1000–3500 ml/min was used. Total decomposition of toluene of 97 % was achieved at the oxygen content in carrier gas of 60 %. For measurements with air as a carrier gas, the highest efficiency was 95 %. We also tested the SPME technique suitability for the quantitative analysis of exhausts gases and if this technique can be used efficiently in the field to extract by-products. Carbowax/divinylbenzene and Carboxen/polydimethylsiloxane/divinylbenzene fibres were chosen for sampling. Tens of various high-molecular substances were observed, especially a large number of oxygenous compounds and further several nitrogenous and CxHy compounds. The concentrations of various generated compounds strongly depend on the oxygen content in gas mixture composition. The results showed that the fiber coated by Carbowax/divinylbenzene can extract more products independently on the used VOC compound. The Carboxen/polydimethylsiloxane/divinylbenzene fiber is useful for the analysis of oxygenous compounds and its use will be recommended especially when the destruction is done in the oxygen rich atmosphere. With the higher ratio of oxygen in the carrier gas a distinctive decline of CxHy compounds amount have been observed. We also tried to describe the significant production of some compounds like benzyl alcohol, benzeneacetaldehyde, even in oxygen content is proximate 0 %. Experimental data demonstrated that it is necessary to use several SPME fibres for full-scale high-molecular products analysis.

1. Introduction

VOCs (volatile organic compounds) are organic chemical compounds that have high enough vapour pressures under normal conditions to significantly vaporize and enter the atmosphere. They are sometimes accidentally released from the exhaust of industrial processes into the environment contribute strongly to air pollution causing photochemical smog or destruction of the ozone layer as well as they can become soil and groundwater contaminant. In recent years, insist on the quality of indoor environment as well. Common artificial sources of VOCs include paint thinners, wood preservatives or cleaning solvents. Regarding the medical risks, it is known that many VOCs are toxic,
several of them are known as human carcinogens [1, 2]. Conventional techniques for the abatement of VOCs, such as thermal and catalytic oxidation are widely spread techniques. They are known for their ability of total destruction but they suffer from low energy efficiency given the high operating temperatures. Technologies based on non-thermal plasmas could offer an alternative and they are capable of removal of various pollutants [3]. Moreover, undesirable toxic by-products can be formed.

Gliding arc discharge (GlidArc) is an interesting possibility to generate a non-thermal plasma discharge at the atmospheric pressure [4, 5]. Toluene is used for experiments as a model compound. By-products are sampled by SPME and analyzed by gas chromatograph linked to mass spectrometer. Our experiments were focused on the analysis of the high-molecular discharge products and total conversion measurements. We tested the SPME (solid phase microextraction) technique suitability for the discharge exhaust gas analysis and if this technique can be used efficiently in the field to extract VOCs by-products.

2. Experiment

2.1. Plasma source
The GlidArc is a well-known kind of the plasma discharge. Our plasma reactor consists of a single pair of diverging knife-shaped copper electrodes (thickness 1 mm, size 60 mm x 40 mm each), whose minimal distance is 0.6 mm. Electrodes are positioned in the fast gas flow. The applied DC voltage during our experiments was from 3.5 kV up to 4.5 kV with the discharge current of 35 mA. Gliding arc discharge was created in various gas mixtures of nitrogen, oxygen and argon at the atmospheric pressure. Just before entering the reactor, carrier gas was enriched by toluene, which was chosen as the model VOC. The gas mixture flow rate was 2800ml/min. The details of the experimental setup are on the figure 1.

![Figure 1](image)

Figure 1. Schematic experimental setup of apparatus as configured for measurements and collection of specimens.

2.2. Solid Phase Microextraction
Samples were taken with SPME (Solid Phase Microextraction) fiber, presentive CW/DVB (Carbowax/divinylbenzene) recommended for alcohols and polar comp and second CAR/PDMS/DVB (Carboxen/polydimethylsiloxane/divinylbenzene) used for gases and other low molecular compound sampling. SPME is a relatively new and attractive alternative sampling method. This technique is very useful for volatile and semi volatile compounds because it is rapid and simple with no need for organic...
solvent. The method, with the due calibration, can allow also the quantitative determinations of different compounds. SPME has gained a wide spread acceptance as the technique of preference for many applications including flavours and fragrances, forensics and toxicology, environmental and biological matrices. As well, this technique is powerful for trace analysis of organic pollutants in the environment and shows some interesting performances for VOCs sampling in air [6, 7]. For quantitative analysis, it is very important to explore the dependence of the analyte mass in the fiber as a function of the extraction time.

The GC/MS separation was performed in a CP-SELECT 624 CB fused silica capillary column. For the detection and identification of reaction products an ion trap mass spectrometer (Saturn 2100, Varian, Walnut Creek, CA, USA) was used.

3. Results

3.1. High-molecular products analysis
The areas of total absorbed high-molecular products of the toluene destruction in the nitrogen – oxygen gas mixture (21% O\textsubscript{2}) are given in the figure 2. Total quantity of absorbed compounds is approximately twice time higher if Carboxen/polydimethylsiloxane/divinylbenzene fiber is used for extraction, but these experiments also showed that Carbowax/divinylbenzene is better for full-scale high-molecular products analysis.

![Figure 2](image)

**Figure 2.** Carrier gas nitrogen, total gas flow 2800 ml/min, applied voltage 4 kV, current 35 mA, sampling time 2 min.

We observed tens of various compounds, especially a large number of oxygenous compounds and further several nitrogenous and C\textsubscript{x}H\textsubscript{y} compounds. The main products of this treatment are benzaldehyde, phenol and benzyl alcohol. Increasing content of oxygen gives rise to the formation of oxidation products (figure 3), the most abundant being benzaldehyde, obtained by many process, in all probability by oxidation of toluene, phenol - can be formed by the partial oxidation of benzene, benzyl alcohol or benzeneacetaldehyde.
Figure 3. Dependence of several oxygenous compounds quantity on the oxygen concentration, total gas flow 2800 ml/min, applied voltage 4 kV, current 35 mA, sampling time 2 min.

Apparently, almost 69% of total absorbed amount on the fiber is still unexpanded toluene. The main nitrogenous products (figure 4) were nitropropanetriol and 1-nitro-2-methylpropane. We also remarked some significant C\textsubscript{x}H\textsubscript{y} products, see figure 5, like ethylbenzene, which should be produced by combining the benzene and ethylene, styrene (commonly produced by catalytic dehydrogenation of the ethylbenzene) and bibenzyl, obviously the toluene dehydrocoupled product. For better understanding of whole process, some other analysis techniques like optical emission spectroscopy will be necessary to use. Then we can come to conclusion about active particles which are important for destruction of VOC in GlidArc.

Figure 4. Dependence of nitrogenous compounds quantity on the oxygen concentration. total gas flow 2800 ml/min, applied voltage 4 kV, current 35 mA, sampling time 2 min.
3.2. Conversion

Figure 6 presents the results of the final organic carbon conversion and toluene conversion, sampled by CW/DVB fiber. These results showed that the highest removal efficiency for toluene is obtained for the experiments with 61% of oxygen in carrier gas. With raising concentration of O\textsubscript{2} in gas flow, toluene conversion is increasing up to 97%. On the other side, if we assume that almost all organic by-products are extracted by the fiber, the highest organic carbon conversion is 87%, it is achieved with the 21% of O\textsubscript{2} in carrier gas.

![Figure 6. Conversion as the function of oxygen concentration, sampling time 5 min.](image)

4. Conclusion

The presented work gives the results about applicability of the solid phase microextraction in the analysis of volatile organic compounds destruction in the non-thermal plasma. The concentrations of various generated compounds strongly depend on the gas mixture composition. The results showed that CW/DVB fiber can extract more products independently on the used VOC compound. With the increasing ratio of oxygen in the carrier gas a slight decline of C\textsubscript{x}H\textsubscript{y} compounds amount, distinctive increasing of oxygenous compounds amount and exiguous growth of nitrogenous compounds have been observed. Future experiments will be concerned with the low-molecular products analyses.
Acknowledgments
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