

VOC DECOMPOSITION IN SURFACE DISCHARGE

FRANTIŠEK KRČMA, JANA VYHNALÍKOVÁ,
LUCIE POLÁCHOVÁ, HANA GROSSMANNOVÁ
and ZDENKA STARÁ

*Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, Brno 612 00, Czech Republic
krcma@fch.vutbr.cz*

Introduction

VOCs (volatile organic compounds) are organic chemical compounds that have vapor pressures under normal conditions high enough to significantly evaporate and enter the atmosphere. They are sometimes accidentally released from the industrial processes into the environment, where they can damage soil and groundwater. Vapors of VOCs escaping into the air contribute significantly to the air pollution (e.g. they cause photochemical smog and also contribute to the global warming). In recent years, their influence on the quality of indoor environment has started to be a serious task, too. 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 carcinogens¹.

Conventional techniques for the abatement of VOCs, such as thermal and catalytic oxidation, are able to completely decompose the VOCs, but they suffer from the low energy efficiency given by the high operating temperature. The biological degradability of VOCs is also very problematic due to low concentration of VOCs in the gas phase. This degradation way is also impossible for many VOCs based on aromatic ring that could not be biologically destroyed. Technologies based on non-thermal plasmas could offer an alternative and they are capable to remove various pollutants in the gas phase². The plasma decomposition process of VOC is rather complex and the hydrocarbons are attacked in several ways. In the plasma reactor, the hydrocarbons are partly transformed into oxygenated compounds and into CO and CO₂. Unfortunately, undesirable toxic by-products can be formed.

Various non-thermal atmospheric plasma sources have been studied with respect to VOC destruction^{2–4}. This study presents the first results obtained using recently developed surface discharge that is nowadays widely used mainly in the surface treatment processes⁵.

Experimental set up

The schematic draw of the experimental device is shown in Fig. 1. The discharge reactor consisted of a surface discharge electrode 10×10 cm² connected to the HF power supply. The Al₂O₃ plate in the distance of 2 mm above the electrode was installed. The reactor side walls were made from Teflon with one fused silica window oriented in parallel to the gas flow through the reactor. The gas inlet into the reactor was realized by the system of equidistant holes (distance of

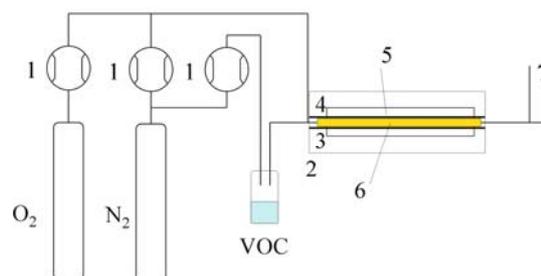


Fig. 1. Scheme of the experimental set up; 1 – mass flow controllers; 2 – Teflon discharge reactor; 3 – surface discharge electrode; 4 – Al₂O₃ plate; 5 – Quartz window; 6 – discharge; 7 – sampling point for the chemical analyzes

5 mm, i.d. 1 mm); the outlet was possible through the open electrode gap on the opposite side. This system guaranteed nearly homogeneous flow of the reacting gas mixture through the discharge.

The synthetic dry air was used as the carrier gas and it was enriched by the VOC (hexane, cyclohexane or xylen) just in front of the reactor. VOC concentration in the reactor was constant at about 1 %.

The exhaust gas analyses were carried out by three different ways. The simple gas analyzer Testo 350 XL was used for the detection of low molecular weight discharge products as CO, NO₂, NO, H₂, etc. The analyses of high molecular weight products were made by *ex-situ* GC-MS. Samples of exhaust gas for these analyses were taken by active carbon sorption tubes or by solid phase micro extraction (SPME) technique using Divinylbenzene/CarboxenTM/polydimethylsiloxane (DVB/CARTM/PDMS) fibers⁶. The GC-MS analysis was done using spectrometer GC 8000 with the quadrupole mass spectrometer MS TRIO 1000 (both made by Fision Instruments Ltd.). Quartz capillary (30 m long) with polydimethylsiloxane stationary phase (0.25 μm) was used for the separation.

The optical emission spectroscopy using Jobin Yvon TRIAX 550 spectrometer was applied to characterize the surface discharge plasma. The molecular bands of nitrogen (1st and 2nd positive and 1st negative systems) were observed with high intensities, some bands of CO were recognized, too. The rotational temperature of about (850 ± 100) K was calculated from the rotational structure of nitrogen second positive 0–2 band. Vibrational temperature of about (1900 ± 150) K was calculated using nitrogen second positive –2 sequence bands. Both rotational and vibrational temperatures were more or less independent on the VOC compound and also the dependence on discharge power was negligible. The discharge reactor construction allowed also partial space resolution of spectroscopic observations. However, no significant changes in the plasma parameters were determined along the whole reactor.

Results and discussion

The results of the laboratory experiments are presented in this part. The implicit concentrations of low molecular inorganic products as CO, NO₂, NO or H₂ and relative con-

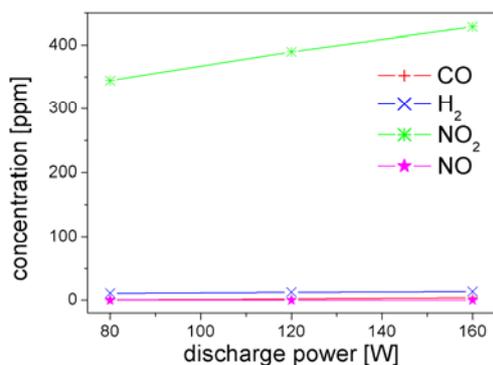


Fig. 2. Concentrations of low molecular products generated by surface discharge in synthetic air without VOC

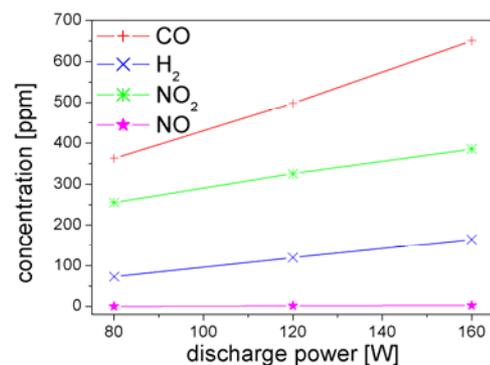


Fig. 4. Concentrations of low molecular products generated by surface discharge in synthetic air with cyclohexane

concentrations of combustion high molecular products of hexane, cyclohexane or xylene are displayed. The resulting concentrations depended on energy input and gas composition as it is shown on following figures and tables. Only nitrogen dioxide was generated in the discharge without VOC and its concentration was directly proportional to the discharge power. Fig. 3–5 show the results obtained during the selected VOCs destruction. The concentrations of CO and H₂ resulting from combustion were again directly proportional to the applied discharge power and their concentrations depended on the VOC. NO₂ was generated in the significant amount in all cases; in contrary, no measurable value of NO species was observed.

According to the results and the mechanism of VOC oxidation studied in the literature⁷, benzene rings of cyclohexane and xylene in the collisions with active species (mainly O and OH radicals) are firstly oxidized to dihydroxybenzenes and subsequently to quinones. Both continue to yield ring-cleavage products (i.e. aldehydes and carboxylic acid groups). Finally, carboxylic acids such as formic and acetic acids are mineralized to CO and CO₂. Though mixture of nitrogen and

oxygen are used as the carrier gas, no nitrogen compounds were detected in the treated gas samples.

Electrons produced in surface discharge in atmospheric air initiate gas phase reactions to produce remarkable quantity of ozone and nitrogen oxides. As it can be seen from Fig. 2, production of significant amount of NO₂ is higher when input power is increased. Destruction and resulting very low concentration of NO is primarily due to the oxidative properties of ozone molecules. The influence of an admixture of a VOC on the production of NO₂ was studied as well. Fig. 3–5 show the behavior of NO₂ production for three different admixtures. Xylene admixture leads to an increase in the NO₂ concentration, on the other hand cyclohexane and hexane admixtures lead to slight decrease with the increasing discharge power. Therefore we can't conclude the existence of negative or positive effect of the VOC admixture to the NO₂ formation. The large occurrence of CO is detected during the plasma treatment of VOC as well. Increasing energy input is leading to higher efficiency of VOC decomposition resulting in higher concentration of CO, which is up to 700 ppm for treated amount of VOC (initial concentration of about 1 %).

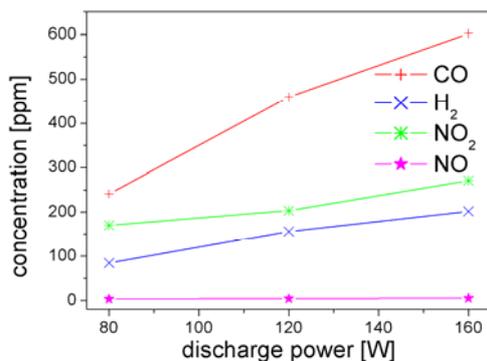


Fig. 3. Concentrations of low molecular products generated by surface discharge in synthetic air with hexane

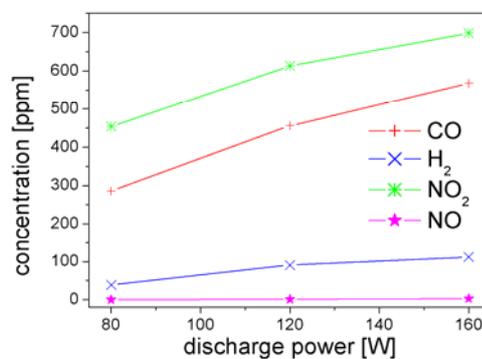


Fig. 5. Concentrations of low molecular products generated by surface discharge in synthetic air with xylene

Table I

Chromatographic peak areas of selected products identified in the exhaust gas during the decomposition of hexane at two different discharge powers and ratio of peak areas A_{160}/A_{120}

Specie	120 W	160 W	F
Nox	9110000	8480000	0.93
Hexane	3550000	4430000	1.25
2,5-dihydro-2,5-dimethyl-furanone	1930000	1890000	0.98
2-hexene	1180000	253000	0.21
2-hexanol	726000	785000	1.08
2-pentanone	710000	638000	0.90
2-hexanone	668000	692000	1.04
3-methyl-2,4-pentadione	668000	663000	0.99
2-hexene-1-ol	456000	434000	0.95

Table II

Chromatographic peak areas of selected products identified in the exhaust gas during the decomposition of cyclohexane at two different discharge powers and ratio of peak areas A_{160}/A_{80}

Specie	80 W	160 W	F
Nox	9750000	2800000	0.29
2-hydroxy-cyclohexanone	2640000	238000	0.09
3-hydroxy-cyclohexanone	607000	663000	1.09
1,5-pentandiol	470000	62000	0.13
2-cyclohexene-1-one	505000	264000	0.52
1,6-hexandiol	323000	113000	0.35
1,2-cyclohexandiol	182000	199000	1.09
cyclopentandiol	56000	56000	1.01

Table III

Chromatographic peak areas of selected products identified in the exhaust gas during the decomposition of xylene at two different discharge powers and ratio of peak areas A_{160}/A_{80}

Specie	80 W	160 W	F
NOx	11900000	8600000	0.73
1,3-dimethylbenzene	21300000	7850000	0.37
2-hexanol	9660000	559000	0.06
ethylbenzene	6290000	2720000	0.43
4-methylbenzaldehyde	996000	627000	0.63
benzaldehyde	694000	465000	0.67
methylbenzene	658000	340000	0.52
cyclohexanol	449000	317000	0.71

Tables I–III provide a summary of the most significant high molecular weight combustion products analyzed by GC/MS system. Many different especially oxygenated compounds

originated from the added VOC were detected. When oxygen reacts with nitrogen it is possible to form different nitrogen oxides: N_2O , NO , N_2O_3 , NO_2 , N_2O_4 , N_2O_5 . The summation of all of these oxides is marked as NO_x in the tables. Third columns show the correlation factor F between concentrations of products at the highest and the lowest value of input power. It can be clearly seen that this factor is mostly lower than 1. This means that higher input energy would lead to the shift in the product distribution towards low molecular inorganic compounds.

Influence of oxygen content

The oxidation properties of plasma are related to the occurrence of highly reactive species. Of course, generation of these species is highly dependent on the gas composition. In order to investigate the effect of different synthetic gases on the decomposition of VOC, oxygen and nitrogen can be used separately as a carrier gases. Some experiments were carried out when oxygen was added in the gas stream up to 30%. The examples of chromatograms obtained at these conditions are shown in Figs. 6–9. The results presented in Tables IV–VI show that the oxygen addition led to a slight increase of oxygen compounds generation, only.

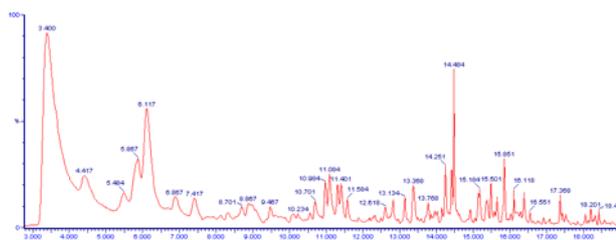


Fig. 6. Chromatogram of exhaust gas sampled by SPME technique during hexane decomposition in nitrogen with 30% of oxygen at discharge power of 160 W

Table IV

Comparison of chromatographic peak areas of selected compounds identified in the exhaust gas during the hexane decomposition at two different oxygen concentrations at discharge power of 160 W

Peak time [s]	Specie	10 % O_2	30 % O_2
3.3	NOx	10200000	16000000
4.3	2-hexanol	2350000	2880000
6.867	2-hexene	638000	783000
8.867	2,5-dihydro-2,5-dimethyl-furan	610000	746000
9.467	4-methyl-3-pentanal	446000	632000
11.084	2-hexanone	490000	588000
13.368	1,3-dimethylbenzene	202000	455000
14.484	2,5-hexanedione	1310000	1220000
16.385	3-methylpentanal	266000	192000
17.368	5-ethylidihydro-2(3H)furanone	212000	173000

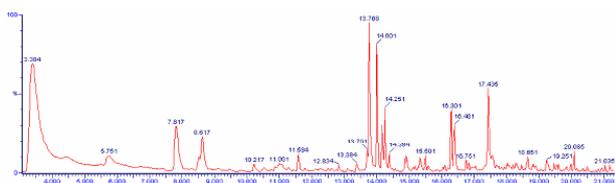


Fig. 7. Chromatogram of exhaust gas sampled by SPME technique during cyclohexane decomposition in nitrogen with 30 % of oxygen at discharge power of 160 W

Conclusion

This article gave some results relevant to the surface discharge environmental application. The objects of research were hexane, cyclohexane and xylene decomposition at the atmospheric pressure. The dependences of low molecular products concentration versus discharge power were studied. GC/MS analyses allowed the better understanding of high molecular products formation.

The role of oxygen content in the carrier gas for the VOC removal process was also investigated. The presented result indicated that the most of carbon in the decomposition of VOC was converted to carbon oxides rather than to hydrocarbons. The main problem of VOC removal in a plasma system is the by-product formation. Unfortunately, the surface discharge plasma generates high concentrations of carbon monoxide and nitrogen dioxide. This main disadvantage can be successfully (but not completely) solved by the additional application of catalytic system.

Table V

Comparison of chromatographic peak areas of selected compounds identified in the exhaust gas during the cyclohexane decomposition at two different oxygen concentrations at discharge power of 160 W

Peak time [s]	Specie	10 % O ₂	30 % O ₂
3.367	NOx	14600000	15100000
5.734	2-butenal	1430000	996000
6.734	2-hexanol	390000	319000
7.817	cyclohexane	2150000	2030000
8.617	3-methylbutanal	1470000	1340000
13.768	cyclohexanol	2650000	2160000
14.001	2-methyl-cyclopentanol	1950000	1520000
16.301	2-hydroxy-cyclohexanone	838000	728000
17.435	dihydro-4-methyl-2(3H)furanone	1570000	1350000
18.651	3-hydroxy-cyclohexanone	298000	266000
19.668	cyclobutanol	365000	586000

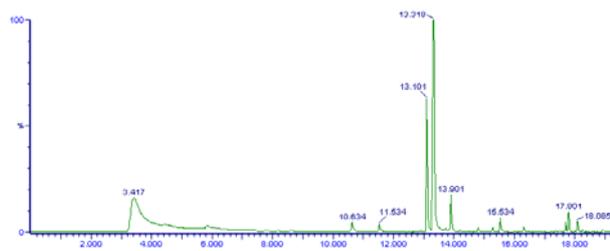


Fig. 8. Chromatogram of exhaust gas sampled by SPME technique during xylene decomposition in nitrogen with 30 % of oxygen at discharge power of 160 W

Table VI

Comparison of chromatographic peak areas of selected compounds identified in the exhaust gas during the xylene decomposition at two different oxygen concentrations at discharge power of 160 W

Peak time [s]	Specie	10 % O ₂	30 % O ₂
3.417	NOx	11300000	13200000
5.851	2-hexanol	2100000	2580000
10.634	methylbenzene	461000	438000
13.101	ethylbenzene	3490000	3410000
13.318	1,3-dimethylbenzene	10500000	10500000
13.901	1,4-dimethylbenzene	954000	1000000
14.801	dihydro-3-methyl-2,5-furandione	180000	186000
15.534	benzaldehyde	433000	393000
17.801	4-methylbenzaldehyde	454000	451000
19.568	ethylbenzaldehyde	37000	68800
19.935	3-fenyl-2-propenal	490000	356000

This work was supported by the Czech Ministry of Education, Youth and Sports, research project MSM 0021630501 and by the Czech Science Foundation, project No. 202/03/H162.

REFERENCES

- Jones S. P.: *Atm. Envir.* 33, 4533 (1999).
- Kim H. H.: *Plasma Proces. Polymers* 2, 91 (2004).
- Mutaf-Yardimci Ö., Savaliev A., Fridman A., Kennedy L. A.: *J. Appl. Phys.* 87, 1632 (2000).
- Fridman A., Gutsol A., Cho Y. I.: *Adv. Heat Transf.* 40, 1 (2007).
- Šimor M., Ráhel' J., Černák M., Imahori Y., Štefečka M., Kando M.: *Surf. Coat. Technol.* 172, 1 (2003).
- Grossmannová H., Cigánek M., Krčma F.: *J. Phys.: Conf. Series* 63, Article No. 012011 (2007).
- Yan J., Du Ch., Li X., Sun X., Ni M., Cen K, Cheron B.: *Plasma Sources Sci. Technol.* 14, 637 (2005).