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## Field-tests at VKG Oil AS oil-shale processing plant in Kohtla-Järve, Estonia

### Introduction

This report of second series of field tests is the continuation of the earlier report concerning first measurement series in VKG Oil AS oil-shale processing plant. Present measurements included variation of the input power and different gas analysis techniques. Most importantly, the use of FTIR spectroscopy allowed in-situ analysis of results and detection of inorganic species like CO, CO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, NO<sub>x</sub> and HNO<sub>3</sub>. Similarly to previous experiments tests were carried out at an absorber in the shale oil storage unit.

### Experimental details

The plasma-unit was a stack type dielectric-barrier discharge reactor designed for the purpose of such field tests (described in previous report). The input power of the reactor was changeable up to the value of approximately 165 W.

The scheme of the experimental setup used in the second set of experiments is shown in the figure 1. Part of the exhaust gas was directed through the plasma reactor. The exhaust gas was sometimes diluted with atmospheric air with the use a valve and a mixing point. A filter was used before the plasma reactor to purify the gas from possible oil-mist. A fan was used after the plasma reactor to force the mixing of exhaust gas with the atmospheric air. 100 mm pipes were used to connect these devices. Two sampling points were used before and after the reactor to measure the velocity of the gas with Testo 445 termo anemometer and obtain the air samples for MS/GC analysis. The gas flow rate was additionally measured by a home-built flow-meter utilizing differential pressure method. The device was calibrated by an commercial flow-meter. The flow rates were usually in the range of 1-10 m<sup>3</sup>/h. The corresponding SIE values were in the range of 50 to 250 J/L.

For the MS/GC analysis, two samples of air were obtained simultaneously for same exhaust gases due to varying working conditions of the site. The analysis allowed quantitatively measure for different aromatic VOC species (benzene, toluene, xylene, ethyl-benzene). Qualitative analysis was carried out for various other VOC-s based on the chromatograms and mass-spectrum. FTIR sampling point was usually in the outlet of the reactor and the reactor was switched ON and OFF to obtain the effect of plasma treatment on the VOC concentration. Various plasma ON times were used to obtain suitable averaging of the results. Preliminary information concerning the VOC concentrations was obtained from the highest peak corresponding to CH<sub>x</sub> vibrations characteristic for most types of VOC-s. Calibration data of FTIR was available for some specimens (O<sub>3</sub>, N<sub>2</sub>O, HNO<sub>3</sub>, CO, C<sub>3</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>8</sub>) and quantitative data could be obtained from FTIR.





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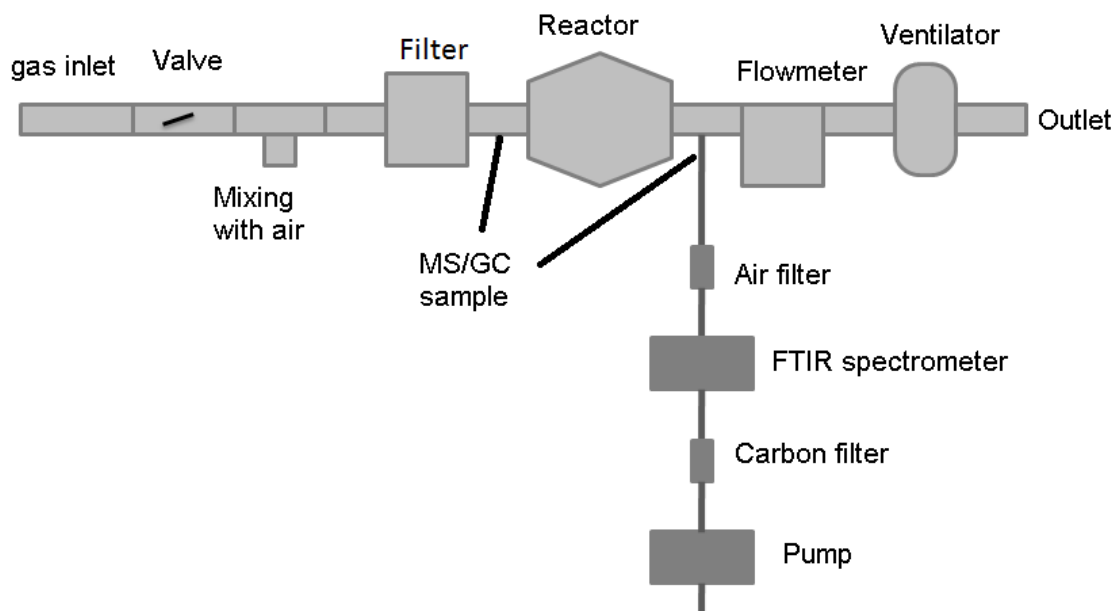


Figure 1. Scheme of the experimental setup and the picture of the setup in action.

## Results

The tests were carried out at the outlet of an absorber which was used for the cleaning of the exhaust of storage tanks. The absorber was not the same as the ones described in the first report. Preliminary analysis with FTIR indicated large variation in the outlet concentrations of VOC-s at various work conditions of the units. Occasionally, there was large increase of the concentration above the saturation limit of FTIR while afterwards the concentration decreased below the detection limit of the apparatus. This large variation made the experiments complicated and large amount of data had to be collected for FTIR analysis.

The air samples for MS/GC analysis were collected before and after the plasma reactor over 5 min time period and is an averaged value. Concentrations of aromatic species obtained by MS/GC at various times and conditions were relatively small and varied considerably. One example of concentrations obtained in the inlet and outlet of the reactor (before and after plasma treatment) is shown in Table 1. At the used conditions (80 J/L), the concentrations of investigated aromatic compounds decreased about 40 % from the initial values. The total aliphatic VOC concentration was not obtained with the MS/GC analysis setup used in current study.



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Table 1. Concentration of various aromatic species in the exhaust gas of absorber before and after the plasma treatment (80 J/L).

VOC	Before mg/m <sup>3</sup>	After mg/m <sup>3</sup>
Benzene	3	1.9
Ethylbenzene	NA	NA
Toluene	1.6	0.9
Xylene	NA	NA

The Gas-Chromatogram for the same conditions as Table 1 is shown in figure 2. The analysis method was somewhat different compared to the first experiments and the resulting chromatogram looks also different.

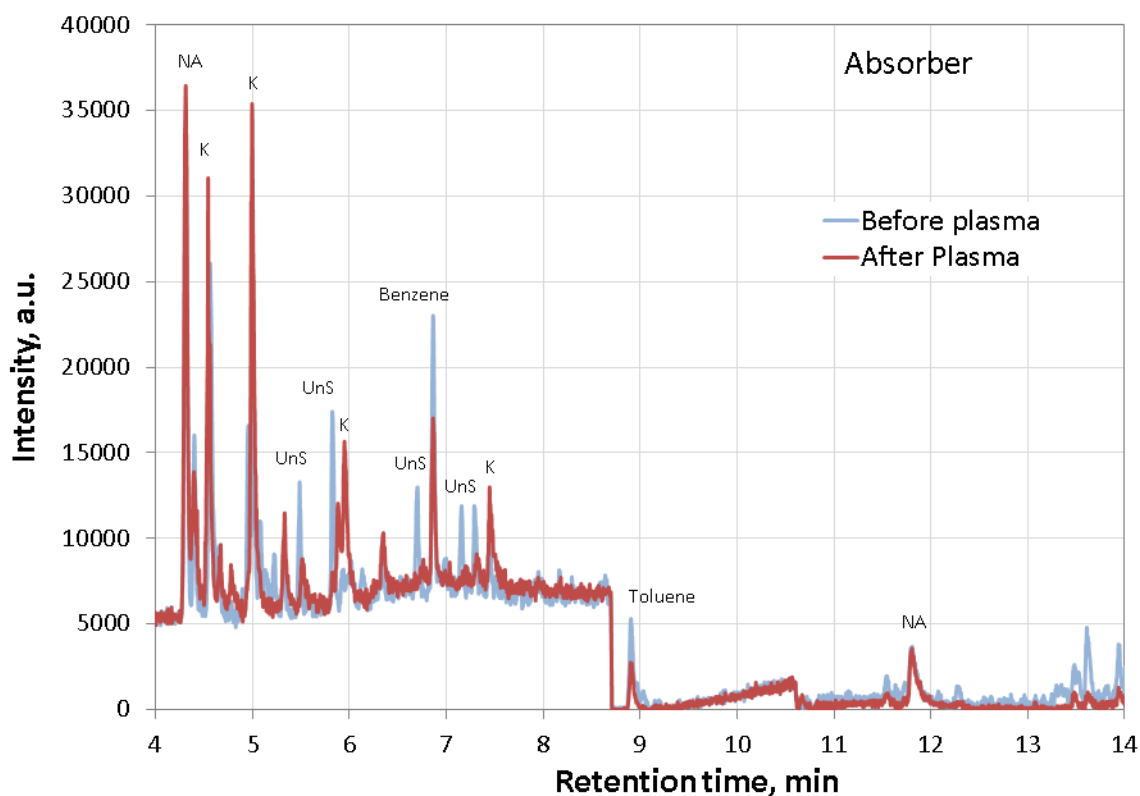


Figure 2. Comparison of GC-MS chromatograms obtained before and after the plasma treatment in the case of absorber. The peaks marked as NA are due to the peculiarities of the GC measurements and always present at same intensities. The peaks marked with UnS denote unsaturated species while peaks marked with K denote ketones and aldehydes.



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In addition to aromatic compounds Benzene and Toluene, there were several peaks corresponding to various unsaturated VOC species (alkenes, dienes), alcohols and possibly saturated VOC-s (not verified). Peaks corresponding to heavier VOC species were also present but were not assignable to specific compounds due to missing parts of mass-spectrums for these species. The plasma treatment resulted in considerable decrease of the peaks corresponding to unsaturated VOC-s and heavy species (more than 50 %) which was similar to the results of first series of experiments. Signal from some VOC species (mostly recognized as dienes) vanished almost completely. Present MS/GC chromatogram additionally featured new peaks after plasma treatment which corresponded to partially oxidized VOC-s: acetaldehyde, acetone, butanal and other ketones. These species are known to be the product of oxidation of unsaturated hydrocarbons [Jarrige 2006, Hill 2008].

The dilution of absorber outlet by ambient air decreased the concentration of VOC-s in the exhaust but general features of the plasma treatment remained similar (Appendix). Unsaturated VOC-s were practically absent after plasma treatment while smaller amount of ketones appeared in the chromatogram compared to exhausts with higher inlet concentrations of VOC-s. The relative decrease of aromatic species was also somewhat smaller. Even larger dilution of the exhaust of absorber decreased the VOC-s to the detection level of MS/GC. There was practically no decrease of aromatic compounds in this case.

The FTIR spectra obtained from the exhaust of absorber (fig. 3.) had characteristic bands between 2800 and 3200  $\text{cm}^{-1}$  which could be assigned to various CH bonds. The bands corresponding to alkanes (saturated VOC) are usually between 2800 and 3000  $\text{cm}^{-1}$  while alkenes (unsaturated VOC) give also bands between 3000 and 3100  $\text{cm}^{-1}$ . Other organic compounds have also bands in this range. Several other bands were also present at lower wavenumbers most notably in the range of 1400 and 1600  $\text{cm}^{-1}$  and below 1000  $\text{cm}^{-1}$ . These are characteristic to alkenes (unsaturated VOC). There was also a series of narrow bands with maxima at 3050  $\text{cm}^{-1}$  which can be attributed to methane.

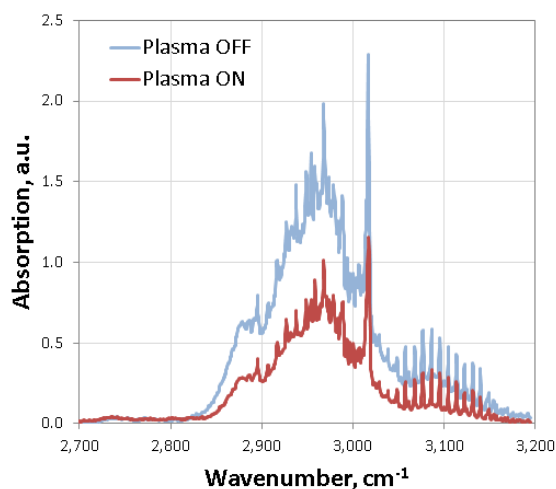


Figure 3. FTIR spectra of exhaust gas from absorber with and without plasma treatment at 180 J/L.





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The plasma treatment decreased considerably the bands around  $3000\text{ cm}^{-1}$ . The intensity of these bands decreases up to 50 % from initial values while the broad band above  $3000\text{ cm}^{-1}$  decreased even more. The narrow bands of methane on the other hand increased during the plasma treatment. There appeared also new bands at  $1270 - 1300$  and  $1700 - 1750\text{ cm}^{-1}$  which are attributable to partially oxidized organic species (formaldehyde, acetone and other ketones) and confirm the results of MS/GC. These species expectedly also give some additional adsorption bands at  $2970\text{ cm}^{-1}$ .

In addition to bands corresponding to organic species, there occurred other new bands after plasma treatment, most notably a band at  $1000-1100\text{ cm}^{-1}$  which corresponds to ozone. The calibration data was available for ozone and according to this data the concentrations of ozone reached 200 ppm. The band corresponding to CO between  $2000$  and  $2200\text{ cm}^{-1}$  also appeared during plasma treatment and the concentrations of CO reached 400 ppm. The FTIR spectra featured also bands corresponding to  $\text{NO}_x$  species. The formation of HCN was not detectable from FTIR spectrum. The concentrations of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  varied too much to reliably detect changes in the values of these species during plasma treatment.

With the assumption that the absorption maximum around  $3000\text{ cm}^{-1}$  is related to the total VOC concentration, the percentage of outlet concentration of VOC-s during the plasma treatment at various inlet concentrations is shown in figure 4. The maximum decrease was about 50 %. The MS/GC data shown in table 1 and figure 2 corresponds to the decrease of about 40 % (blue diamonds). The inlet concentrations corresponding to different points in the graph varied more than 3 times and in the limits of measurement error, the removal percentage was similar. However, the values had large scatter due to variation of inlet concentrations during plasma treatment which made the analysis rather complicated.

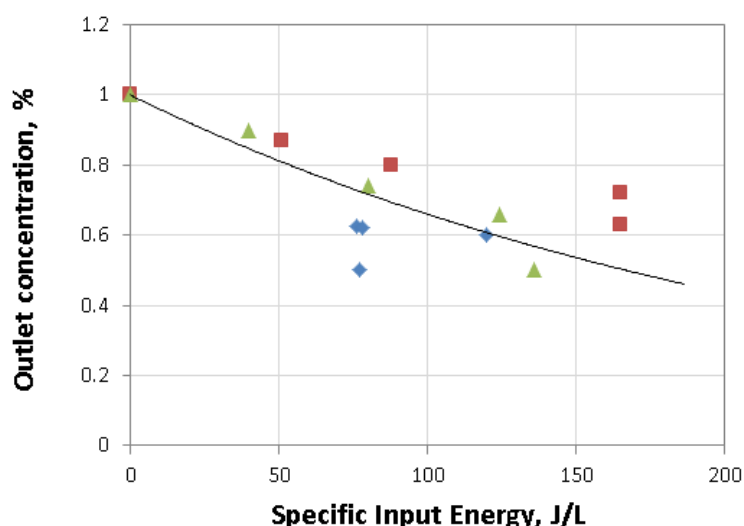


Figure 4. The outlet concentration during plasma treatment as a fraction of the concentration without plasma treatment in the case of exhaust from absorber.



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The decrease of FTIR bands around  $3000\text{ cm}^{-1}$  due to plasma treatment was less pronounced compared to the decrease of most of the peaks in GC-MS. One possible explanation is the relative importance of alkane peaks in the FTIR spectrum. The alkanes as saturated VOC-s [Jarrige 2006] are removed least efficiently and thus the decrease in FTIR could be less pronounced. Most of the peaks in MS/GC correspond probably to dienes, alkenes (olefins) and cyclic (not aromatic) compounds and the decrease of these compounds is more pronounced. The partially oxidized plasma species will also give bands around  $3000\text{ cm}^{-1}$  and this also counts for the relatively strong presence of VOC-s according to FTIR data.

### General remarks

Usually, the plasma was switched on only for few minutes but several measurements were done with longer plasma treatment times. Longer plasma treatment time improved the removal efficiency due to increased temperature of the reactor. Separate measurements in the laboratory demonstrated that the temperature of reactor increased to levels above  $100^{\circ}\text{C}$  (depending on plasma power and gas flow rate) whereas characteristic heating time was more than 30 min. During field tests, we wanted to compare the results obtained at similar conditions and had to use shorter treatment times where heating effect was less important. However, in working conditions where the treatment time is longer, one could expect somewhat improved removal of VOC-s.

At the used concentrations the dilution of exhaust gas is not justified because the removal percentage was the same for diluted and non-diluted gas. This is consistent with the previous results and indicates that the reactions of plasma species and most of the VOC-s do not proceed with sufficient efficiency. The presence of considerable amount of ozone also confirms this conclusion. One possible route for improvement of efficiency could be the use of catalyst which may decompose the ozone and further oxidize partially oxidized VOC-s and CO.

The removal efficiencies of VOC-s in the exhaust of the absorber tested during the present studies were smaller than efficiencies obtained during previous tests with other absorber but it is not possible to clearly state the reasons. One explanation could be larger amount of saturated VOC-s in the exhaust and heavier fraction. In previous studies, when the exhaust had larger fraction of heavy species, the removal efficiency also decreased considerably. The water vapour may also vary in the exhausts of absorber and this may result in different removal efficiencies for the aromatics.

### Suggestions for further experiments

In the case of highly varying concentrations as observed in the case of absorbers, the data would be more reliable when two FTIR spectrometers could be used: one before and other after plasma reactor. This would allow to determine average removal effect.

The water vapour concentration and  $\text{CO}_2$  concentration should be measured by other means than FTIR.

It would be highly valuable to get calibrated MS/GC data for larger set of VOC-s. This probably needs co-work with Institute of Chemistry in University of Tartu. FTIR and other supplementary analysis methods are still necessary for the measurement of  $\text{CO}_2$ , ozone etc.





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In the case of exhausts with high VOC concentrations, the high-power and high temperature devices (radio-frequency or microwave torches) could be more efficient but the power efficiency of these devices has to be confirmed.

## Conclusions and outlook

The field tests reported in this paper specified the energy input effect of the plasma technology for the exhaust of an oil-shale processing unit. The removal efficiency of VOC-s increased up to 50 % at high plasma input energy values of 250 J/L. Similarly to the tests carried out earlier, the unsaturated species were removed more efficiently compared to saturated and aromatic compounds. The direct comparison of the results was not possible due to different MS/GC analysis methods used in the studies.

The exact concentrations of partially oxidized VOC-s formed during the plasma treatment could not be obtained due to the presence of a large number of different species and the lack of calibration of the detection method for all these compounds. In addition to partially oxidized VOC species, there formed considerable amount of CO and ozone which could be further removed by the use of an ozone decomposition catalyst. The use of catalyst would probably also improve the oxidation of VOCs.

## References

- J. Jarrige and P. Vervisch 2006 "Decomposition of three volatile organic compounds by nanosecond pulsed corona discharge: Study of by-product formation and influence of high voltage pulse parameters", J. Appl. Phys. 99, 113303.
- S. L. Hill, H.-H. Kim, S. Futamura and J. C. Whitehead 2008 "The Destruction of Atmospheric Pressure Propane and Propene Using a Surface Discharge Plasma Reactor", J. Phys. Chem. A 112 3953-3958.





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## Appendix

