Investigation of Real Car Exhaust in the EUPHORE Chamber

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Introduction

The use of reformulated and alternative fuels has been increasingly tested during recent years in order to improve air quality by lowering the ozone formation of air pollution in urban areas. However, most of these investigations were carried out rather indirectly using e.g. artificial exhaust gas mixtures. The investigations, which are presented here were focused on gasoline and diesel fuel formulation and its influence on atmospheric processes. The main objective was the investigation of real car exhaust in the European Photoreactor EUPHORE in order to improve the knowledge on atmospheric NO_y chemistry, ozone formation and the emission and reactivity of particulates.

Experimental

Gasoline exhaust gases which were sampled from an engine test bed at the Polytechnical University of Valencia were transported to the EUPHORE chamber in 6 tedlar bags, 250 *l* each, kept in isothermal containers to stabilise the exhaust gas temperature and to prevent irradiation by sunlight, see Figure 1.

Exhaust samples of 5 different fuel blends were used for simulation experiments (see Table 1). The total hydrocarbon concentration of these samples varied between 40 and 90 ppmC. Due to technical reasons during exhaust sampling the total hydrocarbon concentration of the other exhaust samples was too low to perform simulation experiments. The experiments were performed with a total hydrocarbon concentration inside the reaction chamber of about 400 ppbC.

Fuel Type	Fuel 1	Fuel 4	Fuel 7	Fuel 8 reference	Fuel 9 reformulated
aromatics, % v/v	14	33	2	32	18
paraffins, %v/v	86	54	98	53	54
olefins, %v/v	<1	13	<1	15	22
MTBE, %v/v	0	0	0	5	5

Table 1: Characteristics of the different gasoline fuel blends.

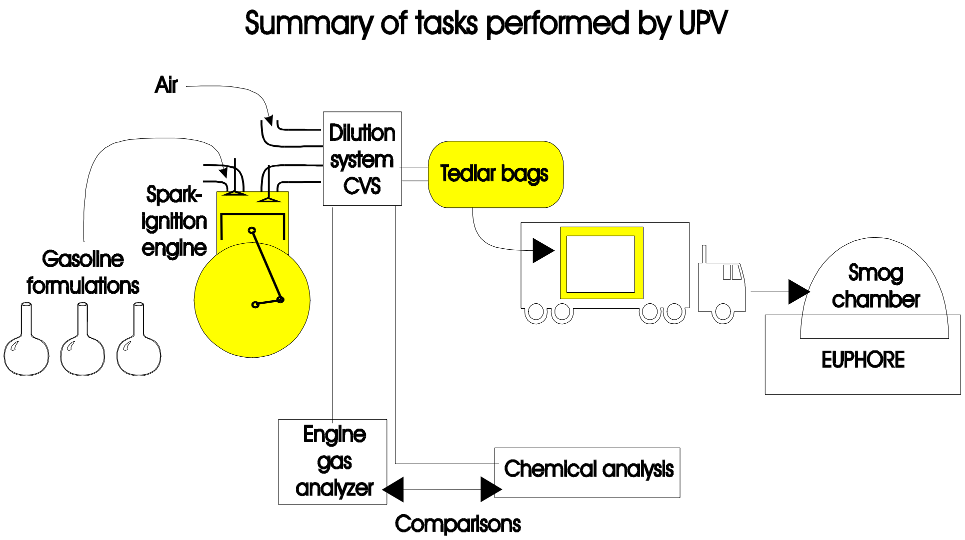

Fig. 1: Schematic diagram of the set-up for the gasoline fuel experiments.

The composition of the gasoline fuel types varied from a mainly aliphatic mixture (>98%) to blends with a high percentage of aromatic compounds (>30%). Two of the gasolines, the reference fuel (present Euro Grade fuel) and the reformulated blend, contained the fuel additive MTBE. The composition of the exhaust gas samples was determined at the Polytechnical University of Valencia (UPV). The exhaust gas samples consisted of a very large number of different components, only a few main compounds had relative ratios higher than 5% C/C.

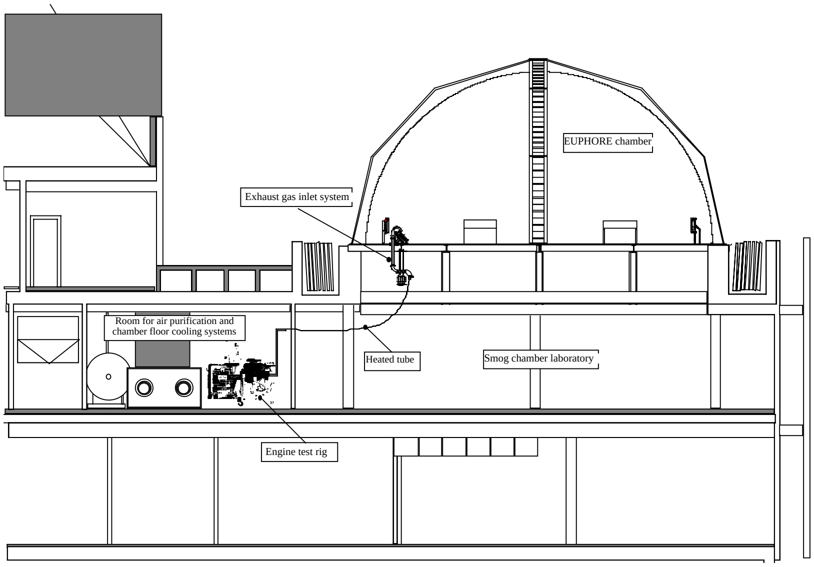

Fig. 2: Schematic diagram of the set-up for the diesel fuel experiments.

In addition to the work on gasoline fuels, a diesel fuel matrix was defined, produced and analyzed in terms of spec. bulk properties and of composition. Different aromatic hydrocarbon and a low sulfur content basically characterized the diesel fuels. For the experiments with diesel fuel a simple motor test bed was set up close to the European Photoreactor EUPHORE, which allows the operation of a commercially available small size diesel engine from a passenger car. The diesel exhaust was injected directly into the EUPHORE chamber through a heatable and temperature-controlled sampling line. In the EUPHORE chamber the concentration-time profiles of several chemical species including particulates were monitored by various analytical techniques. The schematic set-up for the diesel exhaust experiments is shown in the Figures 2 and 3.

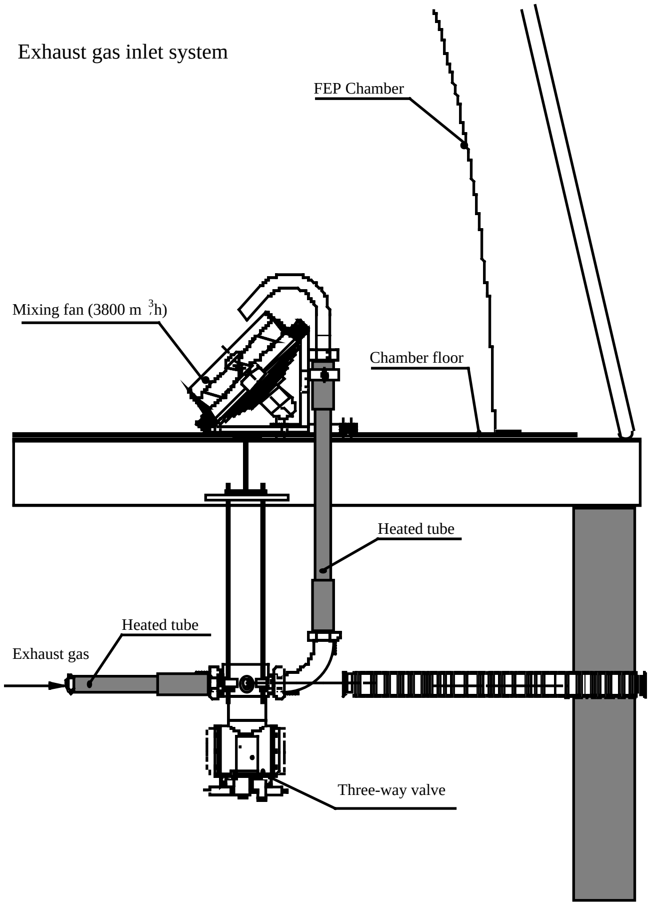

Fig. 3: Mixing unit for the injection of diesel exhaust gases into the EUPHORE simulation chamber.

Results and Discussion

The experiments in the EUPHORE simulation chamber clearly revealed the impact of different parameters on the photochemical processes during gasoline exhaust gas oxidation: radiation, initial NO_x concentration and composition of the fuels; see Figure 4.

Ozone time profiles with different initial NO_x concentrations during gasoline exhaust gas experiments are plotted in Figure 5.

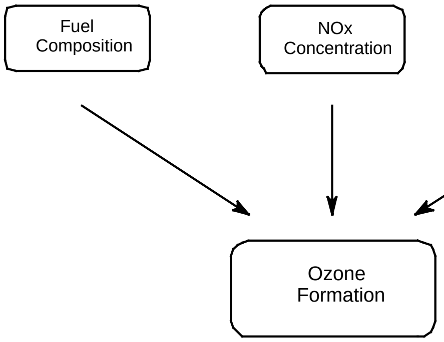

Fig. 4: Parameters which influence the ozone formation.

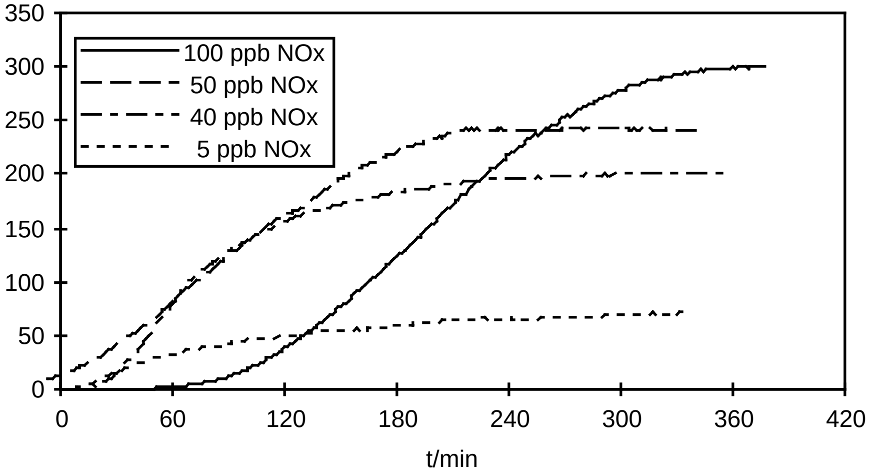

Fig. 5: Ozone time profiles during exhaust gas experiments with different initial NO_x concentrations, reference fuel.

Experiments performed in EUPHORE are characterized by using natural sunlight to irradiate the reaction mixture and initiate the oxidation processes. Therefore, the experiments strongly depend on weather and season. While the initial NO concentration in the smog chamber can easily be controlled, it is not possible to manipulate the radiation intensity by the use of photolysis lamps like in indoor photoreactor experiments. As a consequence, radiation intensities at different wavelengths have to be measured carefully for every experiment.

Experiments with simple VOC mixtures indicate that MTBE does not have a significant impact on the radical chains during the oxidation of other VOCs. The contribution to ozone formation from MTBE oxidation only adds to the ozone formation in the system without MTBE.

If ozone formation from other compounds is already very fast, MTBE oxidation does not show a significant impact. If ozone formation is comparably slow like from alkanes, MTBE competes with these hydrocarbons and contributes to ozone formation.

With respect to the ozone formation potential of MTBE being similar to *i*-octane and much less than that of most aromatic hydrocarbons the substitution of aromatic compounds in fuel blends by MTBE might lead to a reduction of local ozone formation from evaporated fuel or exhaust gas, see Figure 6.

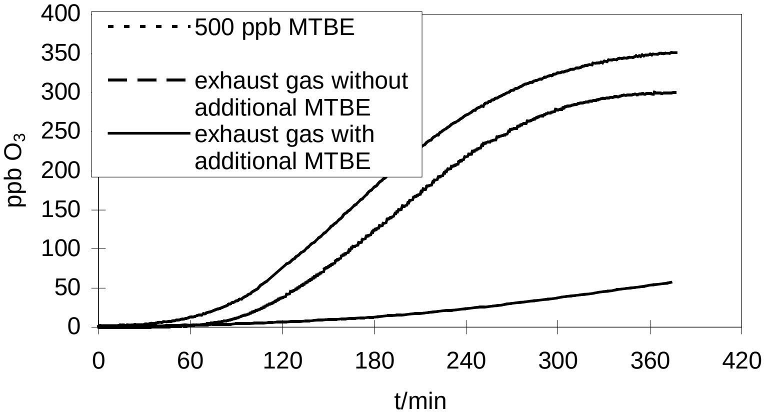

Fig. 6: Ozone formation for reference fuel exhaust gas with and without additional MTBE; 100 ppb NO_x.

During future work on this topic mixtures with a few more compounds should be investigated and experiments with similar total hydrocarbon concentrations and substitution of aromatics by MTBE should be compared.

From the one-day simulation experiments performed during this project it cannot be concluded whether MTBE might contribute to regional ozone formation because of its longer tropospheric lifetime. Since MTBE and its oxidation products are water soluble and the photolysis rates by sunlight are fairly low, deposition will probably be the most important loss process for these compounds.

Because of the strong influence of the radiation intensity, a direct comparison between exhaust oxidation experiments from different fuel types is only possible for very similar reaction conditions. In cases when the conditions are not very similar, reliable modeling of the photochemical processes is required to enable the comparison of different simulation experiments, especially those with VOC mixtures. The difficulty arising at this point is the missing mechanistic knowledge with regard to the oxidation of aromatic hydrocarbons. As long as the atmospheric degradation of aromatics is not fully understood it will remain infeasible to correctly model the behavior of VOC mixtures containing aromatics. Further, the loss of NO_x in these systems and the identification of the NO_z compounds should be a matter of special interest.

From the experiments with exhaust gas samples from differently blended fuels it can be concluded that within the same time period the ozone formation from the oxidation of paraffins is much less than from aromatic and olefinic hydrocarbons, see Figure 7.

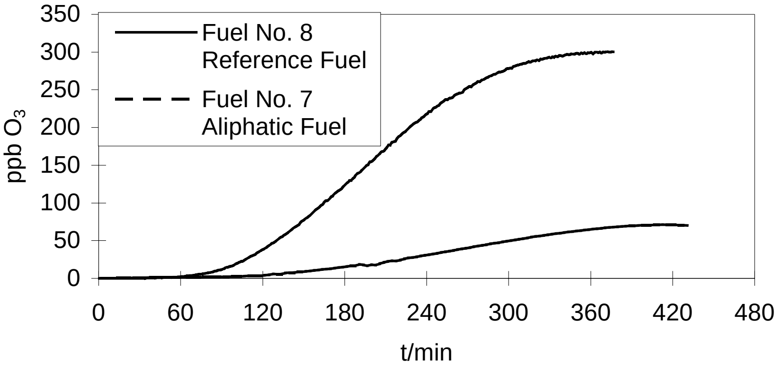

Fig. 7: Ozone formation for different fuel blends under similar conditions; 100 ppb NO_x

The substitution of aromatic hydrocarbons by olefins does not significantly affect the overall ozone formation. The use of MTBE as a fuel additive offers the possibility to reduce the aromatic content of the blends and thus the atmospheric reactivity of the exhaust gas.

In Figure 8 typical concentration-time profiles for HONO, HNO_3 and SO_2 are shown after the injection of diesel exhaust into the EUPHORE chamber. The injection time was 2 min. The engine was operated on the motor test bed under idle conditions using the European standard reference diesel fuel. The injection of the diesel exhaust caused a rapid increase of the concentration of the different species and then remained almost constant. After three hours a sodium carbonate denuder was installed in the gas sampling system, which caused a significant decrease in the HONO, HNO_3 and SO_2 concentrations. Surprisingly, the HONO concentration did not go to zero when the denuder was switched on. This is probably caused by an NO_2/SO_2 interference in the HONO detection system. Four hours after the diesel exhaust injection the denuder was switched off and the concentrations increased again reaching the levels measured before the denuder was switched on. After five hours the chamber was opened and the gas mixture was exposed to sunlight. A decrease in the HONO concentration was observed which is in reasonable agreement with known HONO photolysis rate constants. However, the concentration values did not go to zero as expected, indicating again an NO_2/SO_2 interference in the HONO detection system. Further experiments are necessary in order to clarify this problem.

In Figure 9 typical time profiles for the SMPS volume and number concentration of particles after the injection of diesel exhaust into the EUPHORE chamber are shown. Injection of diesel exhaust caused a rapid increase of the SMPS volume and number concentration. Exposure of the exhaust mixture to sunlight did not show an effect on the time behavior.

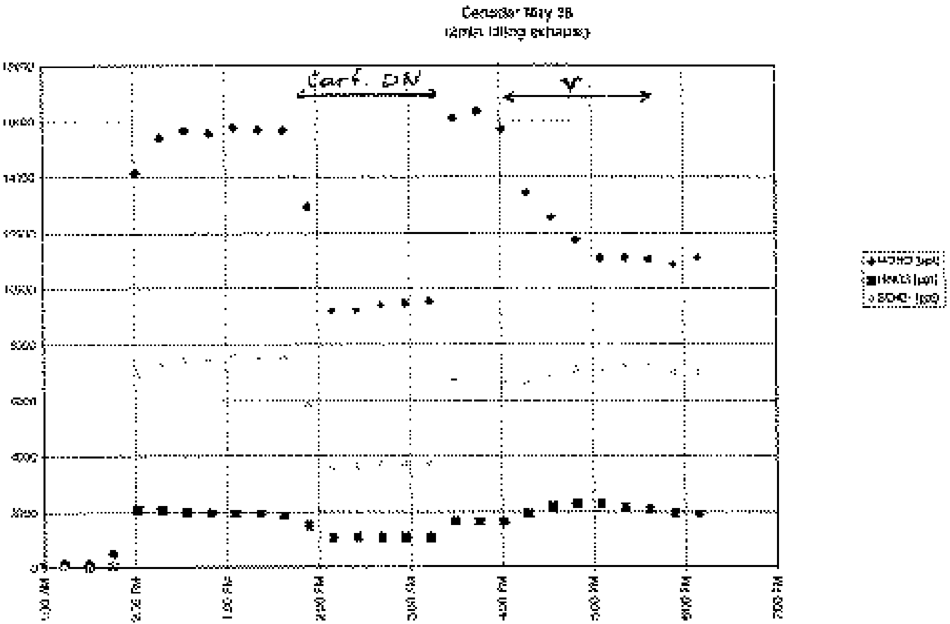

Fig. 8: Typical concentration-time profiles (r.h. 50%) for HONO (◆), HNO_3 (■) and SO_2 (σ) after the injection of diesel exhaust into the EUPHORE chamber. The injection time was 2 min. The engine was operated under idle conditions.

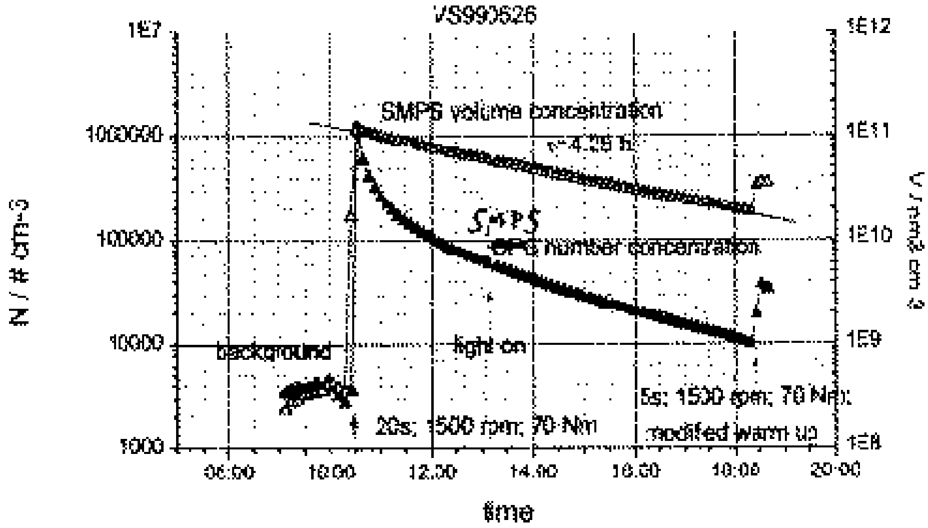

Fig. 9: Typical time profiles (r.h. 50%) for the SMPS volume and number concentration of particles after the injection of diesel exhaust into the EUPHORE chamber.

In Figure 10 typical particle size distributions after the injection of diesel exhaust into the EUPHORE chamber are shown. The size distribution is bimodal with a first maximum at a particle size of 33 nm and a second maximum at 107 nm directly after the exhaust injection. After three hours the size distribution exhibits a maximum at a particle size of 90 nm which is caused by agglomeration of the ultra-fine particles. In addition, Figure 10 illustrates a size distribution which was obtained directly after the injection of diesel exhaust when the diesel engine was warmed up by a different operating procedure. The size distribution exhibits a maximum at 80 nm particle size. This clearly shows that the particulate emission is strongly dependent on the engine operating conditions and engine pre-treatment.

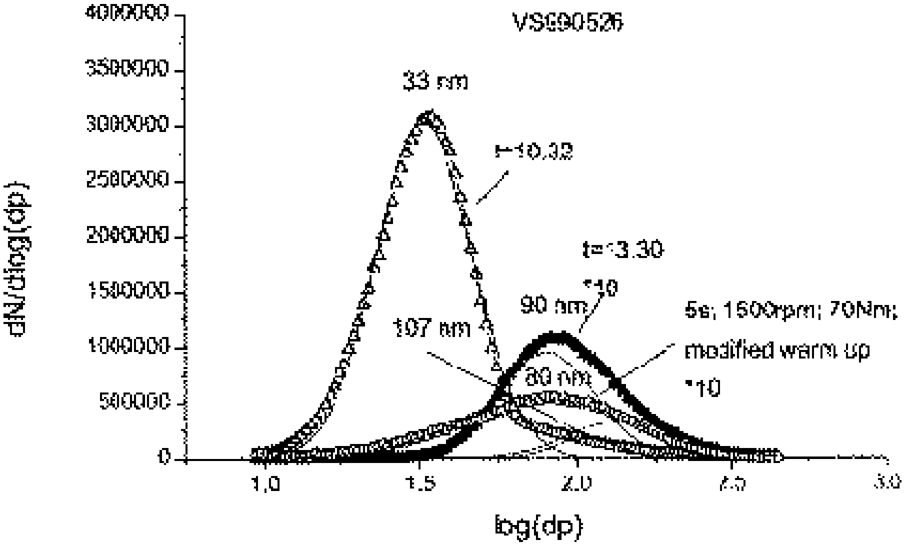

Fig. 10: Typical particle size distributions after the injection of diesel exhaust into the EUPHORE chamber.

Conclusions

The experiments performed with gasoline fuels clearly showed that the fuel composition has a strong impact on ozone formation. The composition of the exhaust gas depends on fuel blending and, therefore, the amounts of alkanes, alkenes and aromatic compounds in the exhaust vary. The experiments demonstrated that exhaust gases with a high aromatic content form more ozone within the same time than mainly aliphatic exhaust gases. The experiments carried out with the European standard reference diesel indicate that significant HONO quantities are either directly emitted from the engine or formed rapidly in the simulation chamber. In addition, the diesel exhaust experiments showed that the emission of particulates is strongly dependent on the engine operating conditions and engine pre-treatment.

Further knowledge of the atmospheric oxidation of fuel components and exhaust gas is still needed.

Acknowledgements

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