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EMISSION OF VOLATILE ORGANIC COMPOUNDS FROM DIESEL ENGINE FUELLED WITH OIL–WATER EMULSIONS

Exhaust gas from compression ignition engine fed with oil–water emulsions containing 10 vol. % of water or H₂O₂ (30 vol. %) water solution in commercial diesel oil have been analysed and the results compared with the composition of flue gas when diesel oil alone was used. The analyses concerned concentrations of NO, total NO_x, carbon monoxide, the sum of hydrocarbons as well as volatile organic compounds. When emulsion was used, considerable reduction of nitrogen oxides (however for low engine load only) and slightly lower smokiness of flue gas was reached; on the other hand, it caused higher concentrations of CO, aromatic hydrocarbons and the highest increase, even up to 10-fold, of acetaldehyde concentration, a typical product of incomplete combustion of organic compounds.

1. INTRODUCTION

Continuous increase in the number of motor vehicles and the distances travelled are observed all over the world and their growth rate seems unpredictable. In particular, the number of automotive vehicles increases very rapidly in the Far East countries, China or India, due to their technological boom. Also in Poland, the number of registered vehicles has distinctly increased compared with previous years (Table 1) [1].

Conventional fuels, including petrol and diesel oil, are mixtures of various hydrocarbons. As an effect of their complete combustion under ideal conditions, both in spark-ignition engines fuelled with petrol and in compression ignition engines fed with diesel oil, just harmless compounds, like CO₂ and water, should be generated. In practice, this type of combustion never occurs and like in all combustion processes of hydrocarbon fuels, a whole series of air pollutants can be found in flue gas – carbon

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monoxide, hydrocarbons, and among them especially dangerous polycyclic aromatic hydrocarbons (PAHs), nitrogen oxides, sulfur oxides and particulate matter (PM). Motor vehicles are responsible for significant fraction of total emission, first and foremost the nitrogen oxides (38.5%), carbon monoxide (22%), and, to a slightly lower extent, non-methane volatile organic compounds (16%) [1].

Table 1

Number of recorded vehicles in selected sectors

Sector	Year			
	1970	1990	2000	2007
Motor cars	479 000	5 261 000	9 991 000	14 589 000
Trucks	274 000	1 045 000	1 879 000	2 521 000
Buses	78 000	80 000	82 000	88 000

Pollutant emission depends on the fuel type and the way it is combusted in an engine. In the case of compression ignition engines fed with diesel oil where combustion always takes place with large excess air, the main problem consists in emission of nitrogen oxides and smoke – specific diesel particulate matter (PM), so called “diesel soot”. Diesel PM consists of insoluble material – particles of condensed carbonaceous material with ash from the engine oil and fuel additives, adsorbed water, sulfur compounds (sulfuric acid or sulfates) and adsorbed soluble organic fraction (SOF), which is a complicated mixture of organic compounds, including both volatile organic compounds (VOCs) and PAHs, soluble in methylene chloride.

Pollutant emission of vehicles can be reduced with primary methods which lead to improve the conditions of fuel combustion (to burn less fuel and more efficient) by optimisation of engine construction and the whole fuel supply system. Another solution is to use unconventional drives (e.g. electric or hybrid) and fuels. Most often it refers to biofuels, e.g. esters of plant origin fatty acids (fatty acid methyl esters – FAME) having been added in various proportions to diesel oil. Mixtures of diesel oil and esters allow one to reduce pollutant emission, first of all the PM (by 20–50%), carbon monoxide (11–25%) and hydrocarbons (20–32%), however the NO_x emission may increase [2, 3].

Another proposal consists in feeding diesel engines with oil–water emulsions where water droplets are surrounded by film of liquid fuel. High temperature existing in combustion chamber causes evaporation – at first of water and then of the fuel. Evaporating water supports atomizing of fuel droplets which favours full combustion of fuel at somewhat lower temperature. As an effect of emulsion combustion, the concentration of basic pollutants in flue gas, i.e. diesel soot and nitrogen oxides, are reduced. Oil–water emulsions properties depend on water volume fraction in fuel. In practice, it is up to 30%. Elf Company’s fuel, brand name Aquazole, including about 13% of water and 2% of stabilizing additives in low-sulfur diesel oil, ensures NO_x

reduction by 15–30% and soot by 10–50%. At the same time, engine power reduces by about 4% and fuel consumption rises by 10–15% as compared with diesel oil alone [4]. In any way the concentrations of CO and organic compounds can increase [5].

The purpose of the work was to compare chemical compositions of exhaust gases of diesel engine fuelled with pure commercial diesel oil and those of oil–water emulsions containing 10 vol. % of distilled water or the same content of 30% water solution of H₂O₂.

2. EXPERIMENTAL

Tests were carried out with a diesel engine S301D with a hydraulic load brake HWZ1 equipped with an extensometer force transmitter with accessories allowing one to measure and to control operating parameters of the engine. In order to simulate characteristic standard mode of driving, examinations were performed for three rotational speed values of engine crankshaft, 1200, 1400 and 1600 rpm and two levels of engine torque (*Mo*) of 10.72 and 21.28 N·m. Measurements were taken for the following operating points of the engine:

- 1) $n = 1200$ rpm, $Mo = 10.72$ N·m
- 2) $n = 1200$ rpm, $Mo = 21.28$ N·m
- 3) $n = 1400$ rpm, $Mo = 10.72$ N·m
- 4) $n = 1400$ rpm, $Mo = 21.28$ N·m
- 5) $n = 1600$ rpm, $Mo = 10.72$ N·m
- 6) $n = 1600$ rpm, $Mo = 21.28$ N·m

Apart from commercial diesel oil for summer season (ON), two oil-water emulsions were prepared, one with 10 vol. % of distilled water in ON (ON+) and one with 10 vol. % of 30 vol. % H₂O₂ solution (ON++). Emulsions were prepared in the Institute of Machine Construction and Operation, Wrocław University of Technology using ultrasonic washer.

2.1. ANALYTICAL MEASUREMENTS

Concentration of formaldehyde was determined by the colorimetric method, according to Polish Standard PN-71/C-04593, after absorbing the aldehyde in water. The remaining VOCs were adsorbed on active carbon and, after desorption with CS₂, they were analyzed with gas chromatograph, using a Hewlett-Packard HP 5890 Series II apparatus, with a FID detector and a HP PONA capillary column (50 m long with stationary phase film 0.5 μm thick). Exhaust samples were taken from the outlet system via a probe. The gas was split into two streams – formaldehyde was absorbed in

washers containing 10 cm³ of distilled water, VOCs were adsorbed and concentrated on active carbon. Samples were taken simultaneously using a two-channel aspirator. Flow rates of flue gases in each system were 20 dm³/h and the sampling time was 30 min. A scheme of the testing stand is shown in Fig. 1.

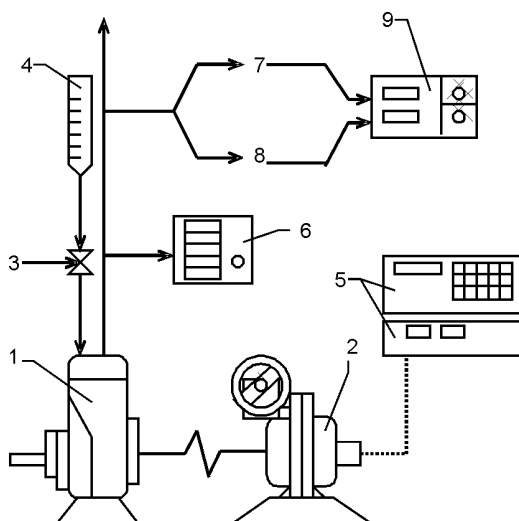


Fig. 1. Scheme of testing stand: 1 – engine, 2 – load brake, 3 – fuel supply, 4 – test fuel supply system, 5 – rotational speed and torque meters, 6 – flue gas analyzers, 7 – absorbing washer, 8 – pipe with adsorbent (active carbon), 9 – two-channel aspirator

3. RESULTS AND DISCUSSION

Experiments by the gas chromatographic method revealed a series of compounds, of which those of the biggest chromatographic peaks were determined qualitatively and quantitatively. Within the group of aldehydes, apart from formaldehyde determined by the colorimetric method, exhaust gas contained acetaldehyde, propanal and acrolein, alcohols (amyl, *n*-buthyl and isobuthyl), methyl isobutyl ketone, aromatic hydrocarbons (benzene, toluene, xylene) and alkanes (heptane, octane, decane).

The concentrations of aromatic hydrocarbons (AHC), aldehydes and other compounds determined for the specific working points of the engine are shown in Fig. 2.

When diesel oil alone was used, higher concentrations of aromatic hydrocarbons were observed for the higher load of engine, and – independently of its rotational speed – they amounted to about 0.25 g/m³. At this engine load, combustion of oil–water emulsion produced somewhat lower concentrations of AHC but serious, almost twofold rise of the concentration of these compounds took place during combustion of oil–perhydrol emulsion, especially at the engine test points 2, 3 and 4.

When engine was fuelled with diesel oil only, the concentrations of aldehydes, except series 3, were slightly lower than that of AHC and amounted to 0.1 g/m^3 . Combustion of both emulsions caused a considerable higher concentration of aldehydes than during oil combustion; especially at the lowest rotational engine speed of 1200 rpm they were almost 8-fold and over 10-fold higher for the lower and higher engine load, respectively. Such result is particularly dangerous – aldehydes are recognized as strongly irritating compounds for human being and on the other hand for their great potential to create photochemical smog with nitrogen oxides.

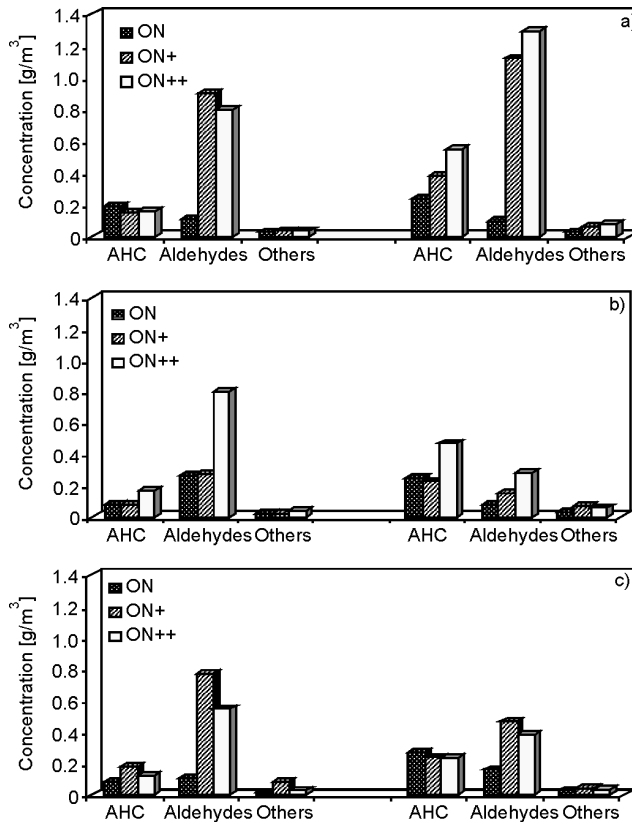


Fig. 2. Total concentrations of aromatic hydrocarbons (AHC), aldehydes and other identified organic compounds (alkanes, ketones and alcohols) depending on the fuel combusted, at the rotational speed of: a) 1200 rpm, b) 1400 rpm, c) 1600 rpm; $M_o = 10.72 \text{ N}\cdot\text{m}$ – on the left-hand side, $M_o = 21.28 \text{ N}\cdot\text{m}$ – on the right-hand side

The part of remaining organic compounds in total VOCs emission was much lower but also in this group higher concentrations of organic compounds were observed when the both emulsions were combusted than when diesel oil only was used.

Among hydrocarbons, benzene occurred in the highest concentrations (maximum 0.126 g/m^3). Its concentration increased with increasing both load and rotational speed of engine. Similar trend of concentration changes was observed for the remaining AHC, however their concentrations were substantially lower and reached 0.11 and 0.037 g/m^3 only for xylene and toluene, respectively. Much lower concentrations, at least two orders of magnitude with respect to benzene, occurred for alkanes and they were similar for all compounds determined.

In the group of oxy-derivative compounds, aldehydes were determined in the highest concentrations and among them, acetaldehyde, typical product of incomplete combustion of VOCs representing organic compounds of various chemical structure [7–9]. The concentration of acetaldehyde varied within 0.03 to 0.063 g/m^3 . Concentrations of other determined aldehydes were lower and amounted about 0.04 g/m^3 , 0.03 g/m^3 and 0.02 g/m^3 for propionaldehyde, acrolein and formaldehyde, respectively. Concentrations of remaining oxy-derivative compounds were much lower and did not exceed 0.007 g/m^3 . Both these compounds – benzene and acetaldehyde are particularly hazardous – which is proved by very stringent their maximum available concentrations in air (Table 2).

Table 2

Maximum available concentrations of selected compounds in air [9]

Compound	Classification (No. CAS)	Maximum available concentration [$\mu\text{g/m}^3$]	
		1 hour	Year
Benzene	71-43-2	30	5
Acetaldehyde	75-07-0	20	2.5

As was shown above, combustion of both emulsions increased the concentration of VOCs; the same tendency was observed for benzene and acetaldehyde. The concentrations of those compounds, depending on the fuel combusted, are presented in Figs. 3 and 4.

Benzene concentrations for all tests were lower at a lower rotational speed and load of engine. When oil alone was combusted, benzene concentrations at $Mo = 10.72 \text{ N}\cdot\text{m}$ lowered from 0.054 to 0.032 g/m^3 for 1200 and 1600 rpm, respectively. Oil combustion at a higher engine torque ($Mo = 21.28 \text{ N}\cdot\text{m}$) resulted in distinctly (2–4-fold) increase of benzene concentration in the waste gases, amounting to 0.125 g/m^3 . Combustion of both emulsions, particularly the oil–perhydrol emulsion, brought the increase of benzene concentrations, practically at each point of the engine test, amounting to maximum value of 0.242 g/m^3 at the test point 2.

For combustion of diesel oil at each test point, the concentration of acetaldehyde in the exhaust gases changed within 0.024 – 0.062 g/m^3 . Similar was the concentration of propanal. Formaldehyde and acrolein were detected in much lower concentrations

($0.008\text{--}0.024\text{ g/m}^3$). Engine fuelled with both emulsion produced slightly more acetaldehyde – its concentration increased even 20–30-fold, exceeding the value of 1 g/m^3 .

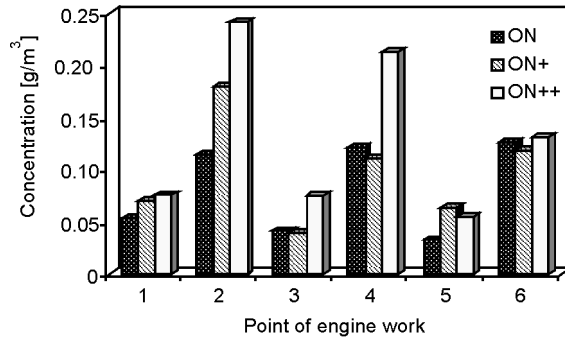


Fig. 3. Concentration of benzene in waste gases during fuels tested combustion

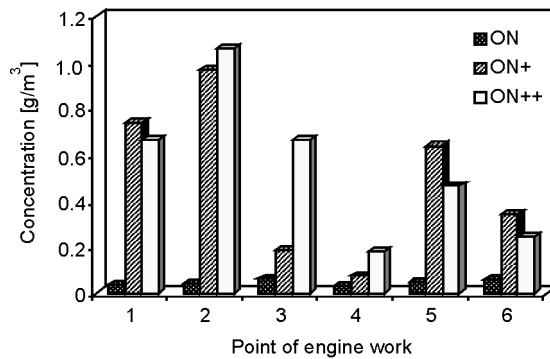


Fig. 4. Concentration of acetaldehyde in waste gases during fuels tested combustion

Combustion of oil–water emulsion probably contributes to deterioration of combustion parameters in terms of the abatement of local combustion temperature and additional oxygen atom, contained in water molecule enabled incomplete oxidation of fuel hydrocarbons to acetaldehyde only. On the other hand, when both emulsions were combusted, only formaldehyde was produced in lower concentrations at every engine test point, than when oil alone was burnt.

4. CONCLUSIONS

Combusting of oil–water emulsions leads to reduced emission of the most important air pollutants generated by compression ignition engines – nitrogen oxides and

diesel soot [10]. However, it also contributes to higher concentrations of volatile organic compounds in flue gas, including dangerous aromatic hydrocarbons or aldehydes. Despite improved degree of fuel dispersion in oil–water emulsions, combustion of organic compounds originating from oil may be inhibited by the presence of water – ballast decreasing local temperature of combustion. It should be emphasized that tests were made using an old-design engine and, under such conditions, complications with combustion of a fuel other than diesel oil are more evidently highlighted.

Oil–water emulsions can be successfully applied to any direct injection diesel engine without engine construction or settings changes. Fundamental disadvantage of this fuel is a low durability of such emulsions. Special additives are necessary to be used, so-called emulsifiers, reducing the surface tension, and in this way enhancing fuel durability. At present, oil–water emulsions are used seldom, mainly as fuels for municipal buses in some towns in France or USA.

The performed tests on the combustion of oil–water emulsions showed potential for decrease of emission of some groups of air pollutants, mainly NO_x and soot, however complex systems of flue gas treatment need to be used to reduce the emission of all air pollutants such as carbon monoxide and volatile organic compounds which can be easily oxidized in catalytic reactions.

For the fact that application of emulsions can decrease concentrations of the most dangerous air pollutants generated by diesel engines, research work on combustion of such emulsions should be surely continued.

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