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Researches on a photocatalytic device for toxic hydrocarbons removal from IC engine exhausts

Hydrocarbons, especially aromatic volatile organic compounds (AVOCs) and polyaromatic hydrocarbons (PAHs), emitted by IC engines, indisputably have a negative impact on the environment and public health. Even though current legislation strongly impacts on their low concentration in the exhausts, not quantity but the quality of those substances determines fumes toxicity. The paper presents results of the researches on a photocatalytic device dedicated to BTX (benzene-toluene-xylene) removal from IC engine exhausts, which can be applied in a vehicle cabin ventilation system. According to the results, the system is able to decrease toxic compounds concentration (caused by mobile emission sources) in inlet-air delivered to the vehicle interior. In effect, the system application reduces the users of a vehicle to exposure on contaminants.

Key words: photocatalysis, engine exhausts, vehicle interior, public health

1. IC engine exhausts as a vehicle interior pollutant

Unfavourable health effects of road traffic in cities, especially with large traffic volume, characterised by numerous traffic congestion, are bound in a way direct primarily with the quality of atmospheric air and acoustic climate.

Products of the combustion, such as nitrogen oxides, carbon monoxide, hydrocarbons, particles, and even metal compounds as well as biocide combustion products (substances added to the fuel in order to prevent corrosion of the tank and biodegradation of fuel) emitted into the atmosphere can be easily absorbed by the human body through the respiratory system and dermal exposure. The relation between exposure to increased pollution levels and the mentioned effects is confirmed in many researches [1–3]. The negative impact on health can have itself staying in a car interior where the level of pollutants can be several times higher than in the surrounding air [1–3].

From mentioned compounds emitted by IC engines, especially hydrocarbons (HC) are recognised as toxic, carcinogenic and mutagenic substances. Among them, aromatic hydrocarbons are the most dangerous group.

Aromatic hydrocarbons emitted by combustion engines can be divided into two, important in environmental aspects, groups [1]:

- Aromatic volatile organic compounds (AVOCs) – are organic chemicals that have a high vapour pressure at normal room temperature. Their high vapour pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air, a trait known as volatility.
- Polyromantic hydrocarbons (PAHs) – are hydrocarbons containing only carbon and hydrogen, composed of multiple aromatic rings (organic rings in which the electrons are delocalized). Even though the particles are not volatile (they are relatively heavy) PAHs can be ad-

sorbed on particles, cumulate in the environment and, because of its high toxicity, cause severe problems in ecosystems.

Indisputably interior of a car cabin is an essential environment of contemporary human life. Specificity of car vehicle operation in cities, especially in road congestion conditions, effects in interior atmosphere pollution. Whereas particle matter (PM) is mostly stopped on filters applied in the vehicle ventilation system, a gaseous fraction of the exhausts can easily get into the car interior.

Despite the fact, that the problem of car cabin pollution caused by carcinogenic and mutagenic volatile organic compounds is well known, there are no general standards of its limitation. It can be assumed that a vehicle interior can be treated as an indoor space, like building [1]. In this aspect, the concentration of particularly toxic AVOCs, i.e. benzene, toluene and xylenes (BTX) concentration, very often is a few times higher than the allowable concentration of those substances for indoor space, category A (permissible for human permanent stay – Table 1) [1].

Table 1. Allowable concentration of indoor substances, category A [1]

Compound	Allowable concentration indoor (Category A) [mg/m ³]
Benzene	0,01
Toluene	0,2
Xylenes	0,1

The BTX exposure can effect in serious health problems (long-term exposition) and irritate nervous system which consequence can be a direct influence on vehicle active safety (driver distraction, lowering driver cognitive abilities etc.). This fact should focus the attention of scientists and designers on the problem of effective car cabin inlet air purification and decreasing of gaseous toxins concentration in the vehicle interior.

2. Photocatalytic reactor concept

Gas purifying can be obtained mainly in accordance with widely used physical and chemical processes. Well known is high-temperature oxidation (with or without catalyst) which occurs at temperatures of 200 to 1000°C – effective but not possible to apply in the vehicle ventilation system. The AVOCs can also be adsorbed on the active carbon, often used as a part of a cabin filter system. The capacity of the active carbon layer is relatively small. Most producers recommend to replace an active carbon filters every 6 months to keep its effectiveness. The alternative procedure for HC removal from inlet air is a photocatalytic oxidation (PCO) which is more effective, environmental friendly and free from economic issues [4]. The most common catalytic agent is titanium dioxide, TiO_2 , due to its capability to degrade a wide spectrum of chemical individuals when illuminated with UV light or when in the vicinity of ultraviolet [5–8]. Therefore, it appears that the extent of undesirable, toxic volatile organic compounds removability is dependent upon the UV light length. Furthermore, the reactions can course differently with respect to humidity pressure and temperature [9].

The concept of the reactor was created in Automotive Engineering Division on Mechanical Faculty of Wrocław University of Technology for Dr. Schneider Automotive Poland and is patented as the Vehicle Air Supply System (WO2015PL50072 20151221).

The system, comprising a light source and a photocatalyst between air intake and at least one supply port inside the system wherein the photocatalyst is located, is equipped with elements disturbing a flow of air stream, creating a network of ducts formed by a system of such that the time of exposure of the air stream to the photocatalyst is extended allowing for better mixing of the polluted air and time required for a photocatalytic process to reduce toxins [10].

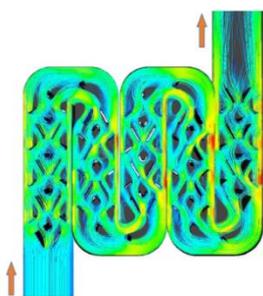


Fig. 1. Photocatalytic reactor concept [11]

The photocatalytic reactor tested here (shown in Fig. 2) was manufactured in additive technology (3D printing). Its constructional complicity was done for the purpose of polluted air disturbance and mixing. Moreover, detailed design and CFD computed channels were to elongate the time of exposure of the polluted air to catalytic agent, and prevent the negative influence of boundary layer occurrence.

The inserts are design in the way enable installation of a tape equipped with UV LEDs. In this case the length of UV light is 395 nm with power of 60 mW of each diode installed in the tape. The angle of illumination was 120 degrees.



Fig. 2. Photocatalytic reactor used in the experiment

In this research as a photocatalytic agent titanium dioxide (TiO_2) was applied to the inserts of the reactor.

The applications procedures which were under consideration assumed varies techniques confronted with each other. The applications procedure described here results from long time investigation and were selected as the most assessable. For example thermal application of the catalytic agent was preliminary selected as one of the most effective procedures due to creation of constant and permanent layer of catalytic agent. However ultimately it was rejected due to significant difficulties and not efficient heating process.

Ultimately the mixture of a titanium dioxide with an adhesive substance was chosen for the investigation (see Fig. 3). The adhesive substance was mixed with a powder creating homogenous gel which was very easy distributed on the surface.

Mixing catalytic agent with the gel can cause immersion of the powder inside the gel which makes it not active. Only pollution contacting the active surface can be subjected to the photocatalysis. For this reason the experiment was repeated after fogging the surface, done in order to uncover layers of the catalytic agent. The results however showed that such action was not required as the not fogged surface was proven to be active



Fig. 3. Catalytic agent mixed with the adhesive substance

3. Research method

In order to simulate the effectiveness of the BTX reduction abilities of a tested reactor during real driving conditions, a test station was constructed. This test station comprises a test vehicle located in the climatic chamber for simulation of various weather conditions (e.g. temperature

and humidity). The photocatalytic reactor was assembled to the ventilation system of a vehicle in order to simulate its later implementation as a bypass to existing systems. During this studies it is assumed that the vehicle is ventilated in a closed loop – the atmosphere from the vehicle interior is aspirated by the system then warmed up or cooled and directed back again to the vehicle's cabin.

Before execution of the experiment, the cabin is set to be filled with pollutions (1:10 air diluted CI engine exhausts, emitted in repetitious conditions). The interior of the vehicle was deprived of most of the materials capable of accumulating the compounds related to exhaust gases directed to the cabin. During the experiment, the cabin of the vehicle is set to be inflated with pollutions provided form the power generator. After inflation, a photocatalytic reactor is engaged, and the BTX reduction process starts. The ventilation system is set to operate in a closed loop. Hence the crude air is directed through the reactor to the ventilation system and back again to the car cabin – as depicted in Fig. 4.

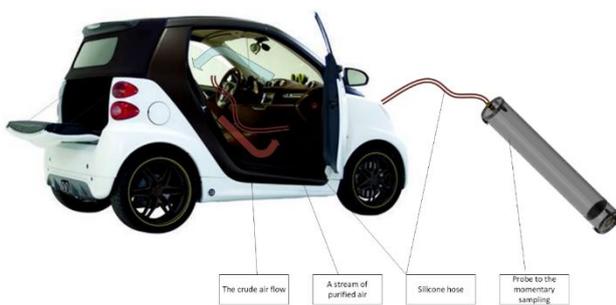


Fig. 4. Schematic representation of the experiment procedure [12]

Considering limited duration of the experiments along with limitation of aspirator flow rate it was necessary to adapt the test station for momentary sampling. The experiment assumed filling the cabin with the fumes and instant sampling in various times of the experiment. The chromatography tests requires specific amount of gases to be provided for analysis, otherwise the accuracy of the results is insufficient. This amount of polluted gas must be gathered instantly from the cabin. For this reason a testing vehicles was equipped in probe to the momentary sampling which aspirate specific amount of gases to the sampling bag. Limited time of the experiment exerted utilisation of at least two probes which gathers the polluted air one after the another allowing to draw characteristic of compound changing with respect to time. The probe is connected to the cabin via a silicon housing which aspirates the gas from the position of the drivers head

Air from the interior of the vehicle was momentary gathered by the probe to the bag for further chromatography tests. the probe is mounted outside the vehicle which requires to use a long silicon house. This in tur requires a large suction power for the bag to be instantly inflated with the polluted air. The exterior of testing vehicle is shown in Fig. 5.

The whole experiment is adjusted in order to consider full gas exchange during one cycle. At specific moments the atmosphere in the cabin was t sampled through the probe.

The test parameters like air flow, temperature and time sets was adjust to real drive conditions, in this research: temperature 290 K and 296 K, flow: 2 m/s, contact time 360 s (approximated time of one full circulation of the air through the system).



Fig. 5. Exterior of the tested vehicle with sampling probe

AVOCs Samples were collected by YEARS aspirator, model ASP-3 II, flow rate adjusted to 30 dm³/h, the amount of gas collected is 10 dm³. The gas was absorbed on active carbon Anasorb® SKC CSC. Activated carbon is poured into a glass tube of 5 cm³ and later it is emerged in 2 cm³ of carbon disulfide. The BTX in the samples was determined by gas chromatography according to the test procedure of the Emission Research Laboratory No. 1/2010 using the gas chromatograph Varian 450 – GC with flame ionization detector (FID), and a column Varian VF-WAXms 30 m × 0.25 mm ID DF: 0.25 um. The work was performed at the set temperature of the column 373 K (110°C), the dispenser 523 K (250°C) and detectors 423 K (150°C). YEARS aspirator, model ASP-3 II, flow rate adjusted to 30 dm³/h, the amount of gas collected is 10 dm³, collected samples. The gas was absorbed on active carbon Anasorb® SKC CSC. Activated carbon is poured into a glass tube of 5 cm³ and later it is emerged in 2 cm³ of carbon disulfide. The glass tube is sealed with a stopper. Extraction takes place in a period of 20 min. After every few minutes the contents of the bottle was shaken in order to ensure adequate mixing of the material. Then 5 µl of the solution was gathered from above of the carbon layer. The gathered sample is injected into the chromatograph. Compounds designated as "residuals" have been converted to the concentration corresponding to n-pentan. In other words residuals are the compounds existing within the gas mixtures but was not identified by the chromatograph. The total relative error of the method was estimated at 20% (according to PN-EN ISO 16017-1: 2006).

4. Results

The results of the experiment are shown in Figs 3 and 4.

Results of the experiment indicate an effective reduction of total volatile organic compounds (41% to 69%) in both temperatures. Despite the fact that there were visible differences between concentration reduction effectiveness in particular BTX compounds (especially xylenes), total BTX reduction is even slightly higher than total VOC (49% to 70%).

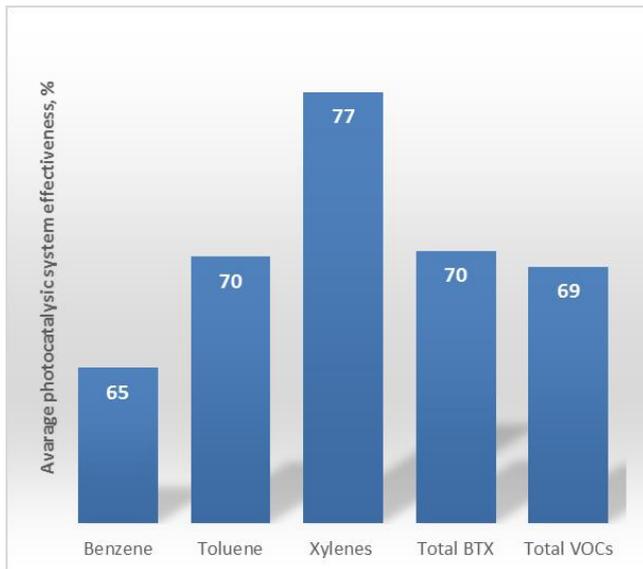


Fig. 3. Average photocatalytic system effectiveness, temperature 290 K

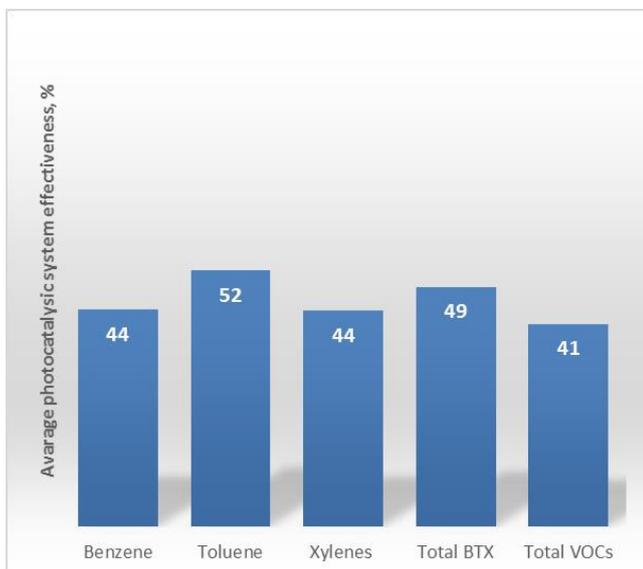


Fig. 4. Average photocatalytic system effectiveness, temperature 296 K

The experiment indicates that temperature can influence VOCs removal properties of the system, what also complies with other researches [11, 13]. The effect of the temperature increase on photocatalytic device effectiveness (Fig. 5) seems to be opposite to effectiveness of conventional catalytic reactors applied for IC engine exhausts cleaning (TWC, DOC), where the temperature increase significantly intensify HC conversion level (their effectiveness is minor in room temperature conditions).

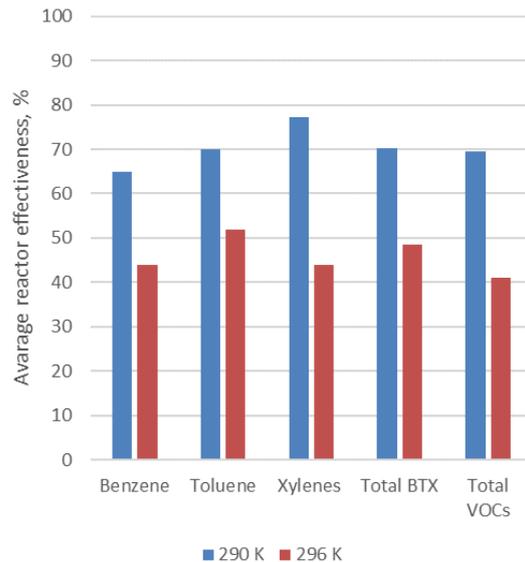


Fig. 5. Average photocatalytic system effectiveness, temperature comparison

5. Conclusions

1. IC Engine exhausts are a source of toxic aromatic volatile organic compounds. Especially benzene, toluene and xylene are substances responsible for many civilizational diseases (including cancer)
2. The BTX irritate nervous system which in consequence can be a direct influence on vehicle active safety (driver distraction, lowering driver cognitive abilities etc.).
3. Cooperation between Wrocław University of Science and Technology and Dr. Schneider Automotive Poland effected of new product development: VOCs removal photocatalytic reactor for vehicle ventilation system.
4. The results of the experiment showed significant effectiveness of the device in BTX reduction (to 70%) in room temperatures.
5. The photocatalytic reactor seems to be prospective solution for air quality improvement in any vehicle cabin.
6. Taking the results of measurements into consideration, it appears that xylene in most cases is the most vulnerable to the catalytic agent purifying properties. Benzene showed opposite tendency. Its removability is in most cases the lowest amount the other compounds.
7. The BTX removal properties are highly dependent upon temperature, UV light length and the time of pollutant exposure to the catalytic agents. This justifies the attempt to improve the existing ventilation nozzles in terms of equipment related to BTX reduction.

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Nomenclature

IC internal combustion
 VOCs volatile organic compounds
 AVOCs aromatic volatile organic compounds
 PCO photocatalytic oxidation
 BTX benzene-toluene-xylenes

GC gas chromatography
 FID flame ionization detector
 TWC three way catalyst
 DOC diesel oxidation catalyst

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