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VOLATILE ORGANIC COMPOUNDS REMOVAL FROM VEHICLE INTERIOR BASED ON PHOTOCATALYTIC SOLUTION

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Abstract

The article presents results of research work which aim was development of solution for volatile organic compounds (VOCs) removal from vehicle indoor air. VOCs, especially benzene, toluene, and xylene (BTX), are air pollutants responsible for many civilizational diseases because of its carcinogenic and mutagenic properties. Concentration of those substances can be even few times higher in micro atmosphere of vehicle cabin than in other indoor atmospheres [1]. The aim of the scientific cooperation between Dr. Schneider Automotive Polska and the Wroclaw University of Science and Technology (WUST) is research on innovative (international range), product development – photocatalytic reactor characterized by Volatile Organic Compounds, especially BTX removal properties. The BTX reduction effectiveness, caused by photocatalytic reactor application in vehicle ventilation system, was subjected to in-depth analysis. The results showed difference on not only maximal benzene, toluene, and xylene reduction (separately) but also in the pattern of response surface. In some tested parameters, the hazardous compounds (as a BTX sum) were reduced for almost 70%. The photocatalytic reactor seems to be prospective solution for air quality improvement in any vehicle cabin.

Keywords: *automotive vehicle, benzene-toluene-xylene compounds, vehicle interior, indoor air, photocatalysis*

1. Introduction

Volatile organic compounds (VOCs) are carbon-based compounds, with 2 to 10 carbon atoms, that have vapour pressures high enough to significantly vaporize and enter the atmosphere. Many different kinds of VOCs can be found in the air: alkanes, alkenes, alkynes, halogenated hydrocarbons, aromatic hydrocarbons, terpenes, aldehydes, ketones, and alcohols. Some of these compounds are toxic or carcinogenic, and therefore there are limit values for their concentrations in the air [1, 2].

Substances from VOCs group have negative impact for human body. Due to the popularity of occurrence, the most dangerous are benzene, toluene and xylenes known as BTX. The most exposed is respiratory system as it is the main way of VOCs penetration into organism.

The cancer, as well as non-cancer risks of exposure to aromatic hydrocarbon in car cabin varies between different groups such as [3]:
– male drivers,
– female drivers,
– male passengers,
– female passengers.

The health risk is the highest for the male driver and is [3]:

- 1.04 times higher than for female driver,
- 6.67 times higher than for male passenger,
- 6.94 times higher than female passenger.

The reason of such a health risk statistics is a direct exposure to sources of emission at the driver's position.

The content of VOCs measured in the indoor air of car depends on cars age, materials used in car, cabin tightness, ventilation, humidity and temperature. The emission of VOCs inside car cabin comes mostly from synthetic panels, synthetic fabrics, rubber, rugs and applied adhesive joints.

The first methods to measure VOCs in cars were developed over 20 years ago. Since then they are continuously developed and improved. The methods are distinguished between measuring the complete car cabin interior and individually material samples. Before 2013, a couple of countries had standards to test the concentration of VOCs in cabin [4].

In Germany, the VDA (Verband der Automobilindustrie) had methods to determine the emission of smell and volatile substances from components and materials used in car.

In China, the standard GB/T 27630-2011 was used to check the emission of chosen Volatile Organic Compounds and aldehydes from cars materials.

In Japan, the Japan Automobile Manufacturers Association (JAMA) tested the VOCs content in cabin since 2007. JAMA test method is still used in buses and trucks.

Some of the car manufacturers have had their own test procedures and criteria of acceptance of VOCs emission and odour; however, they are not available outside of the companies. It is known that Volvo's materials were measured and Oeko-Tex 100 certified. In addition, Ford tested some cars models paying special attention to content of allergens, in which some VOCs might be found.

In 2013 international standard ISO 12219-1 was released in which the procedure of measuring Volatile Organic Compounds, including Very Volatile Organic Compounds, in car cabin was described. The method assumes that tested car is brand new, within 28 days since production. Before inspection, the car is supposed to be transported or stored avoiding high temperature. Test report should include precise description of the materials used in car cabin.

Referring to the ISO standard the car should be put in a chamber with a temperature of 23°C and 50% relative humidity. The test consists of three phases: ambient mode, parking mode and driving mode. Each of them establishes that windows and doors of the car are closed.

For the time being ambient mode the car is parked, engine is off. Firstly the car has open doors for an hour, after that the doors are closed and for at least 8 hours stays in temperature of 23ºC. During last half an hour double samples are taken- to measure VOCs and aldehydes.

Tests of parking mode take 4 hours. After 3.5 hours of car parked at elevated temperature samples are taken. For last half an hour double probes are captured to measure formaldehyde (VVOCs). The temperature is nor determined. Capacity of heating should be 400 W/m^2.

In driving mode, the engine is on; exhaust gases are discharged from the cabin. Ventilation should be running at maximum speed, Air condition, if present, should be set on 23ºC and an automatic airflow. The samples are taken during first 30 minutes, double to measure VOCs and aldehydes. This mode illustrates the exposure to VOCs during driving car after parking in a hot place. At this time being the exposure is the highest, as the higher the temperature, the higher concentration of Volatile Organic Compounds.

In table below (Tab. 1) an overview of chosen studies, measuring content of VOCs in car cabin air is shown. Most of the car manufacturing countries at some point were involved, which indicates they are aware of emissions from car interior materials and indoor air quality: PL – Poland, DE – Germany, IT – Italy, CN – China, JP – Japan, TW – Taiwan, US – the United States.

In most cases, middle class cars were studied for VOC content in the cabin. The car brand or specific model also was not indicated. All studies show that concentrations of VOCs decrease with the car's age and the number of travelled kilometres. The worst-case conditions of exposure are in new cars.

Tab. 1. Studies concerning VOCs content in air of car cabin [4]

Cars	Country	Age	Year	Conditions	Temperature	Findings of VOC
9	PL	1 day	2012	Outside, ambient	21-25ºC	Total > 260 VOC, 107 VOC all cars
9	PL	< 1 month	Before 2013	Outside, ambient	18.9-23.8ºC	Total 228 hhv. 200, 105 VOC all cars
5	PL	< 1 month	2012	Inside, ambient	20-26ºC	18 VOC^T and top-10 VOC identified
10	PL	< week	Before 2013	Outside, ambient	15ºC	BTX^T
4	PL	new	Before 2012	Outside, ambient	25ºC	144-192 identified VOC and TVOC
23	IT	< year	2007	Outside and inside, ambient, parking, driving	varied	16 VOC^T; phthales, aldehydes
1	JP	1 day (to 3 year)	1999 (2002)	Outside, ambient	30-35ºC	162 VOC, SVOC and formaldehyde
101	JP	< 3 years	2004	Outside, ambient	19-35ºC	Median value 101 101 used cars; VOC
101	JP	< 3 years	2004	Outside, ambient	19-35ºC	Median value 101 101 used cars; VOC
4	TW	< months	2004	Outside, ambient	25-32ºC	12 VOC^T
37	CN	1.5 months	2009	Outside, ambient	35ºC	7 $VOC^T; TVOC$
3	CN	1 new, 2 used	2007	Chamber, ambient	25ºC	Top 20 VOC; TVOC
3	CN	< 1 month	Before 2015	Outside, ambient	24/29/35ºC	5 VOC^T, 3 aldehydes
2	DE	1 month, 3 years	< 2007	Chamber, parking	65ºC	47 VOC, 6 aldehydes
6	DE	New; 20, 40 days	Before 1996	Chamber, parking	65ºC	VOC, aldehydes, phthalates, amines, nitrosamines
6	AT	New	2005	Outside, parking	60ºC	Sum VOC, Formaldehyde; phthalate
2	US	<6 months, 1 used	2003	Outside, parking	63ºC	Top 10 VOC and TVOC

Most of the studies were carried on outside, in ambient mode and in normal temperature about 15-35ºC. Three studies were conducted in chamber, where the temperature, humidity, supply of filtered air, airflow, as well as velocity of the air outside the car is controlled. Four of them were in parking mode with elevated temperature to over either 60 º C, which indicates the sun, when parked outside, or lighting of lamps, when parked in chamber.

Generally, there are three types of removal processes of volatile organic compounds from the air, physical, chemical, and biological. The first type, sorption on the relevant materials combined with the accumulation of eliminated from the vapour phase compounds, without changing their properties. The second type is the chemical reactions leading to conversion of the other connections, preferably in simple compounds, not cumbersome, such as carbon dioxide and water [5].

The basis of the second type of process is that in the given conditions (especially oxygen concentration in the air), these compounds are thermodynamically unstable and only kinetic considerations prevent them to transmit in the equilibrium connection (having the dominant carbon dioxide and water carbon portion) [5].

A third type of process of the removal of volatile organic compounds is biological one. In fact it

^{T} – analysis of selected substances

a specific type of chemical catalytic, performed by the organism, which reacquire in this way the energy from the environment. This is a valuable method, which, however, in some conditions seems hardly useful because of the slowness of the process and the necessity to ensure growth gathering of microorganisms suitable for the conditions [5].

Given that under typical operating system removal of volatile organic compounds from the vehicle passenger compartment should not lead to the accumulation of these combined connections (with the threat of their uncontrolled release), should instead be resistant to the operating conditions (including insensitive to temperature fluctuations) [5].

In the present study, catalytic processes are considered. Additionally, taking into account that the heat balance of the vehicle passenger compartment should not be disordered, particular attention was given to the photocatalytic processes, and among them those which utilizes titanium oxide, (TiO_2) [5].

TiO_2 occurs naturally in three forms, as tetragonal rutile, tetragonal anatase, and orthorhombic brookite. Of these, particularly anatase has a high catalytic activity (in some crystallographic planes), although the presence of rutile in a sample increases its catalytic activity.

In practical applications, it is crucial to provide the TiO_2 nanoparticles into the stream of gas (air). It this case a typical porous material can be used, such as silica, alumina, zeolites or activated carbon where the TiO_2 was applied as a coating of emulsion paint of acrylic type [5].

2. Photocatalytic reactor in vehicle ventilation system as effective solution for VOCs removal

Ventilation is a process of air exchange between inside and outside of car cabin. It has a significant effect on dynamics of transporting pollutants from:

– outside into cabins,
– surfaces of different interior fittings.

In the Fig. 1, it can be seen the typical air pollutant species, their sources and transportation of air pollutants under different ventilation settings.

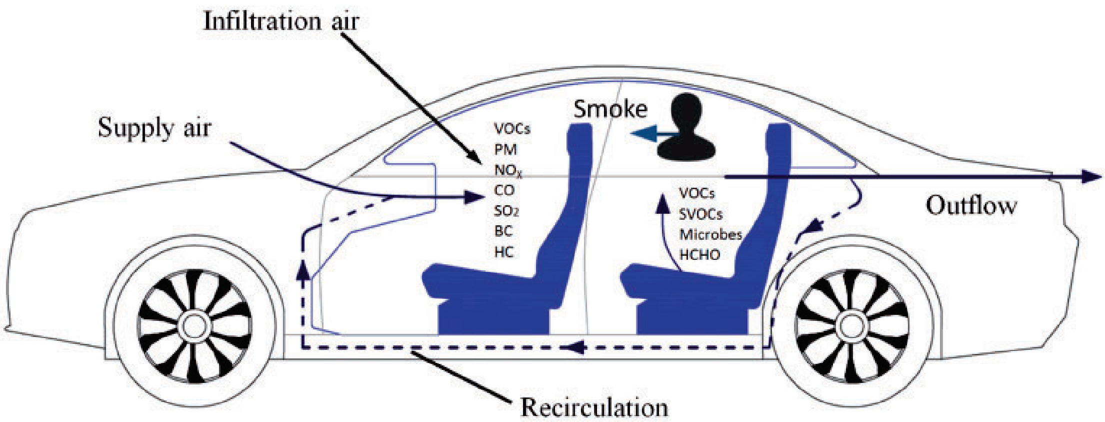

Fig. 1. Schema of sources of air pollutants in car cabin [3]

In literature more authors and test proving, that emission of VOCs from interior materials depend on the airflow and air velocity in the cabin, can be found. Wensing experimented, that during driving with a high speed provide significantly higher airflow in the cabin than when driving with lower speed. You and others found a correlation between the concentration of TVOCs and the airflow in the cabin. The correlation is a function of the air velocity in the surrounds. Increase of air velocity from 0.1 to 0.7 m/s results in increase of the airflow rate from 0.15 to 0.67 h^{-1} and decrease of TVOCs concentration from 1780 to 1201 $\mu g/m^3$. The level of TVOCs may differ up to about 50% depending on the wind and air velocity in the surroundings of the vehicle and moreover on the effect of the airflow from the vehicle's ventilation system [4].

The aim of the scientific cooperation between Dr.Schneider Automotive Polska and the Wroclaw University of Science and Technology (WUST) is research on innovative (international range), product development – photocatalytic reactor characterized by Volatile Organic Compounds (VOCs), especially benzene, toluene and xylene (BTX) removal properties.

3. Test station

In order to simulate 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 the 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 HVAC system, than wormed up or cooled and directed back again to the vehicles cabin.

Before execution of the experiment, the cabin is set to be filled with pollutions. In the case of laboratory station, the pollutions are produced by a power generator supplied with gasoline. Such a solution guaranties free moderation of the pollution amount introduced to the cabin, hence allow performing a variability of experiments. The interior of the vehicle was deprived of most of materials capable of accumulating the compounds related to exhaust gases directed to the cabin. It was found that the compounds accumulated in such material (for example in sits, headlining or, material on side doors) are gradually released which resulted in emissivity indications during verification tests. Ultimately the interior of the vehicle constitutes only non- fibre texture elements.

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 sat 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. 2. Whole experiment is adjusted in order to consider full gas exchange during one cycle. At specific moments, the atmosphere in the cabin is going to be sampled by means of the probe.

The test parameters like airflow, temperature, and time sets were adjust to real drive conditions (based on Dr.Schneider and WUST own researches):

- temperature (x_1=17ºC to 28ºC). The photocatalysis process can alter when occurring in various temperature. One of the main function of HVAC system is the ability to moderate temperature inside the cabin, thus this factor could not be neglected. The range of the temperature was set for the minimal and maximal which can be adjusted in standard HVAC system,
- flow (x_2=2 m/s to 8 m/s). Every HVAC system provides the possibility to alter the flow rate directed to the cabin. The flow is usually controlled by changing the set of a blower switch. For the sake of this research, the minimal and maximal flow rate corresponding to the switch adjustments was measured by means of anemometer. The first adjustment of the blower switch corresponds to the flow rate of 2 m/s, and the last (third) adjustment of the switch corresponds to 8 m/s,
- time (x_3=2 min to 6 min). The time of the purifying process has a tremendous importance in photocatalysis. The first sample was taken 2 minutes after pollutions implementation to the car cabin in order to ensure adequate mixing and equal distribution of polluted air. The maximal time (6 minutes) corresponds to approximated time of one full circulation of the air through the HVAC system. It therefore, constitutes one full process of air exchange. Of course, this time vary with respect to the intensity of flow. However, considering relatively little difference of maximal and minimal flow rate the time of one cycle of air exchange does not vary significantly.

Samples were collected by YEARS aspirator, model ASP-3 II, flow rate adjusted to 30 dm^3/h, the amount of gas collected is 10 dm^3. The gas was absorbed on active carbon Anasorb® SKC CSC. Activated carbon is poured into a glass tube of 5 cm^3 and later it is emerged in 2 cm^3 of carbon disulfide. Volatile organic compounds 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-WAX ms 30 m × 0.25 mm ID DF: 0.25 um. The work was performed at the set temperature of the column 373 K (110ºC), the dispenser 523 K (250ºC) and detectors 423 K (150ºC). YEAR's aspirator, model ASP-3 II, flow rate adjusted to 30 dm3/h, the amount of gas collected is 10 dm^3, collected samples. The gas was absorbed on active carbon Anasorb® SKC CSC. Activated carbon is poured into a glass tube of 5 cm^3 and later it is emerged in 2 cm^3 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 solution is gathered from above of the carbon layer. Gathered sample is injected into the chromatograph. Compounds designated as "residuals" have been converted to the concentration corresponding to n-pentatonic acid. 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).

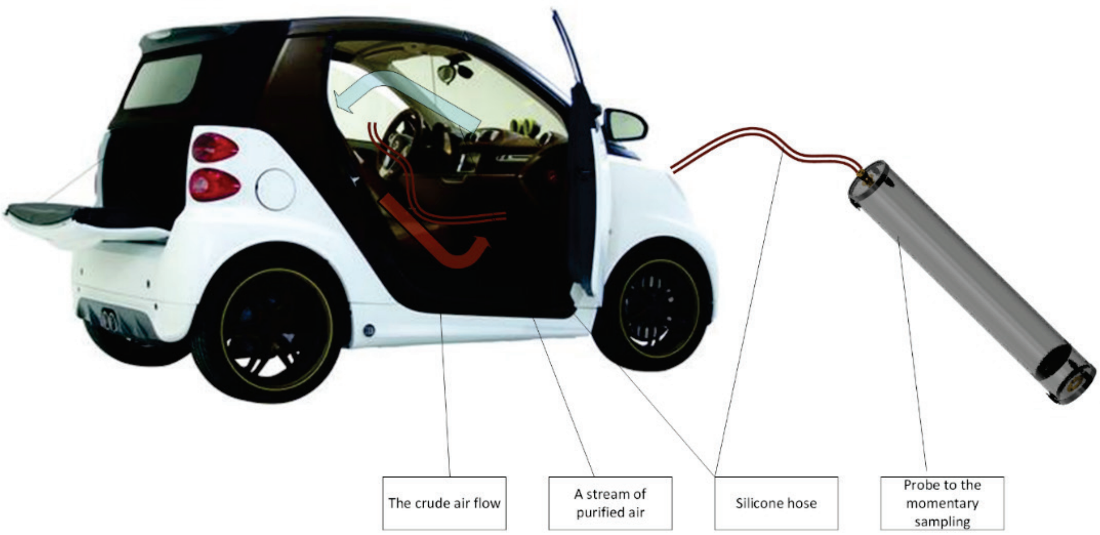

Fig. 2. Schematic representation of the experiment procedure

3. Results of the experiment

The photocatalytic reactor was implemented to the test station. The results of BTX reduction are shown in Fig. 3. As it can be seen the reduction of each compound proceeds differently. The most significant difference is visible in the case of benzene. It appeared that in the case of benzene the minimal reduction occurs approximately in the centre of the map. The minimum in this case exists at approximately temperature of 21°C, airflow of 3 m/s and after 3.5 minutes of the station operation. As anticipated, the maximal effectiveness of BTX reduction exists on the edge of a triangle map, which corresponds to minimal temperature, and the longest time of operation. It was found during previous research that the photocatalysis is the most efficient in the lowest temperature. Furthermore, it is obvious that the longer time of purifying process the greater share of BTX shall be reduced. However, the local optimum in the case of benzene was not anticipated. For this reason the tests was repeated at the condition at which the minimum occurred. The results of these verifications proven such behaviour of benzene.

A summative BTX reduction is shown in Fig. 4. It appears that in this case the local minimum of benzene was dominated by the reduction of toluene and xylene. In consequence, the ternary responds surface indicates maximal effectiveness in BTX reduction at the lowest temperature and the longer time of exposition. Such a behaviour was anticipated basing on previous research.

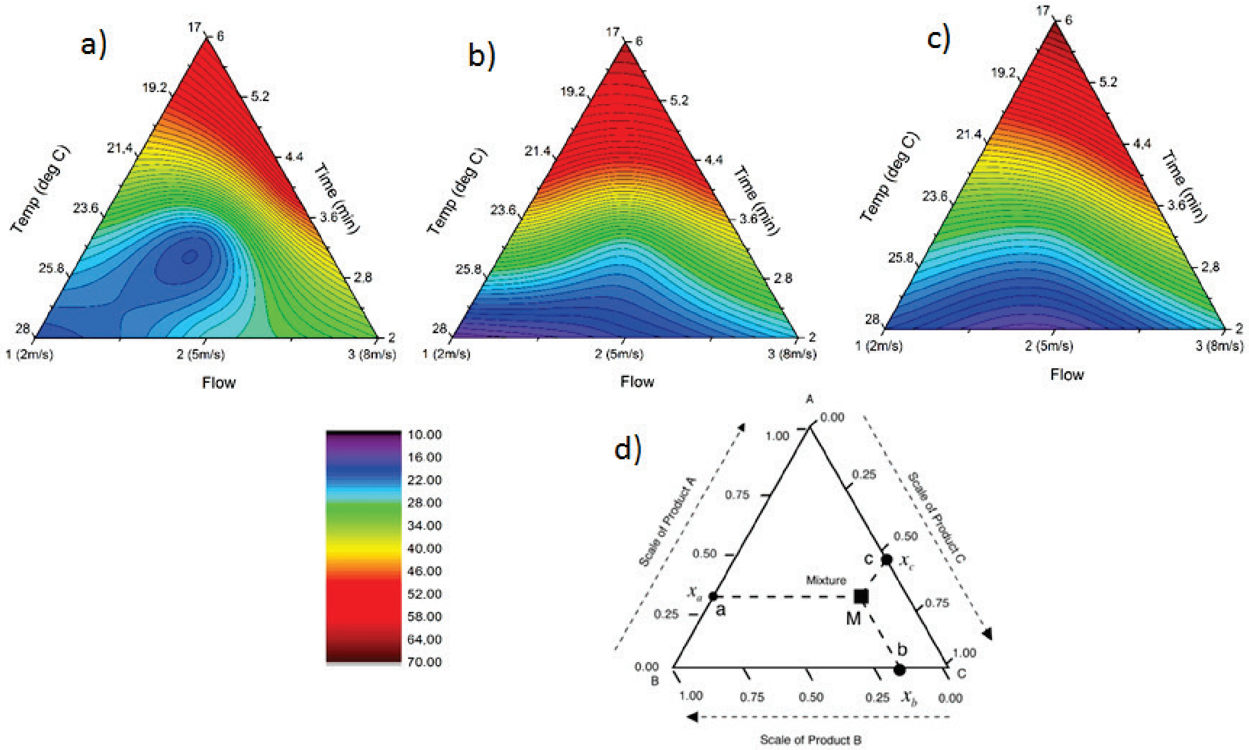

Fig. 3. Ternary responds surfaces for BTX percentage reduction: a) benzene, b) toluene, c) xylene, d) explanation of ternary mixture maps

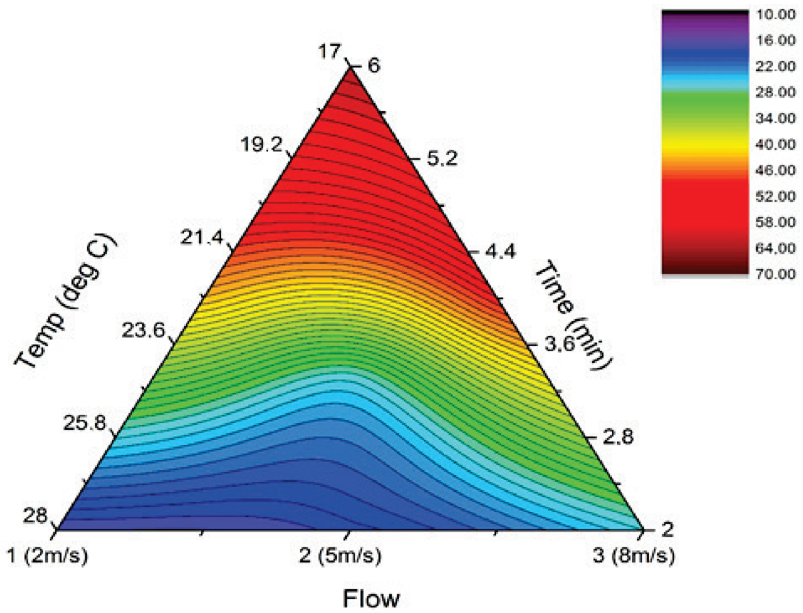

Fig. 4. Ternary responds surfaces for summative BTX percentage reduction catalytic agent mixed with the adhesive gel

The influence of each input factor on the BTX reduction is presented in detail in Fig. 10. The figure contains the percentage share of an input factor (x-axis) and the approximated value of BTX reduction. Three colour lines represent the change of a BTX reduction with respect to the change of each input factor. As it can be seen the effectiveness increases with an increase of time of the experiments (green line). The reduction of BTX decreases with increase of temperature. Importantly, at some point the change of flow becomes invalid.

4. Conclusions

1. Volatile organic compounds, especially benzene, toluene and xylene are substances responsible for many civilizational diseases (including cancer)
2. The problem of in-cabin air pollution by VOCs is important to solve because of high human exposure (public health concern)
3. Cooperation between Wroclaw University of Science and Technology and Dr. Schneider Automotive Poland effects of new product development: VOCs removal photocatalytic reactor for vehicle ventilation system.
4. The BTX reduction effectiveness was subjected to in-depth analysis. The results showed significant difference not only on maximal BTX reduction but also in the pattern of response surface. In some tested parameters, the hazardous compounds were reduced for almost 70%.
5. The photocatalytic reactor seems to be prospective solution for air quality improvement in any vehicle cabin.

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