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Application of low temperature plasma environment for reduction of selected carcinogenic compounds in asphalt industry off-gases

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Bitumen, a by-product of oil-refining, is mainly used in paving and roofing. In paving operations, bitumen is heated and mixed with mineral aggregates. The use of recycled materials and industrial by-products in asphalt mixtures is increasing. Hot bitumen (130–200 °C) emits vapours and aerosols (fumes) that contain various compounds, including polycyclic aromatic hydrocarbons (PAHs) and sulphur-containing organochemicals. Bitumen fumes contain 1–5-ring unsubstituted PAHs, alkylated PAHs, heterocyclic PAHs and terpenoids which may have mutagenic and carcinogenic activities. Additionally some of these compounds are odour causing compounds. One of the effective ways of biochemical and chemical deactivation of odour causing and carcinogenic compounds is application of ozone and low temperature plasma environment. In these conditions the most stable organic compounds including monoaromatic and polyaromatic compounds can be oxidized. In the experiment degradation of volatile organic compounds from asphalt industry, including odour causing compounds, was conducted. With this end in view a special plasmachemical reactor was developed. In analytical part solid phase microextraction and GC-MS was applied for identification and quantitative measurements. It was observed that compounds containing heteroatoms were easily degradable than compounds containing condensed rings and aliphatic substituted benzene rings. The preliminary results of our investigations showed that methods utilizing ozone and/or low temperature plasma environment could be successfully applied for degradation of odour causing and carcinogenic compounds emitted in off-gases originating from asphalt industry. These methods can be however applied in specific conditions, after precise determination of process parameters and identification of the formed products.

1. Degradation processes of carcinogenic compounds in the low-temperature plasma environment

In recent years there has been growing interest in the application of low-temperature plasma methods (non-equilibrium) for the degradation of organic air pollutants (Kuwahara et al., 2011; Monani, 2007; Ogata et al., 2001; Shi, 2006). This consist of the use of reaction environment in which a crucial role is played by highly energetic electrons. The atoms are the carriers of energy which is utilised to initiate chemical reactions. The source of electrons is electric discharges. Energy of electrons and their effect depends on process operating conditions (Ozonek and Fijalkowski, 2007).
Reactions occurring in low-temperature plasma environment can be divided into two groups. The first one contains the reactions resulting from direct influence of electrons on carrier gas molecules. The

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second group includes the reactions between the obtained molecules and the components of the substrate gas which give rise, among others, to ozone formation (Ozonek and Fijalkowski, 2007, Kogelschatz, 2003).

Conditions prevailing in the reaction environment have a fundamental impact on the energetic efficiency of the degradation/oxidation process of organic compounds. The nature of microdischarges, their intensity and amplitude highly depend on the size of the discharge gap, gas pressure, its composition, humidity and temperature, as well as the type and thickness of dielectric and the electric power supply parameters (Morgan, 2009; Kim-Yang et al., 2005).

The main property of low-temperature plasma is the possibility of causing non-equilibrium reactions in ambient temperature. Highly energetic electrons generated in plasma environment are able to effectively degrade pollutants present in off-gases. These electrons provide the energy sufficient to break the bonds of practically every gas molecule as a result of inelastic collisions with pollutant molecules. As a consequence of these reactions, under the influence of ionisation, excitation and dissociation, secondary electrons as well as highly reactive particles (radicals, ions and molecules such as ozone) are also formed. These formed particles being in transition state also affect the conversion degree of pollutants found in effluent gases. The energy of electrons in low-temperature plasma fluctuates from 1 to 10 eV which ensures the excitation of atoms and molecules as well as influences the breaking of chemical bonds.

The main chemical mechanism of the degradation of pollutants and the reaction stages with the participation of active particles that are initiated in low-temperature plasma environment are presented below (Bai et al., 2009):

$$e + O_2 \rightarrow {}^{\bullet}O + {}^{\bullet}O \quad (1)$$
$${}^{\bullet}O + O_2 \rightarrow O_3 \quad (2)$$
$$e + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H \quad (3)$$
$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (4)$$
$$e + X \rightarrow {}^{\bullet}X \quad (5)$$
$${}^{\bullet}X + X \rightarrow \text{products} \quad (6)$$
$${}^{\bullet}O, {}^{\bullet}OH, O_3, H_2O_2 + X \rightarrow \text{products} \quad (7)$$

The efficiency of compound degradation in low-temperature plasma environment depends mainly on: i) capability of generating a large amount of ${}^{\bullet}O$, ${}^{\bullet}OH$ radicals and ozone; ii) rate constants for the reaction of pollutant molecules (odorants) with reactive particles.

All types of devices that make use of electric discharges for the generation of low-temperature plasma operate on the same principle: the energy of electric discharge is utilised to form highly energetic electrons. In the presence of atmospheric pressure the electrons rarely collide with pollutant molecules, however when colliding with the molecules of primary gas (containing pollutants) they form radicals with much longer average lifetimes. These radicals react with exhausted molecules of primary gas which ultimately produces more biodegradable and less carcinogenic compounds (Shi et al., 2006).

2. Experimental part

The research on degradation of carcinogenic compounds produced in bitumen mixing plant located in Lublin, south-eastern Poland, was conducted with the use of plasmachemical reactor of own construction (Ozonek et al., 2008). Before proceeding with laboratory tests, an identification of the odorous compounds arising in the course of technological process by means of chromatographic analysis was made (Cai et al., 2006). The samples of odorous gases were afterwards subject to degradation in the ozone and low-temperature plasma environment.

2.1 Materials and methods

A scheme of laboratory stand used in the tests is depicted in Figure 1. The main element of the experimental set-up for the degradation of carcinogenic compounds arising during asphalt production constitutes a plasmachemical reactor with mesh electrodes. The tests were carried out with different gas flow rates through the discharge zone. The reactor was powered from the system of inverter and high voltage transformer operating with the frequency of 1500 Hz and producing sinusoidally alternating voltage up to 10 kV. The measurement of the active power was carried out with the use of Kyoritsu power meter type KEW6310 with the KEW8128 clamp sensor. The concentration of ozone was measured by means of BMT-964 ozone analyzer by BMT Messtechnik.

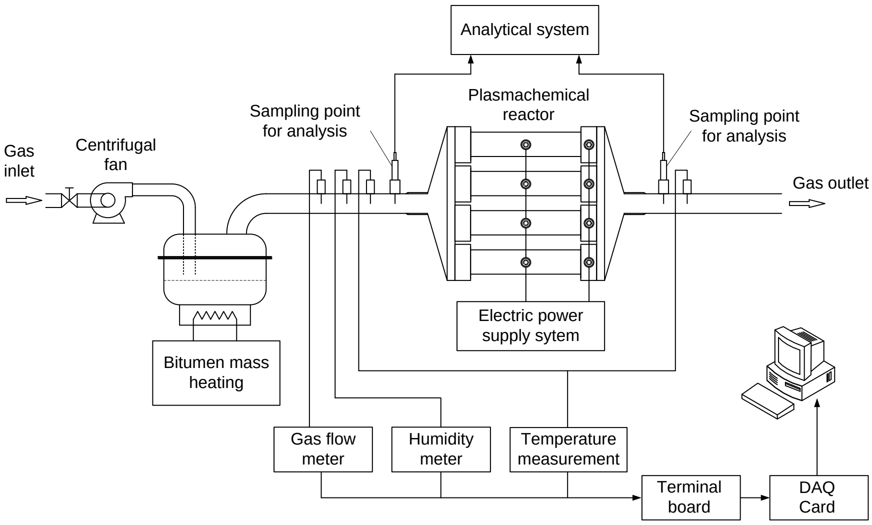

Figure 1: Scheme of laboratory test stand for degradation of malodorous compounds generated in the process of asphalt production under non-thermal plasma conditions

In the experimental set-up several systems are included, namely the electric power supply, the measurement and the analytical system. Conditions prevailing in electric discharge zone as well as the concentration of the generated ozone can be changed through the modification of the voltage powering the reactor. The set-up was equipped with systems for the constant measurement of temperature, humidity, gas flow rate and ozone concentration. The whole experiment was monitored onboard and the measurement data were archived with the use of DAQ card and personal computer.

2.2 Plasmachemical reactor

The structure of the plasma-chemical reactor is of tubular shape. As a dielectric a sodium-silicon glass tube was used with the outer diameter of 37 mm and the thickness of 1.5 mm. The tube was covered on the inside and the outside with mesh electrodes made of acid-proof steel. Single elements were joined in parallel and placed in a casing thus creating a modular plasma-chemical reactor with four discharge elements (Figure 2).

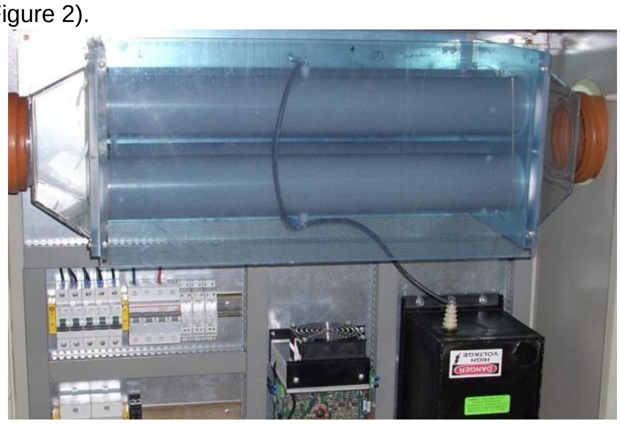

Figure 2: View of the modular low-temperature plasma generator with mesh electrodes

Efficiency and the obtained ozone concentrations are strongly influenced by the conditions prevailing in the discharge zone. The rate of the processes occurring in electric discharge plasma depends on energy density (E_v) defined as a ratio of active power (P) supplied to the reaction zone to the gas flow rate – so-called Becker parameter (Ozonek and Fijalkowski, 2007). In turn, active power of the discharge is one of the key parameters affecting the effectiveness of the generation of ozone and molecules in excited state. The effect the energy density on the obtained concentration of ozone formed in a low-temperature plasma environment is shown in Figure 3.

Measurements were carried out for gas flow rate of $\dot{V}$ = 120 m^3/h. Active power supplied to the reactor was changed at the range of 60÷90 W, the temperature of inlet gas t_{ot}= 30÷40 °C, while the humidity of gas at the inlet of the system was φ = 25 ÷ 40 %. The obtained ozone concentration at the outlet of the reactor varied in function of energy density (Figure 3).

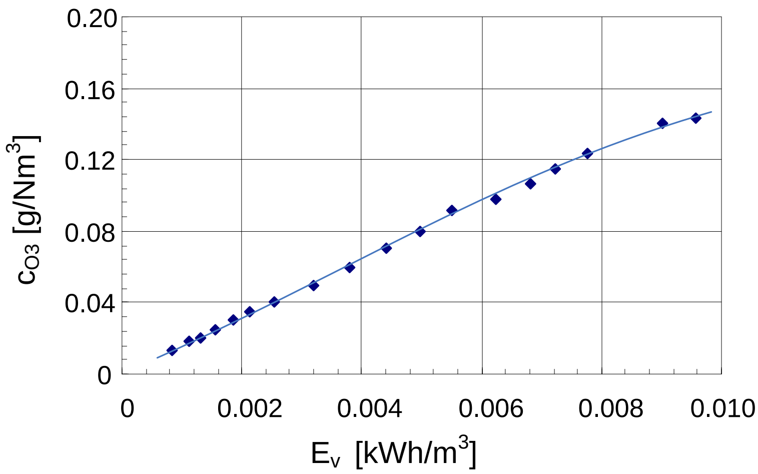

Figure 3: Effect of the energy density (Ev) on the ozone concentration

2.3 Determination and identification of substrates and products of the degradation process

Identification of carcinogenic compounds present in off-gases from bitumen mixing plant was made with the use of gas chromatograph coupled to mass spectrometer Trace Ultra – POLARIS Q, by Thermo Elektron according to the method previously applied by Cai et al. (2006).

For air samples, the five litre Tedlar sampling bags were used. The bags are made of polyvinyl fluoride (PVF) with the thickness of 0.05 mm which is characterized by a very low permeability level as well as low surface-wall adsorption. Extraction of the gas samples was conducted with an SPME method (Solid Phase Microextraction) based on the partition between a mobile phase (gaseous) and a stationary phase coated on the fiber of SPME. In the analysis SUPELCO fibers coated with 100 μm of polidimethylosiloxane (PDMS) were utilised.

During the experiments two kinds of asphalt were applied: the one modified with dicyclopentadiene and the 35/50 asphalt type. The total ion current chromatograms before and after the degradation in low-temperature plasma environment with the participation of ozone as well as retention times of the compounds present in off-gases are depicted in Figures 4 and 5.

Detection of chemical compounds was made on the basis of assigning the retention times to adequate substances. Data for the identification were taken from the NIST 2005 mass spectral library. Determination of the concentration of the substances in question was made on the basis of peak area which represented a particular compound.

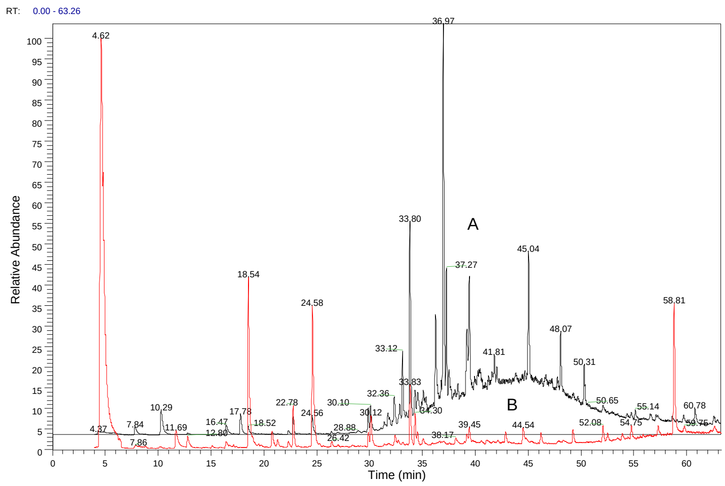

Figure 4: Total ion current chromatogram (TIC) before (A) and after (B) the low temperature plasma treatment of the vapors above the dicyclopentadiene modified asphalt (DCPD) heated to a temperature of about 150 °C

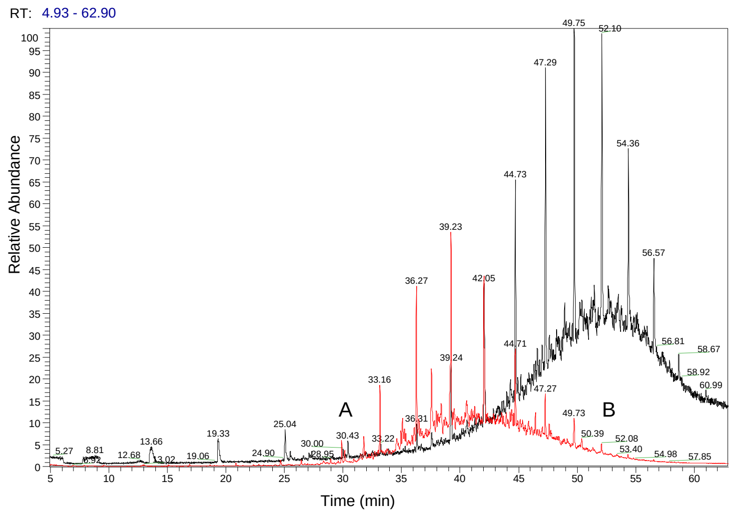

Figure 5: Total ion current chromatogram (TIC) before (A) and after (B) the low temperature plasma treatment of the vapors above the 35/50 asphalt type (SBS) heated to a temperature of about 150 °C

In the analysed samples of effluent gases from bitumen mixing plant alkylated monoaromatic hydrocarbons (styrene, xylenes, ethylbenzene, isopropylbenzene) as well as polycyclic aromatic hydrocarbons (ethylated naphthalenes, anthracene, phenanthrene and their methylated derivatives). Practically in every sample the traces of pyrene were also present.

3. Discussion of the results

Application of plasmachemical reactor containing a discharge element in the form of metal mesh attached to the surface of glass dielectric allowed to obtain technologically interesting results.
Preliminary research results have shown that the method of utilizing ozone and low-temperature plasma environment can be an effective way of treating odour causing and carcinogenic compounds present in effluent gases arising during the bitumen production process. However, these techniques

can be applied only in specific conditions and after conducting precise tests determining parameters of the process and identifying the products formed during the reactions.

The greatest differences between the emission and the degradation degree of organic compounds were observed in the case of SBS and DCPD modified asphalts.

The highest degradation levels were noticed for dicyclopentadiene (asphalt modifier) – 96.3 % and styrene (SBS modified asphalts) – 89.2 %. With respect to samples of non-modified asphalts the highest degradation degrees for bicyclic organic compounds were observed. Moreover, the decrease in aliphatic hydrocarbon chain length was noticed.

It was also observed that compounds containing heteroatoms were easier degradable than compounds containing condensed rings and aliphatic substituted benzene rings.

Application of ozone and low-temperature plasma environment exhibits many advantages, such as low running costs and no wastes.

Degradation degrees of trace pollutants contained in gas mixtures emitted during bitumen production process allow to state that the method could also prove effectiveness as far as full-scale off-gas treatment is concerned.

Acknowledgement

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