

## DECOMPOSITION OF BTX WITH THE APPLICATION OF PRODUCTS OF PLASMA GENERATED IN BARRIER DISCHARGES

*J. Jaroszyńska-Wolińska, A. Mieszawska, K. Pomorska*

Department of Chemical Technology, Technical University of Lublin,  
ul. Nadbystrzycka 40, 20-618 Lublin, Poland,  
e-mail: jwchem@akropolis.pol.lublin.pl

**A b s t r a c t.** In the presented research work model water solutions saturated with Benzene, Toluene, Xylene and their mixtures have been applied. They have been subjected to an ozonization process in static and dynamic conditions. Non-equilibrium plasma has been obtained in a tubular ozonizer made of stainless steel equipped with a glass dielectric. Discharges have been generated by sinusoid current of 5.9 kV voltage (at carrier gas flow rate of 50 L/h). The compound content in the solutions has been subjected to extraction in methylene dichloride prior to the plasma application and after the process completion. Quality and quantity analyses have been performed by means of gas chromatography with the application of flame-ionization detection. In static conditions a decomposition rate reaching 97% has been obtained for Benzene and Toluene. The biggest drop in the hydrocarbon content has been observed in the case of Xylene and the smallest one - in the case of Benzene.

**K e y w o r d s:** ozone , non- thermal plasma, ozone oxidation, decomposition BTX , reduction.

### INTRODUCTION

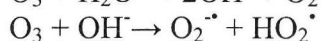
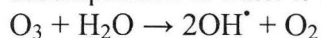
A pollution share of petroleum derivatives in biological degradation of soil and ground waters is big and keeps increasing. Most of the components that get released to the biosphere undergoes biodegradation. However, this way only small quantities of pollutants can get neutralized because the process is comparatively slow. Two main trends can be distinguished among attempted solutions of the problem - it is either procedures aiming at limiting the release of pollutants or elaborating methods for efficient neutralization of the pollutants that got into the environment. There are many methods for removing aromatic hydrocarbons and among them ones that consist in a system of multi-point aeration and air ejection [ 1 ]. Other methods consist in the introduction of microorganisms or intensive oxygenation of ground waters which brings about a development of bacterial flora, or in oxygen biodegradation [ 2 ]. Oxidizing methods seem to be the most efficient. The most important petroleum-derivative pollutants are the following: Benzene, Toluene, and Xylenes. They belong to the group of aromatic hydrocarbons that are

jointly referred to as BTX's as main pollutants hazardous for human health. Biodegradation of Benzene in a water medium can lead to the formation of phenols or catechin and hydroquinone. An application of strong oxidizers can eliminate a formation of intermediate products. Among such oxidizers it is ozone that seems to be the most efficient in neutralizing synthetic and natural organic compounds including the ones that influence taste and smell of water. Its strong selective and oxidizing properties can ensure total destruction of volatile organic compounds with vestigial or untraceable half-products in water at minimum pollutant release to the atmosphere. Recently, aside with a traditional ozone application to the treatment of potable water its other possible applications like sewage treatment, paper pulp bleaching or industrial flue gas cleaning develop to a greater and greater scale. Its dose and a time of contact with water depend on a kind of an oxidized compound and the parameters are experimentally determined. According to [ 3 ] an ozone dose that is needed for a complete oxidization of organic compounds (expressed as solved organic carbon) is 8 g O<sub>3</sub>/ 1 g RWO. Ozone action in processes of organic compound removal can be of two kinds. Depending on a kind of an oxidized compound ozone can either can act as an oxidizer or cause a decomposition as a result of an ozonolysis process. Ozone action on unsaturated compounds like butene makes an example of such decomposition. In the first ozonolysis phase O<sub>3</sub> gets added to the double bonds resulting in the formation of ozonides that subsequently get hydrolyzed as a result of water action. The described changes yield such products as ketones, aldehydes, and hydrogen peroxide (depending on a substrate compound). Ozonolysis causes uncoupling of double bonds in all organic compounds including aromatic ones that include such bonds. Such aromatic compounds can be very frequently found in waters. Both aromatic rings and side chains are a subject to the ozone action. Ozonolysis of BTX's can be run in various conditions and for example when an ozonolysis of Xylene proceeds in the presence of zinc its products are glyoxal, 2,3-butanediol, and pyruvic aldehyde [ 4 ] . Some authors recommend a joint application of ozone and UV radiation to the BTX removal. Unfortunately with that solution, mainly at the application of a small dose of UV radiation, there is a hazard of a formation of side products such as phenols, aldehydes, and carboxylic acid although they are to some extent biodegradable and can be removed on active filter beds.

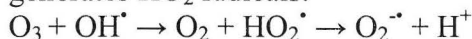
### **Ozone decomposition in water**

Ozone solubility rate in water is comparatively high - 1400 mg/dcm<sup>3</sup> - if to compare it to the oxygen solubility of 70 mg/dcm<sup>3</sup>. Ozone in water solutions gets decomposed much quicker than in the air and a half-life period for ozone in water is from a few seconds up to a few minutes. The process depends mainly on the

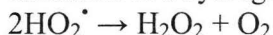
degree and kind of pollution, pH, water temperature, and the initial ozone concentration. In water solutions ozone decomposition runs as two separate processes - autodecomposition and a decomposition caused by hydroxide ions. At pH equal to 7.6 the half-life is 245s and at pH = 10.4 - only 30s. Ozone decomposition in water is of a chain character and runs in a few major stages [ 5 ]:



Hydroxyl radical initiates a decomposition of ozone molecules which generates  $\text{HO}_2$  radicals:



$\text{HO}_2$  radical very quickly reacts with an ozone molecule leading to the formation of a hydroxyl radical  $\text{OH}$  that starts the ozone molecule decomposition cycle again. Two peroxide-hydroxyl radicals can recombine resulting in the formation of a hydrogen peroxide molecule:



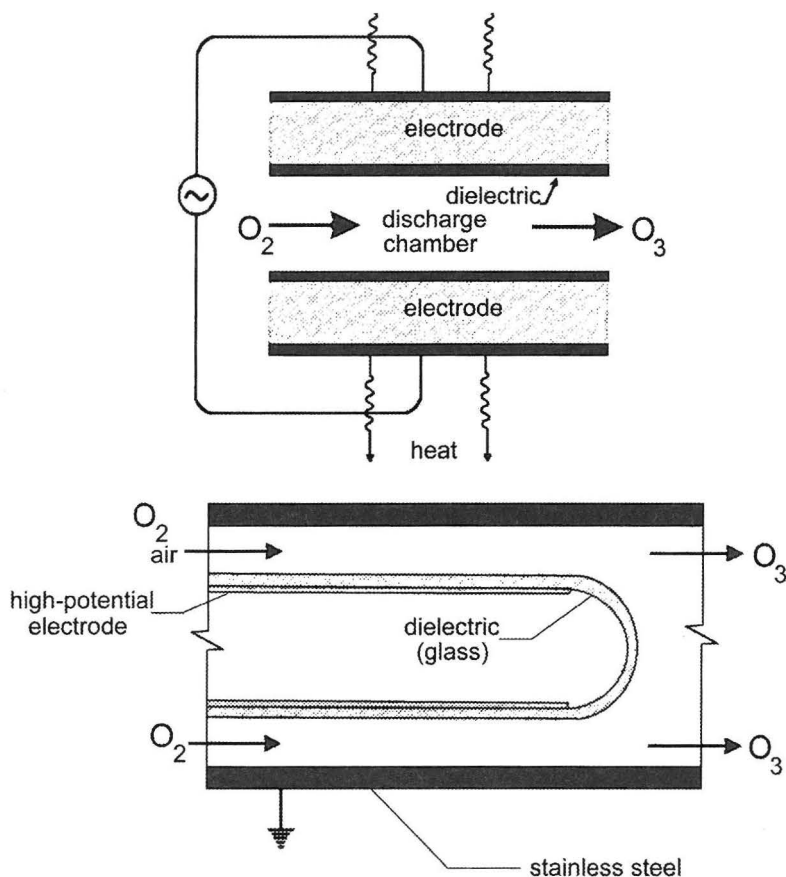
As has been mentioned before, an essential reaction in the process of ozone decomposition in water is a reaction of ozone with a hydroxyl ion which indicates that alkaline medium is advantageous for the process. In water solutions of pH < 3 hydroxyl ions practically have no effect on ozone decomposition [ 6 ]. Hydroxyl radical action on ozone decomposition can be significantly reduced by so called free radical acceptors. Bicarbonates and hydrogen phosphates belong to that group and they increase ozone stability by inhibiting the chain reaction through reacting with  $\text{HO}$  radicals.

Ozone can react two ways with compounds present in water: in a direct reaction of molecular ozone and indirectly by reactions of free radicals that form in the process of ozone decomposition in water.

## EXPERIMENTAL SETUP

In the presented research model solutions saturated with Benzene, Toluene, Xylene, and their mixtures have been applied. Model solutions have been prepared by shaking 1dm<sup>3</sup> of water with single pure compounds of the quantity of 1ml hydrocarbon each time. Solutions prepared this way have been subdued to the decomposition process in static and dynamic conditions. Plasma generation has been performed in a tubular ozonizer, in silent discharges out of a substrate gas - oxygen in that case. The discharge path was the following: inner electrode (high voltage) - dielectric - discharge gap - outer electrode (grounded) and it has been generated by a sinusoidal current of 5.9V voltage. Volumetric intensity of oxygen flow has been 60 L/h. Gas that leaves a discharge chamber aside with ozone can

also contain other components of strongly oxidizing properties as OH radicals or excited oxygen molecules.



**Fig. 1.** Discharge chamber for ozone generation.

A process of decomposition (oxidation) of hydrocarbons has run as a result of passing plasma through a layer of water containing BTX's.

In dynamic conditions a gas has been introduced to model solutions directly after having left the reactor. In static conditions the process has been run by adding water saturated with ozone to mixtures containing BTX's. Samples for an analysis have been prepared by subduing the compound content in the solutions to extraction in methylene dichloride prior to the plasma application and after the

process completion. Quality and quantity analyses have been performed by means of gas chromatography with the application of flame-ionization detection and the "Chromax 2000" software for data collection and processing. The effect of oxidizing agents on BTX's has been determined with taking into account surfaces of the obtained peaks that correspond to a given compound amount in a solution and comparing them to a pattern of control samples.

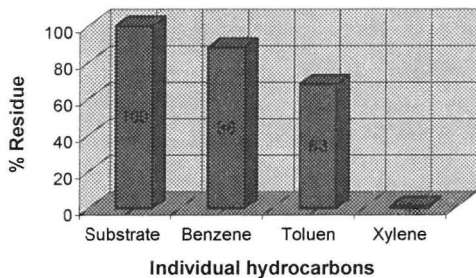
## RESULTS

Benzene, Toluene, Xylene (BTX) and their mixtures have been subdued to the action of oxidizing agents (generated in non-equilibrium plasma) in static and dynamic conditions. In static conditions a sub-stoichiometric dose of ozone has been applied. An efficiency of the generated plasma action on BTX's has been determined by comparing surfaces of the obtained peaks that correspond to a given compound amount in a solution to patterns of extracted control samples. At plasma product action on pure substances in static conditions Benzene presents the smallest rate of reduction - 13%, Toluene undergoes a decomposition of 31%, and Xylene's reduction is almost complete. Figure 2 presents percent residue of individual hydrocarbons resulting from an oxidizing agent action in static conditions as compared to the substrate substance. In dynamic conditions Benzene's reduction rate is 76%, Toluene's - 94%, and in the case of Xylene it is the greatest and amounts to 99%.

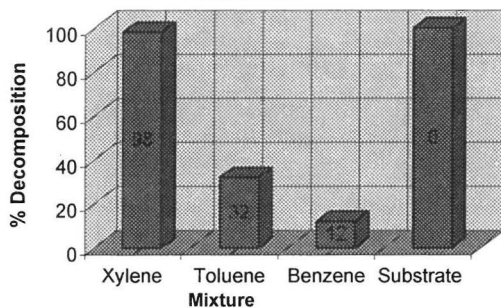
In the case of a Benzene-Toluene-Xylene mixture an insignificant drop of the total BTX content in a solution by 3% on the average has occurred following the oxidation process in static conditions. The amount of Benzene in the solution has decreased by 4%, of Toluene - by 3%, and of Xylene - by 3%. Figures 3 and 4 present a decomposition degree after oxidizing for each of the hydrocarbons in the mixture in static and dynamic conditions.

In dynamic conditions the action of an oxidizing mixture has brought about a drop of hydrocarbon content by ca 88%. Benzene amount in comparison to its initial quantity has decreased by 83%, Toluene - by 92%, and Xylene - by 96%. In a water solution containing a mixture of Toluene and Xylene both in static and in dynamic conditions a much greater decomposition rate of the both hydrocarbons has been observed - on the average of 98%. In dynamic conditions a 99% decomposition of Toluene and a 98% decomposition of Xylene have been found. A nearly complete decomposition of BTX's can be proved by the presence of additional peaks of unidentified compounds aside with peaks of the tested substances in chromatograms. Probably they represent intermediate products of the oxidizing agent (plasma) action on tested substances that are absent from chromatograms of pattern solutions.

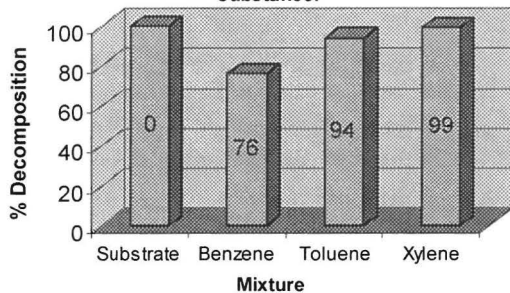
**Fig. 2. Residue degree of individual hydrocarbons in a static conditions as compared to the substrate substance.**



**Fig. 3. Decomposition degree for each of the hydrocarbons after oxidizing in the mixture in static conditions as compared to the substrate substance.**



**Fig. 4. Decomposition degree for each of the hydrocarbons after oxidizing in the mixture in dynamic conditions as compared to the substrate substance.**



## CONCLUSIONS

As it has been stated before, ozone can act on a molecule in a direct way or by the formation of free radicals and it is the reason why a removal of a given substance depends on properties and a structure of the molecule. It can also be assumed that compounds which do not easily enter a reaction with ozone should be removed by free-radical processes at high pH.

The obtained research results can be summerized as follows:

1. A substrate gas after having been passed through a reactor makes an efficient means for the removal of volatile aromatic hydrocarbons (BTX) from a water phase.
2. BTX decomposition in solutions occurs both in static and dynamic processes.
3. In a Toluene-Xylene mixture in a water solution a high reduction rate of 97% has been observed both in static and dynamic conditions.
4. The presence of Benzene in a hydrocarbon mixture significantly reduces the efficiency of the above proposed removal method.
5. Both for pure hydrocarbons and their mixtures the greatest removal rate has been observed in the case of Xylene and the smallest - in the case of Benzene.

## REFERENCES

1. **Nawrocki J., Bilozor S.:** Uzdatnianie wody. Procesy chemiczne i biologiczne. Wyd. Naukowe PWN, Warszawa-Poznań , 2000.
2. **Surgala J., Śliwka E.:** Charakterystyka produktów naftowych w aspekcie oddziaływań środowiskowych. *Chemia i Inżynieria Ekologiczna*, Opole , 1999 T.6 No 8, p.131-147.
3. **Surgala J., Śliwka E.:** Puchowicz A.: Oddziaływania przerobki rafineryjnej ropy naftowej na środowisko. *Ekologia i Technika*, Bydgoszcz , 2001, No 3.
4. **Zieńko J.:** Substancje ropochopochodne w środowisku przyrodniczym. *Ekologia i Technika*, 1996, No 2, p. 4-6.
5. **Jaroszyńska-Wolińska J., Wroński M., Zajac A., Pollo I.:** Kinetics of ozone decomposition in water solution containing phosphoric buffers. *Proc.Reg.Conf.on Ozone Generation and Application to Water and Waste Water Treatment*, Moscow , 1998, p 695-710.
6. **Hoigne J., Bader H.:** Rate constants of reactions of ozone with organic compounds in water , *Wat. Res.*, 1983, p.173-182.
7. **Pollo I., Wroński M., Ozonек J., Wolińska J.**, Dielectric thickness and rate of ozone production, *Polish Journal of Applied Chemistry*, 1995, 39, 503-510.
8. **Jaroszyńska-Wolińska J., Wroński M.:** The influence of high voltage electrode design on electrical parameters of the ozone generator, *Polish Journal of Chemical Technology*, 2002, 4 No 2, p.8-11.
9. **Jaroszyńska-Wolińska J., Wroński., Ozonек., Pollo I.:** Efficiency of an ozone synthesis process realized in ozonizers of various high -voltage inner electrode designs, *Proc.Int.Symp.on High Pressure Low Temperature Plasma Chemistry, Hakone VIII, Estonia*, 2002, 2, p.210-214.

## ROZKŁAD BTX PRZY WYKORZYSTANIU PRODUKTÓW PLAZMY GENEROWANEJ W WYŁADOWANIACH BARIEROWYCH

*J. Jaroszyńska-Wolińska, A. Mieszawska, K. Pomorska*

Katedra Technologii Chemicznej, Politechnika Lubelska,  
ul. Nadbystrzycka 40, 20-618 Lublin, Polska,  
e-mail: jwchem@akropolis.pol.lublin.pl

**S t r e s z c z e n i e.** W badaniach posłużono się modelowymi roztworami nasyconymi mieszaninami benzenu, toluenu, propylobenzenu i ksylenu, które poddawano procesowi utleniania, w warunkach statycznych i dynamicznych, produktami plazmy generowanej w wyładowaniach barierowych. Zawartość związków organicznych przed i po utlenianiu analizowano przy pomocy chromatografii gazowej, po uprzedniej ekstrakcji w dichlorku metylenu. W warunkach statycznych otrzymano 97% stopień rozkładu benzenu i toluenu dla pojedynczych składników. W mieszaninach największy spadek stężenia obserwowano dla ksylenu, a najmniejszy dla benzenu.

**S ł o w a k l u c z o w e :** ozon, plazma niskotemperaturowa, utlenianie ozonem, rozkład BTX, redukcja.