Destruction of molecular compounds in gaseous and liquid medium in microwave discharge plasma

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Abstract. The paper presents the results of experimental studies of molecular destruction in gaseous and liquid medium using microwave discharge plasma at atmospheric pressure. As the gas medium hydrocarbon gas is used, the liquid medium were aqueous solutions of methylene blue and more complex organic compound in the form of humic substances. As a result of the destruction of hydrocarbon gas molecules in microwave discharge plasma new products such as hydrogen, ethylene, acetylene and carbon nanostructured material have been formed. In experiments on destruction of molecular compounds in aqueous organic solutions we used air, nitrogen and argon for plasma gases. It is shown that the process of molecular destruction in aqueous organic solutions in the microwave discharge plasma is based on oxidation-reduction reactions. It is found that the maximum efficiency of removal of organic compounds from the solution occurs when using air as the plasma gas.

1. Introduction

It is known that the gas discharge generates reactive plasma, which is capable of providing the necessary conditions for destruction of molecular compounds and synthesis of unique structures. It finds application in development of new technologies for disposal of waste products, purification of products from pollutants, production of new materials, surface modification of materials, etc.

In recent years there have been intensive studies on possibility of using the microwave discharge plasma in plasma-chemical processes. The choice of this type of discharge is based on the fact that plasma-chemical reactions occur with high energy efficiency due to vibrational excitation of molecules in in nonequilibrium plasma of microwave discharge [1, 2]. This is of a great interest primarily for plasma-chemical processes such as reaction with electron-excited particles, dissociation or degradation of molecular compounds of organic substances.

This paper presents the results of experimental studies of destruction of molecular compounds in the microwave discharge plasma at atmospheric pressure in such medium as petroleum gas, aqueous solutions of methylene blue, humic substances.

2. Experimental set-up

The main element of the experimental setup is a microwave plasmatron. The schematic of which is shown in Figure 1.

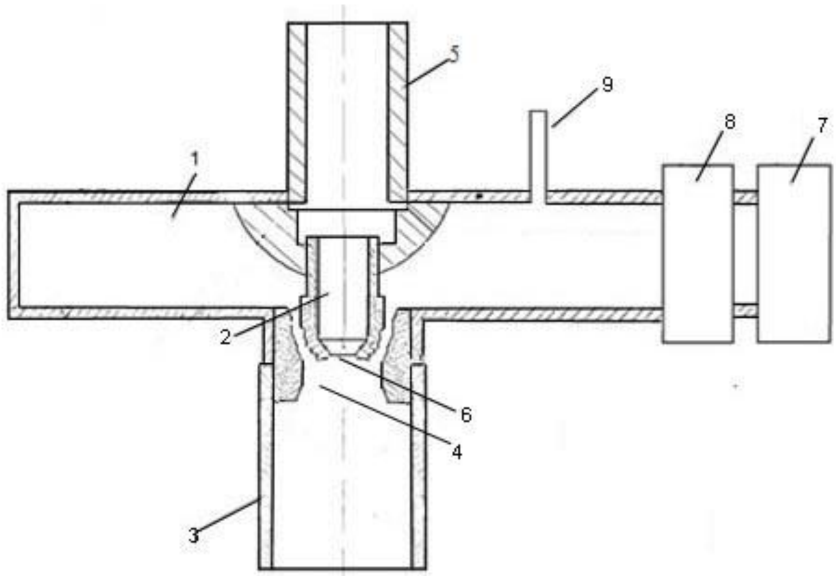

Figure 1. Schematic of a microwave plasmatron
1 - rectangular waveguide; 2 - inner conductor of the coaxial line; 3 - outer conductor of the coaxial line; 4 - discharge chamber; 5 - pipeline; 6 - nozzle; 7 - magnetron; 8 - circulator; 9 – pipe

Structurally, the plasmatron is a waveguide-coaxial junction, consisting of a rectangular waveguide 1 and a coaxial line with a hollow inner conductor 2 and the outer conductor 3, forming a discharge chamber 4. To maintain a stable microwave discharge the plasmatron is provided with an active system of initiation of a discharge, which is described in detail elsewhere [3]. Injection of hydrocarbon gas or aqueous solution into the discharge chamber of the plasmatron is carried out via line 5 through nozzle 6. Power is supplied to the plasmatron from the magnetron 7 with an adjustable output power of up to 2 kW in continuous operation mode with an operating frequency of 2.45 GHz. For breakdown protection of the magnetron a ferrite circulator 8 is used. When working with aqueous solutions the plasma gas is fed into the plasmatron through the inlet 9. The design of the nozzle 6 allows one to spray an aqueous solution, supplied through line 5, in a gas stream similar to an ejector.

The experimental setup works as follows. When working with a hydrocarbon gas, the initiation system of microwave discharge in the chamber 4 is activated first. Then, through line 5 and nozzle 6 the hydrocarbon gas is supplied into the discharge chamber and turns on the magnetron. The microwave energy from the magnetron is supplied into the discharge chamber though waveguide 1 via coaxial-waveguide transition. Near the nozzle 6 due to incident and reflected electromagnetic waves the electric field is increased to the breakdown value. As a result, the microwave discharge is ignited in atmosphere of hydrocarbon gas and nonequilibrium low-temperature plasma is formed. Formation of plasma at atmospheric pressure in hydrocarbon gas proceeds in the absence of oxygen.

When working with aqueous solutions, the solution is fed in the discharge chamber via pipeline 5 through nozzle 6 and the plasma gas is supplied into the plasmatron through pipe 9. In the experiments we studied the following gases: air, nitrogen and argon. The process of microwave discharge and plasma formation proceeds so that the discharge burns in an environment, which contains air and pulverized particles of the aqueous solution.

3. Destruction of molecular compounds in the gaseous medium

The experiments were performed at a flow rate of hydrocarbon gas ranging from 0.4 m^3/h to 1 m^3/h, the level of microwave power delivered to the discharge was varied from 0.8 kW to 2 kW. The degree of destruction of molecular compounds was determined using a chromatographic analysis of gases. Table 1 shows the composition of hydrocarbon gas used in our experimental set-up. Table 2 shows the gas composition after it has passed through the microwave discharge.

Table 1. Composition of the initial hydrocarbon gas

Component	Concentration, %
Methane	93.554
Ethane	3.858
Propane	1.458
Iso-Butane	0.291
Butane	0.262
Isobutyl	0.002
Iso-Pentane	0.027
Pentane	0.013
Carbon dioxide	0.536

Table 2. Composition of the gas after passage through the discharge

Component	Concentration, %
Methane	36.185
Ethane	0.501
Ethylene	1.307
Propane	0.226
Acetylene	2.536
Iso-Butane	0.068
Butane	0.061
Isobutyl	0.000
Cis 2-butene	0.003
Iso-Pentane	0.003
Pentane	0.003
Hydrogen	58.727
Carbon dioxide	0.376

It is seen from Table 1 and Table 2 that in microwave discharge plasma the destruction of the methane and C_{2+} hydrocarbons molecules occurs with the formation of new compounds, such as ethylene, acetylene and hydrogen. Free carbon after discharge settles down in a form of solid particles of carbon material. Analysis of the carbon material using the X-ray diffractometer shows that the material consists of amorphous carbon and carbon nanotubes with a particle size ranging from several nm to several tens of nm.

Figure 2 shows the experimental dependence of the degree of destruction of the gas molecules on the level of microwave power delivered into the discharge. Here, as a parameter, the gas flow rate has been taken. From these results it is clear that the dependence of destruction of molecules on the level of microwave power, delivered into the discharge, has a linear character. The degree of destruction of molecular compounds of hydrocarbon gas increases when adding nitrogen to hydrocarbon gas.

Figure 3 shows the dependence of the degree of destruction K_{distr} of hydrocarbon gas molecules on the relative concentration of nitrogen in hydrocarbon gas β. In [4] authors obtained similar results with methane under the influence of high-frequency discharge. The authors explain this result by a chain mechanism of decomposition of methane molecules, which involves vibrational excitation of nitrogen molecules.

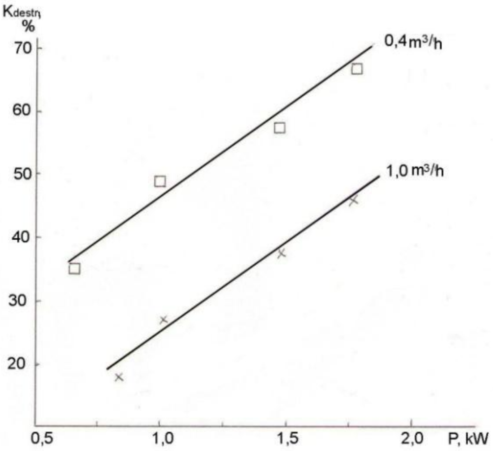

Figure 2. The dependence of the degree of destruction of molecules of hydrocarbon gas on the microwave power level

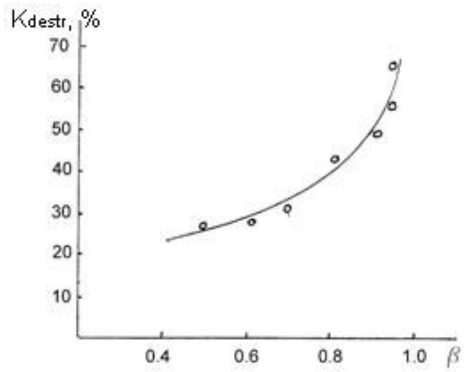

Figure 3. Dependence of the degree of destruction of the hydrocarbon gas molecules on the relative concentration of nitrogen in gaseous medium

4. Destruction of molecular compounds in aqueous solutions

Experiments were conducted at a flow rate of aqueous solution being 3 liters/hour, plasma gas of 3 m^3/h, microwave power level of up to 1.2 kW. In the experiments with methylene blue solution (MB) the concentration of MB in the solution is 4 mg/l, optical density of the solution is 0.35.

Figure 4 shows the optical absorption spectra of the initial MB solution and processed solution with microwave discharge plasma. We observed several absorption maxima in the spectrum: 590nm, 290nm and 200nm. According to the literature [5] absorption at 290nm and 590nm are thought to be due to the chromophore groups of methylene blue and absorption at 200 nm is due to intrinsic absorption of the nuclei of molecules.

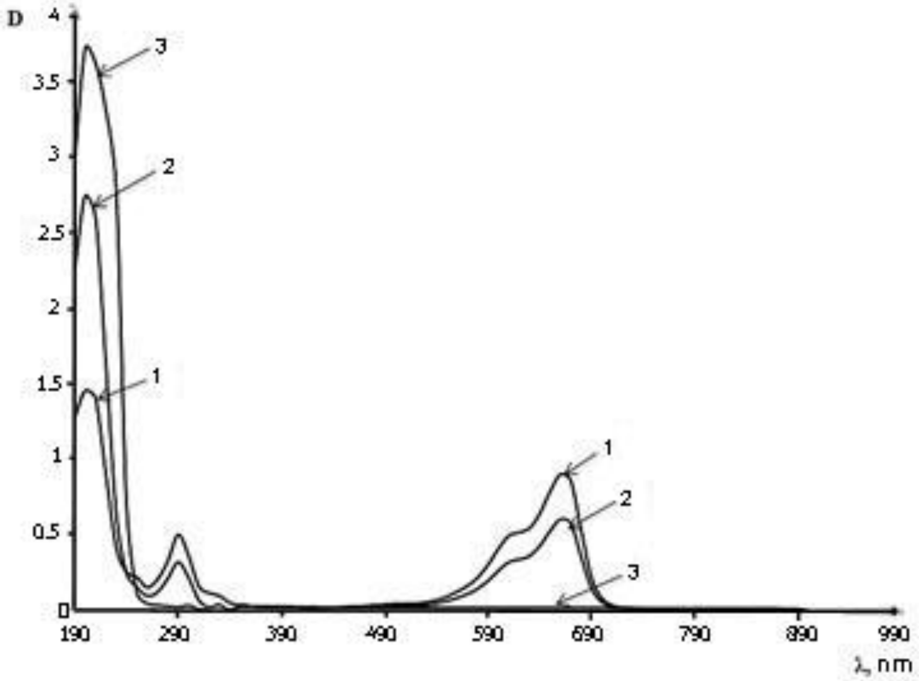

Figure 4. Optical absorption spectra of an aqueous solution of methylene blue.
1 - spectrum of initial solution; 2 - spectrum of the solution after 1 treatment cycle; 3-spectrum of the solution after 2 cycles.

As seen from Figure 4, treatment of MB solution with microwave discharge plasma leads to a reduction in the peak intensity at 290nm and 590nm as compared with the initial solutions spectra (curves 2 and 3). In the area of 200 nm, an increase in the absorption intensity in observed. According to [6], reduction in the intensity of absorption at 290nm and 590nm is due to the destruction of chromophore groups, while an increase in absorption at 200 nm is due to the formation of new compounds according to the schematic shown in Figure 5.

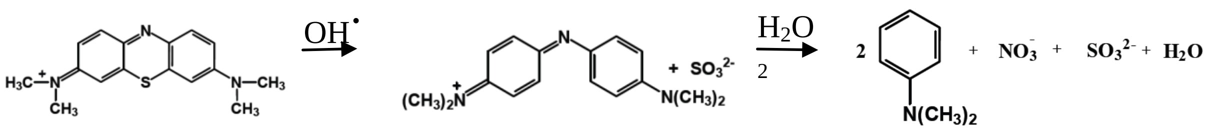

Figure 5. Schematic of the formation of new compounds at the destruction of methylene blue

Along with the change in the absorption intensity there is a decrease in pH. It can be assumed that the reduction in the intensity of the absorption of MB solution is due to the formation of nitrogen-containing compounds, such as HNO_2 and HNO_3 in the solution.

Figure 6 shows the dependence of the decrease in pH (curve 1) and kinetics of the formation of nitrate-ions (curve 2) depending on the number of plasma treatment cycles.

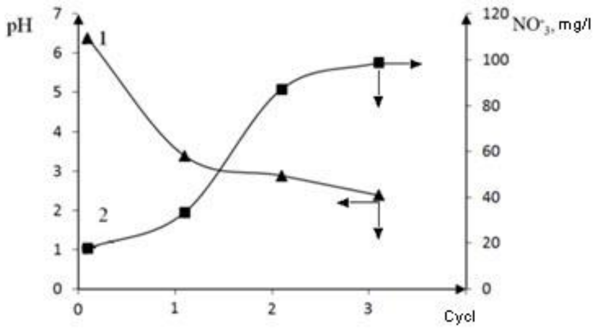

Figure 6. Kinetics of formation of nitrate ions and decrease in pH level

As can be seen in Figure 6, the decrease in pH of the solution is well correlated with the concentration of nitrate ions, which may cause the reduction in the intensity in color of MB.

To exclude the possibility of formation of nitrogen-containing compounds further experiments were performed with argon as plasma gas. Table 3 summarizes the parameters of treated distilled water in air and argon.

Table 3. Parameters of distilled water

Parameters of treated solution	Plasma gas	
	Air	Argon
pH	2.8	6.4
NO_3^-	19.7	0.632
Residual Ozone	2.5	0.71
Permanganate oxidation (PO)	38.6	3.02
Optical density of the solution	0.09	0.11

It can be seen from Table 3 that formation of nitrogen-containing compounds and reduction in pH of the solution is due to the use of air as the plasma gas.

In experiments with aqueous solutions of humic substances we used a model solution with a concentration of humic substances in the distilled water being 8 mg/l, and natural water with a concentration of humic substances being 7.8 mg/l. Table 4 shows the parameters of these solutions before treatment with microwave discharge and after treatment. The plasma gas was air. Each solution was subjected to discharge treatment from 1 to 3 times (1-3 cycles).

Table 4. Parameters of water with humic substances

Tested parameters	Solution of humic substances	Treated and filtered sample		
		Number of cycles		
		1	2	3
pH	5.87[a]	2.83	2.56	2.33
PH, mgO_2/l	2.86[a]	1.07	0.09	0.06
pH	7.10[b]	2.80	2.80	2.80
Fe total., mg/l	8.57[b]	3.30	3.30	3.30
PO, mgO_2/l	2.69[b]	2.10	2.12	2.69
Si, mg/l	11.33[b]	9.40	7.80	6.62
Fe (II), mg/l	$\leq$ 0.05[b]	3.21	3.17	3.23

[a] Model solution of humic substances
[b] Natural water

Table 4 shows that under the action of microwave discharge there a significant change in the parameters of an aqueous solution of humic substances. Reduction in the value of permanganate oxidation indicates a decrease in the concentration of humic substances in the solution. Concentration of humic substances in the solution, which was determined by measuring the concentration of total organic carbon, was reduced from 7.8mg/l. to 2.35 mg/l. The mechanism of destruction of molecular compounds, shown in Figure 5, is also applicable to solutions of humic substances. Under the action of microwave discharge on complex humic substances degradation of their molecular compounds occurs into smaller organic compounds, such as quinoid structures, carboxylic and phenolic compounds, which are difficultly soluble in water. Chemical analysis carried out on the content of divalent iron ions, showed that divalent iron is formed as a result of the treatment by microwave discharge. This indicates the occurrence of redox processes, which were also observed in the experiments with methylene blue.

5. Conclusion

In this study we demonstrated an efficient destruction of molecular compounds in microwave discharge plasma in carbon dioxide and aqueous solutions of methylene blue and humic substances. In the experiments with hydrocarbon gas we obtained the efficiency of destruction of up to 70%. As a result of gas decomposition several substances are formed, such as: hydrogen, ethylene, acetylene, amorphous carbon and carbon nanotubes. The experiments with aqueous solutions show that the main processes that occur during the treatment of aqueous solutions with discharge plasma are the reduction-oxidation reactions. Under the action of microwave discharge plasma on aqueous solution the destruction of complex organic compounds to simple compounds and new elements take place. The results obtained in this study can be of an interest in the development of new environmentally-friendly technologies for utilization of hydrocarbon gases (natural gas, associated petroleum gas, coal mine methane, biogas) and formation of new useful products for cleaning water from organic substances (humic, petroleum products, etc).

Acknowledgement

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