# OPTICAL PROPERTIES AND SOME APPLICATIONS OF PLASMA–LIQUID SYSTEM WITH DISCHARGE IN THE GAS CANAL WITH LIQUID WALL

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Optical properties of plasma-liquid system with discharge in the gas canal with liquid wall and secondary discharge were investigated. We used ethanol as experimental liquid, argon and air – as initiating gas. The emission spectra of plasma discharge in such system were analyzed. Also, we traced change of absorption coefficients in treated liquids. An availability nanoparticle of liquid hydrocarbons in different type of plasma-liquid systems was considered. PACS: 52.77.-j

# **1. INTRODUCTION**

Heterophase plasma-liquid systems based on electrical discharges are of great interest today. Plasma is the source of highly active particles, which are injected through the plasma-liquid boundary into the solution and stimulate chemical transformations there. Typical plasma generators in such systems are electrical discharges with one or two electrodes immersed into the liquid.

The main peculiarity of plasma-liquid systems is an intensive molecule flow from free liquid surface into the discharge volume, which appears because of the evaporation and because of the producing of gaseous products of plasmachemical processes. Therefore plasma generation in such systems occurs under pressure near saturated vapor pressure and higher, when the ionization instability occurs in gas-discharge plasma. Secondary discharges in gas-liquid systems are of great interest. Using of auxiliary discharge inhibits development of the ionization instability in plasma of the secondary discharge, provides high uniformity of parameters on the plasma-liquid boundary and increases a number of external parameters of influencing on the plasma-liquid interaction in real plasmachemical process.

Secondary DC discharge supported by electrical discharge in gas channel with liquid wall in this work. The main feature of such type of the discharge is large ratio of the square of plasma-liquid contact to plasma volume.

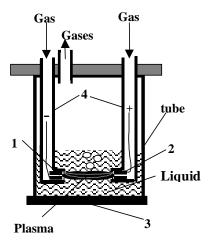
Recently, electrical discharge technique in liquid media has been shown to be a quite simple and inexpensive tool for a synthesis of nanostructures of different materials [1]. Thus, carbon nanoparticles with onion-like structure were synthesized by using a pulsed arc discharge submerged in ethanol. An arc discharge plasma method in hydrocarbon solvents (cyclohexane and toluene) was developed for the purpose of forming tubelike nanocarbons. Amorphous carbon nanoparticles and encapsulated metal nanoparticles were synthesized in liquid benzene by an electrical plasma discharge.

The technique of electrical discharge in liquids offers several advantages because there are no needs in largescale vacuum system (the discharges are performed at atmospheric pressure). Nevertheless, the underlying mechanisms of nanoparticles formation in electrical discharges submerged in liquids have not been completely understood. It should be noted that the carbon nanoparticle-forming material can be supplied by the electrodes as well as in result of the organic liquid decomposition. To meet specific demand of desired applications a controlled production of nanoparticles with a given size, structure, and composition is required [2].

In the present work, an availability nanoparticle of liquid hydrocarbons in different type of plasma-liquid systems with noncarbon electrodes was considered.

# 2. EXPERIMENTAL

The plasma-chemical reactor (Fig. 1) consisted of the vertical cylindrical quartz test-tube supplied by two glass inlet gas pipes (4) with coaxial electrodes (1, 2). The test-tube had a drain pipe at the bottom and an exhaust pipe at the top.



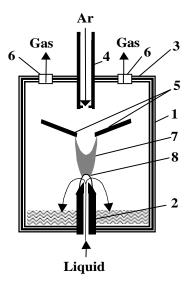
### Fig.1. Plasma-liquid system with secondary discharge supported by electrical discharge in gas canal with liquid wall

The reactor was filled by the work solution; the gas entered into the reactor through the inlet pipes. It formed a counter-flow gas channel with a surrounding liquid wall in the volume between the immersed electrodes (gap  $\sim$ 5 mm) where an electrical breakdown occurred. The gas discharge was powered by the DC source (power  $\sim$ 100 W) or HV source at typical frequency  $\sim$ 7 kHz (power  $\sim$ 30 W). The auxiliary discharge in the liquid was burned between the gas-discharge channel and liquid

wall. The potential of the liquid wall was set by the voltage drop on the secondary discharge powered by the DC source. This source links up via resistance to the one of the electrodes of the auxiliary discharge and to the metallic electrode (3) at the bottom of the test-tube. The liquid in this case had a positive potential. The atmospheric air served as plasma forming and transporting gases; ethanol (C<sub>2</sub>H<sub>5</sub>OH) was used as organic carbon-containing liquids. The gas/liquid flow rates and the discharge time were varied to optimize the process. The gas channel in the system could supply by the vapour flow without gas inputting from the outside under power supply of the discharge more than 50 W.

In the result of the plasma treatment of the test materials in the electro-discharge gas-liquid reactor during the define time (3...10 min), the output products were formed in two phases: (i) liquid phase, and (ii) gas phase. The gas-phase products were taken out from the system into another chamber. The liquid-phase products were collected in the test-tube and analyzed.

Also, treatment of organic liquid for nanoparticles generation was conducted in plasmachemical reactors on the basis of secondary discharge with a "liquid" electrode (Fig. 2).



#### Fig.2. Plasma-liquid system with secondary discharge and "liquid" electrode

Reactor consisted from the glass cylinder (1), which was closed by the cover (3). A free jet of argon ran from the nozzle (4) across two opposite electrodes (5) and formed a bright crescent-shaped electric arc. The exhaust gases came out of a reactor through two holes (6). The current of secondary discharge runs through plasma (7) of arc discharge, a transition layer (8) and a liquid.

The secondary discharge is powered by the DC source. The polarity of secondary discharge was determined by polarity of electrode (2).

Three solutions were used as organic carboncontaining liquids. We used pure ethanol ( $C_2H_5OH$ ) and two mixtures: ethanol with benzene ( $C_6H_6$ ) and ethanol with toluene ( $C_6H_5CH_3$ ), with various concentrations. One type of catalyst (ferrous acetate Fe(CH<sub>3</sub>COO)<sub>2</sub>) was used in all cases.

# **3. RESULTS**

# **3.1 EMISSION**

The research of emission spectra of the electrical discharges in the gas channel with liquid hydrocarbon (ethanol) wall was shown, that their basic components are the lines of hydrogen, system of radical bands  $C_2$ , CH, CN and line of an electrodes material of the auxiliary discharge. The typical emission spectrum of the discharge is given on fig. 3.

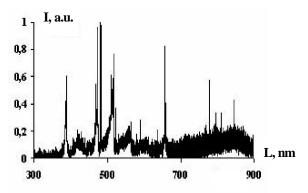


Fig.3. The typical emission spectrum of the discharge in the gas canal with liquid (ethanol) wall

The hydrogen in some regimes of discharges burning was basic component of emission spectra. Atoms of hydrogen, probably, is catalyst for polymerization and formation unsaturated compound of carbon. And the formed compounds can will be distinguished from turning out by usual pyrolysis [3].

In a spectrum the group diffuse bands with main head at 405 nm is observed. Nowadays is convincingly proved, that radiator of these bands is the molecule of threenuclear carbon  $C_3$  [3]. These bands frequently connect to presence of engendering carbon particles, therefore they can represent the certain interest in connection with study of the mechanism of formation polymer nanoparticles in plasma-liquid systems.

Plasma processing of liquid high-molecular hydrocarbons (in this case – ethanol) under normal conditions leads to the synthesis of polymeric particles in our plasma-liquid reactor.

#### **3.2 ABSORPTION**

The plasma treated liquids was investigated by using UV-spectrophotometry. Structural changes in the materials were determined by the comparison of the OAS spectra before and after the plasma treatment. It was found that the absorption band with maximum near 330 nm appears in UV region of the spectra of treated ethanol and toluene (curves 2 and 3 [4] on Fig. 4), which is typical for absorption spectra of fullerenes, dissolved in apolar organic solvents (curve 1 [5] on Fig. 4).

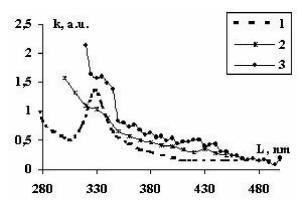


Fig.4. The spectra of treated ethanol – curves 2 and toluene – 3, the absorption spectrum of fullerenes  $C_{60}$ in hexanes – 1

#### **3.3 NANOPARTICLES GENERATION**

In the result of the plasma treatment of the hydrocarbon liquids in the plasma-liquid system with secondary discharge and "liquid" electrode, the output product was formed solid phase – carbon black. The average output amount to 100 mg/h for all regimes with average power imputs ~ 600 watt-hour. Post-process of obtained powder is very difficult and science intensive procedure, which require process refinement.

# CONCLUSIONS

From results of investigation of the plasma-liquid systems with secondary discharge, supported by the auxiliary discharges, the following can be concluded, that the plasma-liquid systems on basis of the secondary discharges in the gas channel with a liquid wall are perspective systems for development of new generation technologies of nano-polymeric particle and reforming of liquid hydrocarbon with the purpose of free hydrogen generation.

#### ACKNOWLEDGEMENTS

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## ОПТИЧЕСКИЕ СВОЙСТВА И НЕКОТОРЫЕ ПРИМЕНЕНИЯ ПЛАЗМЕННО-ЖИДКОСТНОЙ СИСТЕМЫ С РАЗРЯДОМ В ГАЗОВОМ КАНАЛЕ С ЖИДКОЙ СТЕНКОЙ

# Ю.П. Веремий, В.Я. Черняк, В.В. Наумов, В.В. Юхименко, Н.В. Дудник

Были исследованы оптические свойства плазменно-жидкостной системы с разрядом в газовом канале с жидкой стенкой и вторичным разрядом. В качестве рабочей жидкости использовался этанол, инициирующим газом выступал воздух. Проанализированы эмиссионные спектры плазмы разряда такого типа. Прослежены изменения коэффициентов поглощения обработанных жидкостей. Также была рассмотрена возможность получения наночастиц из жидкофазных углеводородов в различных типах плазменно-жидкостных систем.

# ОПТИЧНІ ВЛАСТИВОСТІ ТА ДЕЯКІ ЗАСТОСУВАННЯ ПЛАЗМОВО-РІДИННОЇ СИСТЕМИ З РОЗРЯДОМ В ГАЗОВОМУ КАНАЛІ З РІДКОЮ СТІНКОЮ

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Досліджені оптичні властивості плазмово-рідинної системи з розрядом в газовому каналі з рідкою стінкою та вторинним розрядом. В якості робочої рідини використовувався етанол, в якості ініціюючого газу – повітря. Був зроблений аналіз емісійних спектрів плазми розряду системи такого типу. Досліджено зміну коефіцієнтів поглинання рідин після обробки. Також розглядалася можливість генерації наночастинок з рідких вуглеводнів в різних типах плазмово-рідинних систем.