The Problem of Chemically Active Plasma Nonequilibrium. Review

Chernyak V., Nedybaliuk O., Martysh E., Solomenko O., Fedirchik I., Iukhymenko V., Prysiazhnevych I., Veremii Iu.

[1] *Taras Shevchenko National University of Kyiv, Faculty of Radio Physics, Electronics and Computer Systems, Kyiv, Ukraine, chernyak_v@ukr.net*

[2] *A.J. Drexel Plasma Institute Drexel University 3141 Chestnut Street Philadelphia, PA 19104, USA*

Data on the negative impact of exothermic chemical reactions on the level of non-isothermal plasma are presented. Therefore the transition from the plasma activation of the fuel mixture (fuel/oxidant) to only plasma activation of oxidant leads to a substantial increase in the coefficient of electric energy transformation into chemical energy (α) of produced synthesis gas in hybrid plasma-catalysis system of hydrocarbons reforming (α ≤ 400).

Keywords: non-isothermal plasma, plasma-**c**atalysis system, hydrocarbons reforming

1 INTRODUCTION

Previous studies have shown that in regards to fundamental and applied plasma physics, nonequilibrium plasma-chemical systems, which make the chemical transformations selectively with high energy efficiency are the most interesting. Therefore review is focused on plasma devices, in which not only the electrons temperature but also the vibrational temperature significantly exceed the rotational and gas temperature as a whole. High vibrational temperature in these devices significantly accelerates the direct processes of obtaining useful product, and low translational temperature slows down reverse reactions and provides stability of the products formed in the non-equilibrium plasma. Special emphasis has been made on hybrid plasma-**c**atalysis systems of hydrocarbons reforming. The reduction of energy consumption for the destination product is interconnected with the selective plasma chemical transformation. It is known that achievement of chemical reactions high selectivity and their products purity at plasma chemical systems outlet is possible with usage of non-equilibrium "cold" plasma. Its specific characteristics are: high level of electron energy and concentrations of excited and charged particles at the low gas temperature [1].

High rates of plasma-chemical reactions as a rule are caused by high concentration of excited atoms and molecules in electric discharges. At the same time, the physical and chemical processes in quasi-equilibrium and non-equilibrium plasmas are multi-channel. It is connected with fact that they passed through a large number of vibrational or electron-vibrational levels and there is formation of excited states and excited intermediate products in different quantum states. The presence of deviations from thermodynamic equilibrium of chemically active plasma leads to the fact that the direct and inverse processes are often passed through different quantum states.

So remains the question: how to change the non-equilibrium state level in plasma systems when reactive components are injected to them. We think that it should have the special importance in the case of exothermic processes. Some aspects of this problem are investigated in this paper.

2 THE ENERGY CHANGE OF THE PARTICLES IN CHEMICAL REACTIONS

Traditionally [2] introduced the concept of the reaction path when considering the energy of chemical reactions. So the way reaction of exchange ($A + BC \rightarrow AB + C$) there is a line in the configuration space leading from the initial to the final particles corresponding to the minimum energy of the interaction of atoms and molecules. Cross-section of the potential energy surface along the reaction path is called a profile reaction path. The differences between the potential energies of Q_0 for the initial and final states are characterized by the energy change for the reaction. In particular, the heat of reaction Q is defined as the total change in potential energy Q_0 and change the zero oscillation energy

$$Q = Q_0 + \Delta E_z \quad (1)$$

where ΔE_z is the difference of zero-point energies oscillation source and target molecules $\Delta E_z = E_z - E'_z$. The most chemical reactions have the potential barrier on reaction path.

The occurrence of the energy barrier is required to restructure the electronic structure of molecules involved in the reaction which is reduced to the destruction of the chemical bond BC and the formation of a new bond AB [2]. This energy barrier is named as the activation energy of a chemical reaction.

The using of approach similar to the Fridman-Macheret α-model [3-5] for qualitative analysis of the influence of chemical processes to increase the internal energy of the products indicating an increase in the activation energy of a chemical reaction for exothermic and endothermic processes [6]. Although mentioned earlier the activation energy increasing is much smaller in the case of exothermic processes (Fig.1).

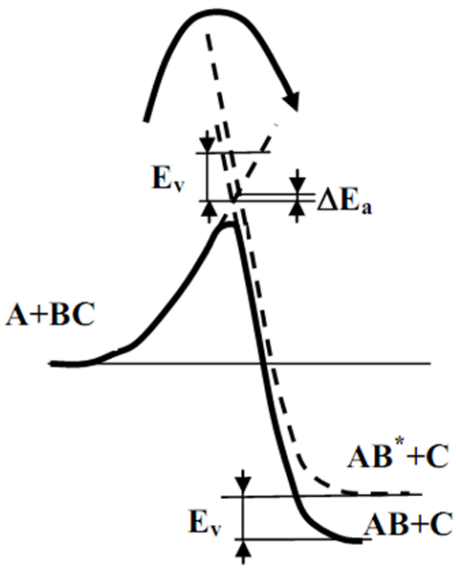

Fig.1: Growth of the activation energy of the exothermic reaction with the excited products in exchange reaction A + BC → AB + C. Solid curve – reaction profile; dashed line represents a oscillatory term, corresponding to an atom C interaction with a vibrationally excited molecule $AB^*(E_v)$

According to Arrhenius law it indicates a lower reaction rate with the internal states of the reaction product pumping compared to the reaction without it.

A large number of data on excitation of the products of elementary chemical processes vibrational levels was obtained in the study of atomic reactions. This research was initiated by Boudart and his colleagues [7]. Theoretical analysis of the energy distribution in reaction products was first implemented by M. Evans and M. Polanyi in 1939 – and based on H. Eyring and M. Polanyi conception of the chemical reaction A + BC → AB + C as three particles A, B and C classical motion as a potential surfaces in one dimension (all three particles are on the same line). M. Evans and M. Polanyi revealed that in the case when the exothermic reaction energy is distinguished at the moment of atom A approaching to molecule BC, basic part of energy is converted into vibrational energy of the reaction product AB. But if this energy is evolved in the process last phase, i.e. when AB and C are divorced, the molecule AB vibrational energy is small and the main part of the released energy takes the form of the reaction products translational energy. The case, realized in practice is determined by the shape of the potential surface i.e. character of the dependence of the potential energy on the distance between the particles [2].

Also the data on chemical lasers [8] analysis indicates that near half of released in the exothermic chemical reactions energy goes into increasing the translational temperature.

When temperature increases there is growth of VT relaxation rate [3] and it also leads to a substantial increase the translational temperature during the exothermic chemical processes.

There are additional factors which increase the translational temperature of heavy component chemically active plasma due to chemical processes [6]:

- the chemical processes in most cases are multi-stage [9],
- direct and inverse processes are took place in statistical systems,
- the low-temperature plasma ability to stimulate chemical processes that do not occur in standard chemical systems. Researches on plasma burning support (S. Starikovskaya and A. Starikovskii 2004, 2006) are shown that non-equilibrium plasma is able to stimulate

the low-temperature fuel oxidation even without the combustible mixture ignition [10]. Kinetics investigations of the hydrocarbons partially-oxidative reforming supported by plasma there revealed simultaneous occurrence of hydrocarbons complete oxidation [11].

- a very high level of energy which is evolved during the exothermic chemical reactions (≥ 1 eV/molecule, f.e. at ethanol full oxidation -13.26 eV/molecule).

All above mentioned indicates that chemical reactions effect on the level of plasma non-isothermality may be extremely high and aimed at reducing the separation among translational temperature and internal states population temperature. It is occurred because the increasing of translational temperature heavy component has its priority in exothermic chemical reactions.

3 EXPERIMENTAL STUDY OF THE INFLUENCE OF CHEMICAL REACTIONS ON THE NON-ISOTHERMAL LEVEL OF PLASMA

Earlier results of studies of the exothermic chemical reactions effect on the level of non-equilibrium plasma of transverse discharge – TD (Fig.2) and the discharge in the gas channel with liquid wall – DGCLW (Fig.3) were presented at [6, 12].

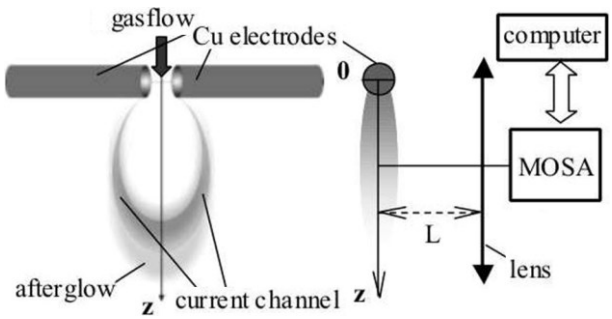

Fig.2: Electric discharge in transversal gas flow

The comparative analysis of plasma parameters of transverse arc and discharge in the gas channel with liquid wall was made for different working gas and liquids (air, distilled water and its mixtures with ethanol). Electron temperature T_e^* of atom excitations, molecule vibration T_v^* and rotation T_r^* temperatures of the generated plasma were determined by optical emission spectroscopy. Discharge realized in air or a lean fuel mixture (Air/C_2H_5OH) in the case of TD, and if DGCLW discharge were implemented in the air channel surrounded by the liquid distilled water and in the air channel surrounded by liquid ethyl alcohol (rich fuel mixture).

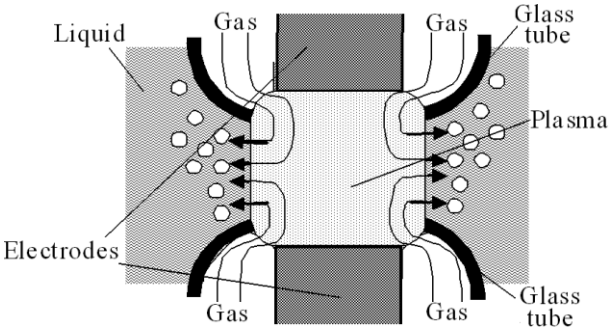

Fig.3: Electric discharge in the gas channel with liquid wall

The main conclusions [6, 12] are:

- TD and DGCLW generate non-equilibrium plasma in the case when working gas is air and working liquid – distilled water. Here the working gas was inactive chemical mixture (dry or moist air).
- Adding fuel to the working gas of plasma system with air leads to a predominant increase of the rotational temperatures and slight increase of the vibrational temperature of the molecules. These temperatures become equal to each other within experimental error. This may indicate that the exothermic reactions reduce the level of the generated plasma non-thermality as a result of additional energy supply for heavy components in the process of complete hydrocarbons combustion.

Adding the final reaction products to the initial reactants can substantially reduce the chemical reactions rates (e.g. extinguishing of the hydrocarbons combustion in the air by adding H_2O or CO_2).

Thus impact on the non-equilibrium plasma by adding CO_2 to plasma-chemical system with a hydrocarbon fuel mixture is in particular interest. These experimental studies have been conducted using the plasma chemical system with an electric discharge with liquid electrode in the TORNADO type gas reverse vortex flow (Fig.4). Detailed description of this setup is shown in [13].

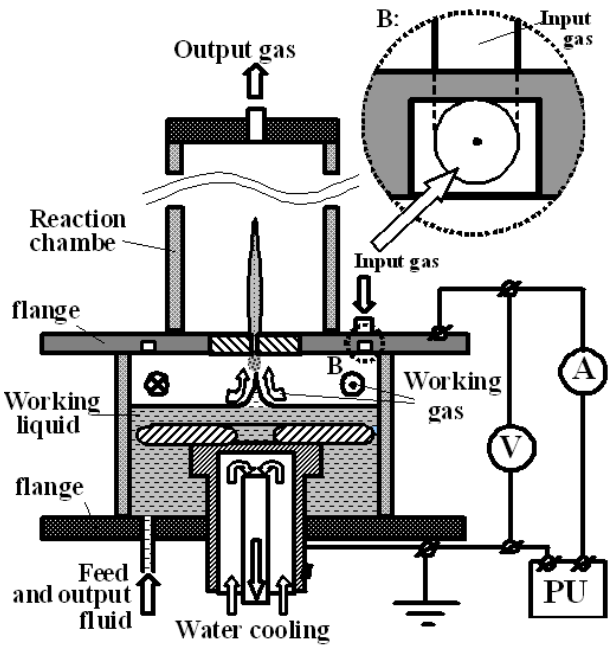

Fig.4: Electric discharge in the reverse vortex gas flow TORNADO type with liquid electrode

The Fig.5 shows the typical dependences of the temperatures of excited electronic (T_e^*), vibrational (T_v^*) and rotational (T_r^*) levels of plasma components from C_2H_5OH concentration in plasma at the constant air flow (55 cm^3/s) current is 320 mA. The stoichiometry of reaction (2) has been performed at ethanol concentration of 4.4 mol/L:

$$C_2H_5OH+0,5O_2=2CO+3H_2+0,14eV/molec. \quad (2)$$

Reaction (2) is endothermic and accompanied by heat absorption. The extra oxygen is formed at its lower values which can stimulate ethanol full oxidation.

On Fig.6 and Fig.7 shows the filling temperatures of excited electronic, vibrational and rotational levels of plasma components for cases when the working fluid is distilled water (Fig.6) and solution of ethanol in water is 1/4 (Fig.7).

In case of using distilled water as the working fluid only a slight tendency to filling temperature of excited hydrogen electronic levels ($T_e^*(H)$) decrease has been noticed from CO_2 percentage increasing in the working gas. Such changes are insignificant given the fact that temperature bias is ± 500 K.

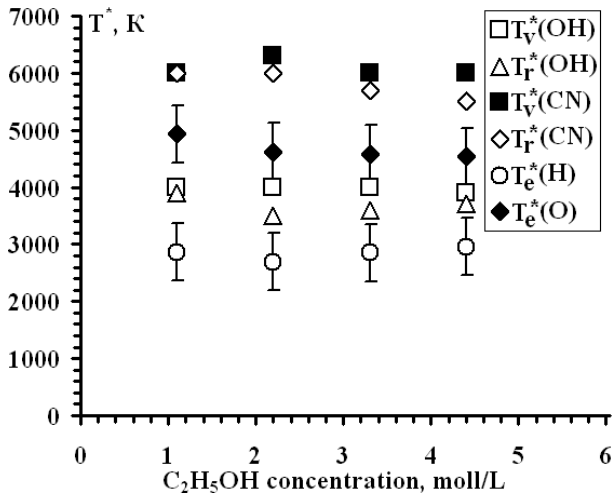

Fig.5: Dependence of T_e^*, T_v^* and T_r^* from C_2H_5OH concentration

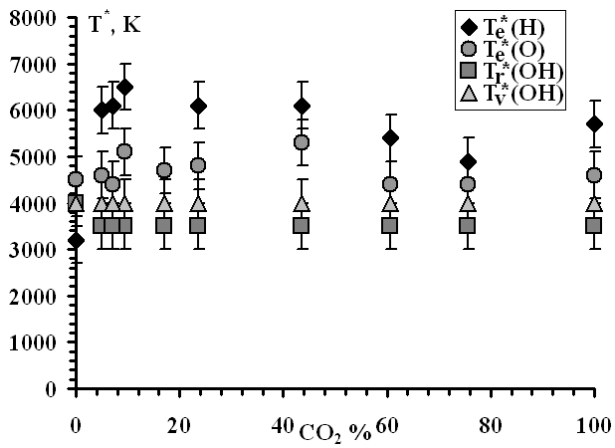

Fig.6: Dependence of T_e^*, T_v^* and T_r^* of interelectrode gap plasma components from CO_2 percentage in the working gas (air/CO_2). The working fluid – distilled water

In case of using the mixture of H_2O/C_2H_5OH as the working fluid adding CO_2 in the studied CO_2/air ration range (I = 300 mA, U = 2-2.2 kV, air flow – 55 and 82.5 cm^3/s, the flow of CO_2 – 4.25, 8.5 and 17 cm^3/s) slightly affects the $T_e^*(H)$ and filling temperatures of excited vibrational molecules levels. The CO_2 concentration increase in the working gas leads to the differences in temperatures of components (reduction of the filling temperature of excited molecules rotational levels).

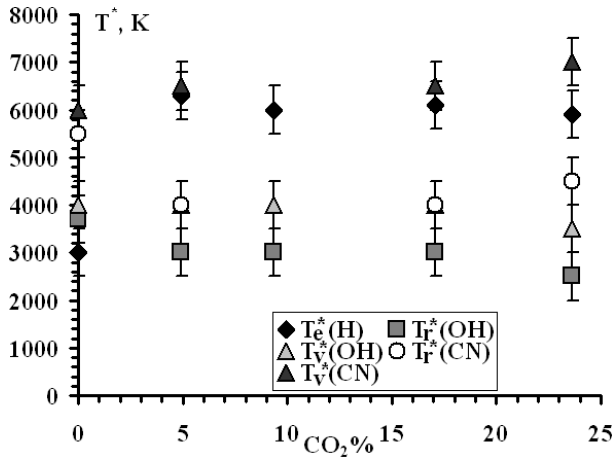

Fig.6: Dependence of T_e^*, T_v^* and T_r^* of interelectrode gap plasma components from CO_2 percentage in the working gas (air/CO_2). The working fluid – bioethanol

4 ENERGY EFFICIENCY OF HYDROCARBONS REFORMING IN PLASMA AND PLASMA-CATALYSIS SYSTEMS

The plasma is a source of chemically active species (radicals, ions, excited atoms and molecules) and particles (electrons, photons) for chemical processes activating. This fact is enabled its use in a variety of technologies. Chemical technologies with plasma are usually constructed exclusively as plasma-chemical systems and hybrid systems. At the last case the plasma devices are fitted into standard chemical system. The first has the feature when plasma is generated either in gaseous medium which is a mixture of starting reactants and some buffer gas (e.g., Ar, N_2) or the starting reactants leading in the pre-ionized buffer gas stream. In the first case as plasma generators usually the various gas discharges are used creating non-equilibrium plasma. The isothermal plasma acts as a heat-transfer medium in the second case. It has the 10^4 K temperature and products rapid quenching is required at the outlet of the reaction zone.

The main features of the hybrid system are the following:

- the reactive species are generated in the plasma and are injected into the reactor where they stimulate chemical processes;
- the cost of electricity on the plasma generation are a few percent of the total process. This effect is called "plasma catalysis" [3]. Combined plasma-catalysis systems are constructed in a variety of configurations this is leaded to plasma and catalysis synergy. One of such configurations is called plasma pre-treatment, when plasma is treated before entering in catalytic reactor. Another configuration, which is called plasma post-processing involves gas processing after exiting catalytic reactor.

Today it can be argued that the problems of hydrocarbons plasma-chemical conversion into synthesis-gas ($CO + H_2$) and other hydrogen-rich mixtures were solved using all known named above plasma-chemical systems and performed for a large number of hydrocarbons. Therefore the particular interest prefers a comparative analysis which is given for the various schemes effectiveness of just this chemical process.

The partially-oxidative and steam reforming and their combinations are most completely investigated. There are following reactions in the case of ethyl alcohol reforming:

$$C_2H_5OH+0{,}5O_2=3H_2+2CO+2{,}65\text{eV/molec}, \quad (3)$$

$$C_2H_5OH+H_2O=4H_2+2CO+3.08\text{eV/molec}. \quad (4)$$

Results of the different methods comparison are given in [14] for plasma ethanol reformer efficiency η by different methods of hydrocarbons conversion into syngas.

$$\eta = \frac{H_2 \times LHV(H_2) + CO \times LHV(CO)}{IPE + \text{fuel injected} \times LHV(\text{fuel})}, \quad (5)$$

where LHV is defined as the lower heating values of each component. IPE is the input plasma energy.

This comparison indicates that selection of plasma reforming method has slight effect on η. But comparison of these methods gives more significant differences between rates of electrical energy transformation into chemical energy (α) by plasma-chemical method and the hybrid one.

$$\alpha = \frac{H_2 \times LHV(H_2) + CO \times LHV(CO)}{IPE}. \quad (6)$$

It follows from the data given in [12, 15], that $\alpha < 3$ for ethanol reforming by plasma-chemical method and $\alpha > 30$ for hybrid plasma-catalysis one [5].

However it should be noted that both components of the fuel mixture (air + fuel) are in-

jected typically to plasma under partially-oxidation reforming by hybrid plasma-catalysis method. Conforming to the data presented in the previous sections it should lead to a decrease in the level of non-equilibrium plasma. That is why the data which are obtained by A. Czernichowski in researches on reforming of glycerol in the hybrid plasma-catalysis system with the low-power (50 W) gliding arc [16]:

- when both components of the fuel mixture are injected to plasma simultaneously the maximum is $\alpha \approx 60$,
- when only oxidant activating by the plasma $\alpha > 250$.

Series of experiments studying the plasma-catalytic reforming of different liquid hydrocarbons was carried out in [17, 18]. The hybrid system based on low power rotating gliding arc with solid electrodes, was used for investigation of the liquid hydrocarbons reforming process. Conversion was realized by partial oxidation. Part of the oxidant flow was activated by discharge. Synthesis-gas composition was analyzed by mass-spectrometry and gas-chromatography. A standard boiler, which operates on natural gas and liquid propane, was used for synthesis-gas burning and calorimetry of its combustion correspondingly.

It was showed that the electric energy transformation coefficient by using this scheme of plasma-catalytic reforming of liquid hydrocarbons into synthesis-gas to several tens times higher ($\alpha \approx 90 \div 400$) than in plasma reforming ($\alpha < 3$ [6]) and higher than well-known analogues ($\alpha \approx 30 \div 40$ [5]); reactor temperature substantially less (about 50 %) as compared with a conventional pyrolysis (450°C°); synthesis-gas component composition varies little and C_2H_5OH conversion efficiency (65÷90 %) in the tested power range. The synthesis gas is efficiently burned in the NAVIEN boiler that runs on natural gas and LPG.

The Fig. 8 shows the coefficient of transformation of electrical energy into chemical energy of produced synthesis-gas (α) and plasma ethanol reformer efficiency (η) as function of the input plasma energy (discharge power) at different LHV_{C2H5OH}.

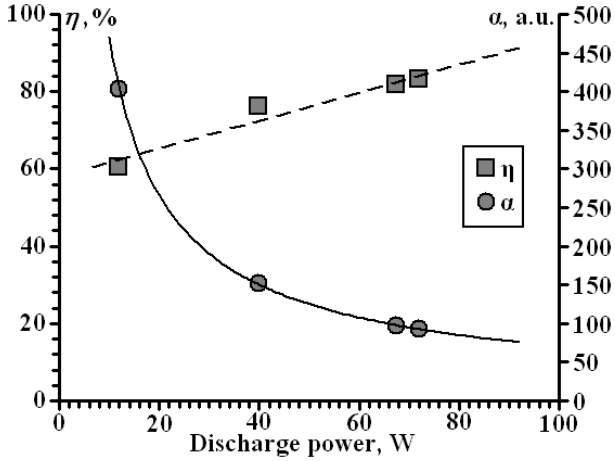

Fig.8: The α and η as function of the input plasma energy (discharge power) at different flow of ethanol (LHV_{C2H5OH} = 8 kW)

5 CONCLUSION

- The effect of chemical reactions on the level of non-isothermal plasma itself can be extremely high and aimed at reducing the separation of the translational temperature from the temperature of energy level.
- Our experimental researches demonstrate that small addition of ethanol into non-equilibrium air plasma leads to full disappearing of difference between population temperature of vibration and rotation states. This difference has initial value in some thousands degrees.
- Introduction of exothermic chemical inhibitor process to the working gas can effectively influence the separation of the rotational temperature from the vibrational one.
- The full oxidation with plasma activation takes place under plasma formation in mixtures with very low fuel consistence.
- The separation of T_v from T_{tr} is increased due to translational temperature significant reduction. It is occurred when an inhibitor of the exothermic process is injected to the plasma-forming gas.
- The transformation ratio of electrical energy into chemical energy is significantly higher at hydrocarbons reforming with plasma-catalysis technologies than with plasma-chemical technologies.
- The transformation of electrical energy into chemical energy under syngas production has strong functional dependence from input plasma energy, especially power area ~ tens

Watts. When this power has change from 20 to 40 Wt, corresponding coefficient of transformation is dropping at five times.

- The transition from the plasma activation of the fuel mixture (fuel/oxidant) to only plasma activation of oxidant leads to substantial increase in the coefficient of transformation of electric energy into chemical energy of produced synthesis-gas in hybrid plasma-catalysis system of hydrocarbons reforming.

Acknowledgements

This work was partially supported by the State Fund for Fundamental Researches, Ministry of Education and Science of Ukraine, National Academy of Science of Ukraine.

REFERENCES

[1] Slovetskij D, Mechanisms of chemical reactions in non-equilibrium plasma, Nauka, Moscow 1980. (In Russian).

[2] Kondratyev V, Nikitin E, Kinetics and mechanism of gas-phase reactions, Science, 1974. (In Russian).

[3] Fridman A, Plasma chemistry, Cambridge University Press 2008.

[4] Levitsky A, Macheret S., Polak L., Fridman A.. Sov. Phys., High Energy Chem. 17 (1983) 625.

[5] Rusanov V., Fridman A, Physics of Chemically Active Plasma, Nauka (Science), Moscow 1984. (In Russian).

[6] Chernyak V, Nedybaliuk O, Martysh E, et al., Problems of Atomic Science and Technology. Series: Plasma Physics 94 (2014) 124-129.

[7] Mc Kinley J, Garvin D, Boudart M J, Chem. Phys. 23 (1955) 784.

[8] Oraevsky A N, Chemical lasers. Handbook on lasers. Sovetskoe radio, Moscow 1978. (In Russian).

[9] *http://www.chem.msu.su/rus/teaching/general.html* (on-line on 5.5.2015). (In Russian).

[10] Starikovskaia S, Kukaev E, Kuksin A.Yu, Nudnova M N, Starikovskii A Yu, Combustion & Flame 139 (2004) 177.

[11] Levko D, Shchedrin A, Chernyak V, Olszewski S, Nedybaliuk O, J. Phys. D: Appl. Phys. 44 (2011) 145206.

[12] Chernyak V, Iukhymenko V, Prysiazhnevych I, Martysh Eu, Problems of Atomic Science and Technology. Series: Plasma Electronics and New Methods of Acceleration 86 (2013) 200-203.

[13] Chernyak V, Nedybaliuk O, Martysh E, Olszewski S, Solomenko O, Shchedrin A, Levko D, Demchina V, Kudryavzev V, Nukleonika 57 (2012) 301-305.

[14] Petitpas G, Rollier J-D, Darmon A, Gonzales-Aguilar J, Metkemeijer R, Fulcheri L, Int. J. Hydrogen Energy 32 (2007) 2848-2867.

[15] Chernyak V, Nedybalyuk O, Yukhimenko V, Colgan V, Solomenko E, Martysh E, Solomenko O, Demchina V, et al., In: Contr. Physics of Low-temperature Plasma (PLTP 2014), May 20-23, 2014, Kazan, Russia. 2, 2014, 130-134. (In Rusian).

[16] Changming Du, Hongxia Li, et al., International Journal of Hydrogen Energy 37 (2012) 8318-8329.

[17] Czernichowski A, In: 19th Int. Symp. on Plasma Chem. (ISPC-19), Bochum, Germany, 2009.

[18] Nedybaliuk O, Solomenko Ol, Martysh E, Fedirchyk I, Problems of Atomic Science and Technology. Series: Plasma Physics 94 (2014) 191-194.