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## OXIDATION OF $n\text{-C}_5\text{-C}_8$ HYDROCARBONS AND CYCLOHEXANE IN A REACTOR WITH BARRIER DISCHARGE. P. 2. SIMULATING CYCLOHEXANE OXIDATION REACTION

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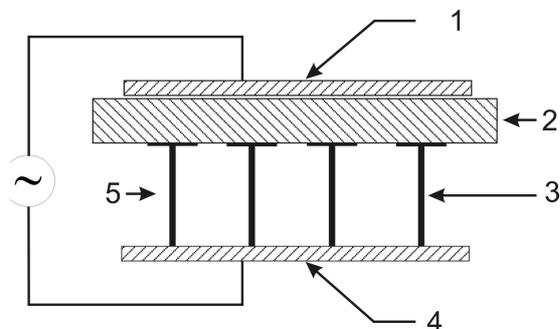
*Numerical model of hydrocarbon oxidation kinetics in a reactor with barrier discharge has been proposed by the example of cyclohexane oxidation reaction. The results of calculations with the use of barrier discharge surface model showed that electron energy and other discharge characteristics in pure oxygen and in the mixture of oxygen with cyclohexane vapors slightly differ that allowed using a simplified model of homogeneous discharge for simulating cyclohexane oxidation reaction. The results of calculation showed good fit with the experimental data.*

### Introduction

The given report continues the series of published works by the results of experiments with steam-and-gas mixtures of  $n\text{-C}_5\text{-C}_8$  alkanes and cyclohexane with oxygen in barrier electric discharge (BD) in the conditions of efficient withdrawal of reaction products from discharge range. In the previous paper [1] it was shown that as a result of oxidation of  $n\text{-C}_5\text{-C}_8$  hydrocarbons alcohols, aldehydes and ketones with the same quantity of carbon atoms as in the initial hydrocarbon are formed. The main oxidation products of cyclohexane are cyclohexanol, cyclohexanone. Oxidation of hydrocarbon mixtures results in forming the same products of the reaction as for the individual hydrocarbons.

The given paper is devoted to simulating cyclohexane oxidation reaction in BD. BD is understood as a discharge occurred in gas under the influence of stress applied to electrodes and in this case at least one of electrodes should be covered with a layer of liquid or solid dielectric.

Modern conception of BD physics is reflected rather completely in scientific literature [2]. A fragment of discharge cell with BD is showed schematically in Fig. 1. Supplying alternating voltage to discharge cell electrodes electric current flows in a gas gap. If voltage at the gas gap is lower than discharge ignition voltage then the current flowing through discharge cell has a capacitive character if it is higher then active discharge current is also added to displacement current. Discharge active current has impulsive character.



**Fig. 1.** Fragment of discharge cell with barrier electric discharge: 1, 4) metal electrodes; 2) dielectric barrier; 3) microdischarge; 5) gas gap

Oscillograms of discharge voltage and current pulse in plasmachemical reactor in which the authors carried out the oxidation of cyclohexane with oxygen are given in Fig. 2 [1].

Current pulses (Fig. 2) in BD are connected with occurrence in discharge volume of luminous channels – microdischarges distributed over the area of electrodes in which an active charge transfer initiating chemical reaction occurs.

Typical microdischarge life time is  $\sim 25\text{...}30$  ns [2] and it complicates experimental researches of its characteristics. This is the reason why mathematical simulation is actual when using BD as plasmachemical reactor for carrying out conversions.

### 1. Microdischarge simulation

Microdischarge was simulated using surface model described by the equation system [3, 4]:

$$\Delta\varphi = -\frac{\rho}{\varepsilon_0}, \quad (1)$$

$$\frac{\delta n_i}{\delta t} + \text{div}(n_i v_i) - \text{div}(D_i \cdot \text{grad} n_i) = S_i, \quad (2)$$

where  $\varphi$  is the potential of electric field,  $\varepsilon_0$  is the electric constant,  $\rho$  is the total charge density,  $n_i$  is the concentration of  $i$  particle,  $v_i$  and  $D_i$  are the drift velocity and diffusion coefficient,  $S_i$  is the sum of sources and drains of  $i$  particle.

Charge space distribution between dielectric barriers and particle concentrations are determined by joint solving Poisson equation (1) and continuity equations (2) for all plasma components.

Electric field and space-time distribution of particles were calculated in axially symmetrical geometry of microdischarge in plane-parallel gap with two dielectric barriers. The accepted assumption is stipulated by slight influence of electric field irregularity in nonplanar gas space with small gap  $d$  (much smaller than cylindrical reactor diameter) on end product output that conforms to direct experimental measurements [5]. Radial derivatives of all magnitudes on the boundary  $r=r_{\text{max}}$  (upper boundary of range of integration by radius) and at the axis of the channel were equal to zero. It was supposed

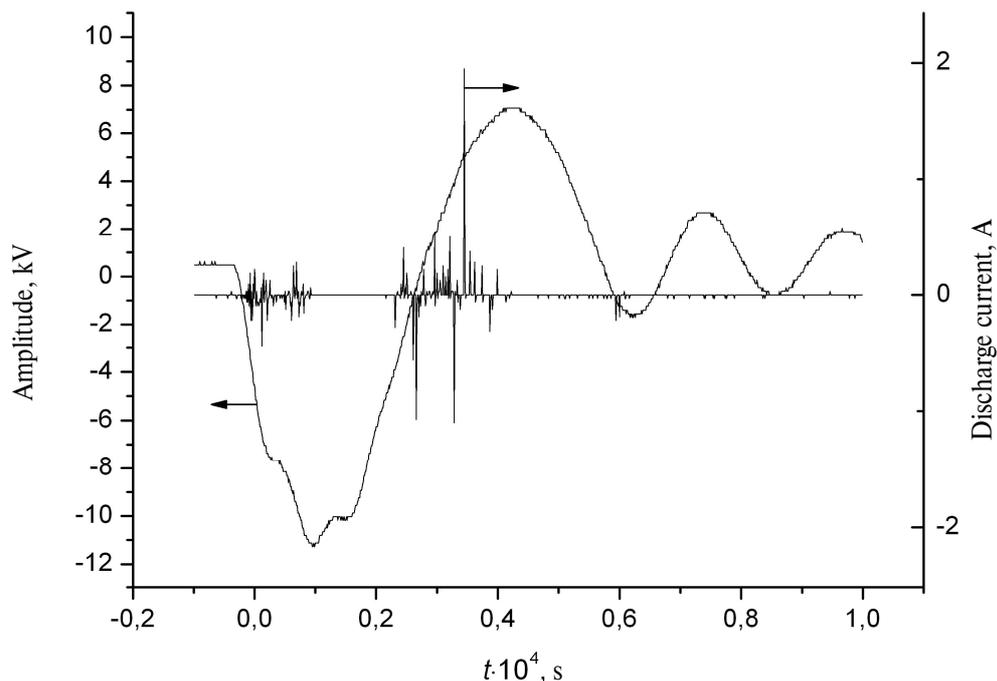


Fig. 2. Oscillogram of discharge voltage and current pulse

that dielectric absorbs electrons, positive and negative ions on the boundaries gas-dielectric therefore respective densities of currents of electron, positive and negative ions,  $j_e, j_-$  and  $j_+$ , were integrated by time for defining surface charges  $\sigma(r, t)$  and respective displacement discontinuity  $\Delta D = \sigma$  on both interphase boundaries. Concentrations of ions  $n_{+0}$  and electrons  $n_{e0}$  in gas gap stipulated by natural radiation background ( $n_{e0} = n_{+0} \sim 10^3 \text{ cm}^{-3}$ ) were accepted as their initial values on channel axis with decrease by Gauss law along its radius to periphery. In other respects, boundary and initial conditions did not differ significantly from similar conditions accepted in [4].

Complete microdischarge model should also include Boltzmann equations for defining electron energy distribution function (EEDF) and calculating particle formation rates. However, owing to high relaxation rate of electron average energy in molecular gas mixtures at atmospheric pressure the velocity coefficients of electron reactions with plasma particles were estimated by functions depending only on reduced electric field strength  $E/n$  [2].

Numeric calculations of microdischarge surface model were carried out using implicit iteration algorithm with analytical grid [5]. The calculations were carried out for plasmachemical reactor used before for oxidation of alkanes  $n\text{-C}_5\text{-C}_8$  and cyclohexane. Sections of electron-molecular processes were taken from papers [6, 7].

The results of calculations of electron concentration distribution and magnitudes of electric field reduced strength along microdischarge channel axis at different moments of time in mixture of oxygen with cyclohexane vapors are given in Fig. 3.

It is seen that electron inhomogeneous distribution along the axis passes to the uniform one rather rapidly (during  $\sim 1,5 \text{ ns}$ ). Electric field distribution in a gap

between barriers becomes constant as well (excluding cathode region). The observed picture is typical for glow-discharge plasma and it remains up to microdischarge disappearance (Fig. 3, a).

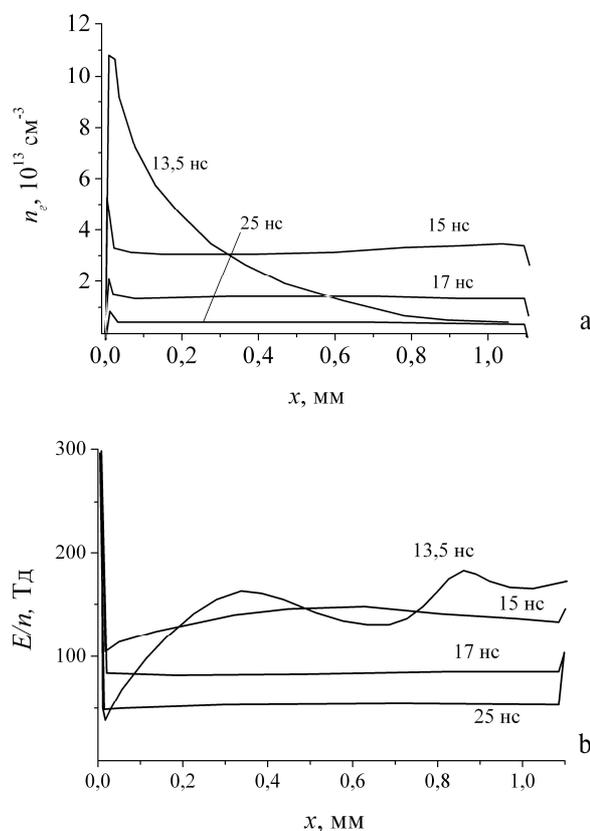
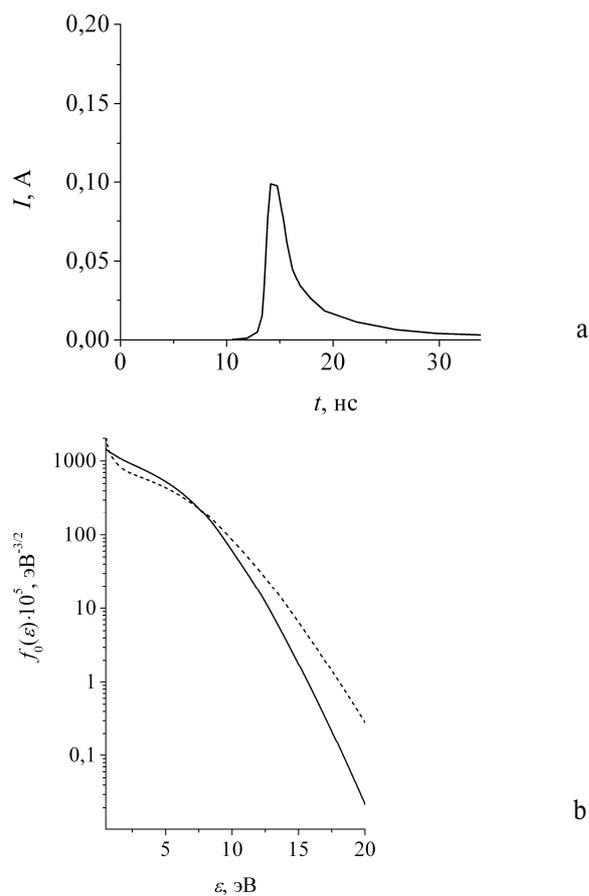


Fig. 3. Distribution of: a) electron concentration; b) magnitude of electric field reduced strength along microdischarge channel axis at different moments of time.  $\text{O}_2:\text{C}_6\text{H}_{12}=9:1$



**Fig. 4.** Results of calculation: a) microdischarge current pulse; b) EEDF in pure oxygen (dashed line) and in mixture of oxygen with cyclohexane vapors (full line).  $O_2:C_6H_{12}=9:1$ ,  $E/n=98,8$

In general the results given in Fig. 3, 4 are typical for barrier discharge in pure oxygen [2].

Comparison of calculation of results of EEDF in pure oxygen and in the mixture of cyclohexane vapors with oxygen (Fig. 4, b) shows that cyclohexane vapors influence considerably, in general, the high-energy part of EEDF. Function kernel in energy region 0...10 eV, the most important for dissociation processes of oxygen and hydrocarbons, do not undergo great changes.

Thus, addition of cyclohexane vapors into oxygen does not result in considerable increase of electron energy losses and change of microdischarge other characteristics. It allows using simpler algorithms in calculations for determining concentration of radicals initiating cyclohexane oxidation process and energy consumption for their formation. Let us give two variants of such calculations:

1. The model of homogeneous discharge according to which the electric field strength in microdischarge channel is considered to be constant. Average particle concentration, electron energy distribution function and parameters of gas-discharge plasma are calculated in self-consistent manner. Such model allows taking into account the influence of varying composition of gas mixture on rate of molecule electron excitation in gas discharge.

2. In the given case when initial hydrocarbon conversion is not high and reaction products are removed efficiently from gas phase change of gas mixture composition may be neglected and homogeneous charge model is significantly simplified. Then initial concentration of particles  $\bar{N}_i$  required for simulating chemical reaction stage may be calculated by the formula [8]:

$$\bar{N} = \eta_i \bar{W}_{ch} \eta_i = \frac{\int N_i dV}{\iint j_{ch} E_{ch} dV dt}$$

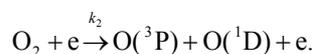
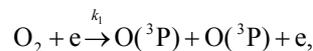
Here  $\bar{W}_{ch}$  is the value of specific energy released in microdischarge channel,  $\eta_i$  is the value of particle formation efficiency,  $N_i$  is the concentration of  $i$  particle at the end of microdischarge pulse,  $j_{ch}$  is the current density inside the channel,  $E_{ch}$  is the value of electric field strength,  $V$  is the volume of microdischarge volume.

The second variant of calculation may be also used for estimating initial concentrations of atoms and radicals formed at one or a series of voltage pulses. Simulating cyclohexane oxidation reaction the latter approach was used as it is the simplest and reduces significantly calculation time.

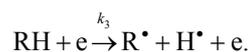
## 2. Simulating cyclohexane oxidation reaction for single voltage pulse

Forming possible cyclohexane oxidation mechanism the following assumptions were accepted: 1) cyclohexane oxidation was considered as chain reaction including events of initiation, continuation and break of chains; 2) only initial compounds undergo BD influence but not intermediate and end reaction products. 3) under the influence of BD gas average temperature rise does not exceed 5 °C [2]; 4) reactions with zero (or almost zero) activation energy are mainly taken into account.

The analysis of the papers devoted to plasmachemical methods of air purification from organic contaminants in reactors with BD shows that the main primary event initiating oxidation reaction is molecular oxygen excitation with electron impact forming atomic oxygen in ground  $O(^3P)$  and excited  $O(^1D)$  states [2]:



Hydrocarbon molecule excitation with electron impact also occurs and judging by reaction products results mainly in forming atomic hydrogen and hydrocarbon radical.



Contribution of reaction into oxidation process is less significant as molecular oxygen dissociation occurs at lower electron energy magnitudes ~6 eV [2] than it is required for breaking C-H- or C-C-bond of hydrocarbon molecule (~8...11 eV) [7].

Then, the formed particles interact with cyclohexane molecule by radical-chain mechanism suggested in [9].

The efficiency values of forming particles  $\eta_i$  were calculated by [8]. For example, for  $\eta_{O(^3P)}$  the expression was obtained

$$\eta_{O(^3P)} = (2k_1 + k_2) \frac{[O_2]}{n} / e_0 v_{drift} (E/n)_{eff} \quad (3)$$

where  $e_0$  is the electron elementary charge,  $v_{drift}$  is the drift velocity of electrons,  $n$  is the number of particles in  $cm^3$ ,  $(E/n)_{eff}$  is the efficient reduced strength of electric field.

Similarly to (3) the expressions for  $\eta_{O(^1D)}$ ,  $\eta_{C_6H_{11}\cdot}$  and  $\eta_{H\cdot}$  are obtained.

Calculating  $\eta_{O(^3P)}$  and  $\eta_{O(^1D)}$  the magnitudes  $v_{drift} = 1,8 \cdot 10^7$  cm/s,  $k_{1,2} = 3,9 \cdot 10^{-11}$  cm<sup>3</sup>/s obtained by data interpolation for pure oxygen were used [8].  $k_3$  magnitude was not found in scientific literature; it was estimated by the formula [10]:

$$k_3 = (2/m_e)^{1/2} \int_{\varepsilon_{nop}}^{\infty} \varepsilon^{1/2} \sigma(\varepsilon) f_e(\varepsilon) d\varepsilon \quad (4)$$

where  $\sigma(\varepsilon)$  is the efficient reaction cross-section,  $f_e(\varepsilon)$  is the EEDF,  $m_e$  is the electron mass,  $\varepsilon_{thresh.}$  is the threshold reaction energy.

Probability of alkanes dissociation from electron-excited states is considered to be close to a unity. Therefore estimating magnitude  $k_3$  the data on sections of excitation of allowed electron transitions in cyclohexane molecule by electron impact were used [7]. Calculated value  $k_3$  amounted to  $4,6 \cdot 10^{-15}$  cm<sup>3</sup>/s that is practically 4 orders lower than oxygen dissociation rates by electron impact  $k_1, k_2$ . It allows ignoring cyclohexane dissociation reaction by electron impact at forming probable oxidation mechanism.

The value of efficient reduced strength of electric field  $(E/n)_{eff} = 22$  used in calculations corresponds to charge burning voltage and obtained from volt-coulomb characteristic measured earlier at cyclohexane oxidation [1].

Initial concentrations  $O(^3P)$ ,  $O(^1D)$  and values  $\eta_i$  corresponding to them are given in Table 1.

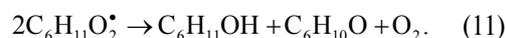
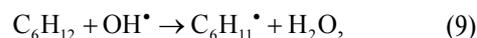
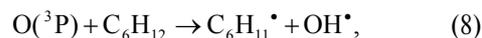
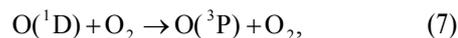
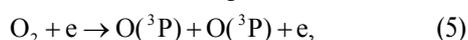
**Table 1.** Initial concentrations  $O(^3P)$ ,  $O(^1D)$  and values  $\eta_i$  ( $W_{mp} = 5 \cdot 10^6$  eV/cm<sup>2</sup>,  $(E/n)_{eff} = 22$ ,  $T = 298$  K,  $[O_2] = 2,2 \cdot 10^9$ ,  $[C_6H_{12}] = 2,3 \cdot 10^8$  cm<sup>-3</sup>) corresponding to them

Particle	$\eta_i \cdot 100$ , mole/eV	Concentration, cm <sup>-3</sup>
$O(^3P)$	11,8	$5,9 \cdot 10^5$
$O(^1D)$	2,9	$1,5 \cdot 10^5$

Elementary stages of probable oxidation mechanism of cyclohexane and rate constants corresponding to them are given in Table 2.

Reaction product composition obtained by mathematical simulation is shown in Table 3. Satisfactory fit between calculated and experimental data allows making conclusion about reliability of suggested reaction mechanism.

The simplified cyclohexane oxidation mechanism may be presented in the following set of reactions:



It is seen that the chain reaction is characterized by short chain – 3 links (reactions 8–10). Chain break occurs by disproportionation reaction of cyclohexyl peroxide radicals (11) forming cyclohexanol, cyclohexanone.

**Table 2.** Elementary stages of probable oxidation mechanism of cyclohexane and rate constants corresponding to them

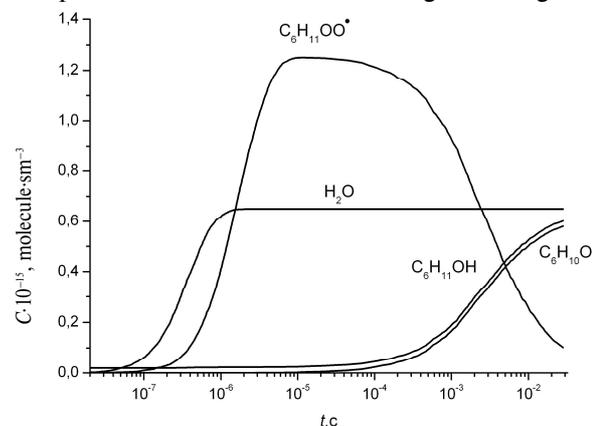
Process	Rate constant, cm <sup>3</sup> /s	Literature
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	$4,0 \cdot 10^{-11}$	[1]
$O(^3P) + O_2 + M \rightarrow O_3 + M$	$1,6 \cdot 10^{-14}$	[1]
$2O(^3P) + M \rightarrow O_2 + M$	$2,0 \cdot 10^{-14}$	[1]
$C_6H_{12} + O(^3P) \rightarrow C_6H_{11}\cdot + OH\cdot$	$1,8 \cdot 10^{-13}$	[12]
$C_6H_{12} + O(^1D) \rightarrow C_6H_{11}OH$	$5,0 \cdot 10^{-11}$	Estimation by [11], [13]
$C_6H_{12} + OH\cdot \rightarrow C_6H_{11}\cdot + H_2O$	$3,7 \cdot 10^{-12}$	[14]
$2OH\cdot + M \rightarrow H_2O_2 + M$	$1,5 \cdot 10^{-11}$	[11]
$C_6H_{11}\cdot + O_2 \rightarrow C_6H_{11}OO\cdot$	$2,7 \cdot 10^{-14}$	[15]
$2C_6H_{11}OO\cdot \rightarrow C_6H_{10}O + C_6H_{11}OH + O_2$	$1,5 \cdot 10^{-14}$	[15]
$C_6H_{11}OO\cdot + C_6H_{12} \rightarrow C_6H_{11}OOH + C_6H_{11}\cdot$	$8,7 \cdot 10^{-20}$	[15]

**Table 3.** Composition of cyclohexane oxidation products

Substance	Experiment [1], wt. %	Calculation, wt. %
Cyclohexanol	49,4	47,1
Cyclohexanone	40,8	44,5
Water	9,5	8,4
Other	0,2	–

Low temperature in discharge reactor zone and practically «nonchain» character of reaction makes the technique of cyclohexane oxidation in reactor with BD explosion-proof that is certainly an advantage on traditional oxidation techniques where nonexplosiveness is one of the main problems.

The calculated dependences of cyclohexane oxidation product concentrations in BD are given in Fig. 5.



**Fig. 5.** Calculated dependences of concentration  $C$  of cyclohexane oxidation products in BD on time  $t$

It is seen that typical formation time of cyclohexanol and cyclohexanone is  $\sim 10^{-2}$  s, water –  $\sim 10^{-6}$  s.

A good fit between compositions of cyclohexane oxidation products obtained experimentally and theoretically allows writing down gross-equation of this process:



As at oxidation of hydrocarbons n-C<sub>5</sub>-C<sub>8</sub> and cyclohexane the mixture of alcohols and carbonyl compounds with the same number of carbon atoms that is in

original hydrocarbon and ratio of alcohols and carbonyl compounds in reaction products  $\sim 1:1$  is formed, the similar (12) gross-equations may be also written down for oxidation process of hydrocarbons n-C<sub>5</sub>-C<sub>8</sub>.

On the basis of the obtained results the conclusion may be made that the studied approach to simulating cyclohexane oxidation reaction in BD allows describing rather adequately this process. The results of investigations are of interest at developing the processes of plasma-chemical conversion of organic substances in charges at atmospheric pressure, for example, in BD.

## REFERENCES

1. Kudryashov S.V., Ryabov A.Yu., Shegoleva G.S., Sirotkina E.E., Suslov A.I. Oxidation of n-C<sub>5</sub>-C<sub>8</sub> hydrocarbons and cyclohexane in reactor with barrier discharge. P. 1. The results of experimental investigations // Bulletin of the Tomsk Polytechnic University. – 2006. – V. 309. – № 6. – P. 92–96.
2. Samoylovitch V.G., Gibalov V.I., Kozlov K.V. Physical chemistry of barrier discharge. – Moscow: MSU Press, 1989. – 174 p.
3. Eliasson B., Egli W., Kogelschatz U. Modeling of dielectric barrier discharge chemistry // Pure and Appl. Chem. – 1994. – V. 66. – № 6. – P. 1279–1286.
4. Braun D., Gibalov V., Pietsch G. Two-dimensional modeling of the dielectric barrier discharge in air // Plasma Sources Sci. Technol. – 1992. – V. 1. – P. 166–174.
5. Okazaki K., Nozaki T., Uemitsu Y., Hijikata K. Direct conversion from methane to methanol by a pulsed silent discharge plasma. // Proc. of 12<sup>th</sup> International Symposium on Plasma Chemistry. – Minneapolis, Minnesota, USA, 1995. – P. 581–586.
6. BOLSIG [Electron program]. – <http://www.siglo-kinema.com/bolsig.htm>
7. Slovetskiy D.N. Plasma chemistry / Ed. by B.M. Smirnova. – Moscow: Energoizdat, 1981. – Issue 8. – P. 189–229.
8. McCulla W.C., Rososha L.A., Neely W.C., Clothiaux E.J., Kushner M.J., Rood M.J. Treatment of hazardous organic wastes using wet air plasma oxidation // Proc. 1<sup>st</sup> Idaho National Engineering and Environmental Laboratory Plasma Applications to Waste Treatment Workshop, Idaho Falls. – Idaho, USA, 1991. – P. 1–25.
9. Kudryashov S.V., Shegoleva G.S., Sirotkina E.E., Ryabov A.Yu. Hydrocarbon oxidation in reactor with barrier discharge // Khimiya Vysokih Energiy. – 2000. – V. 34. – № 2. – P. 145–148.
10. Polak L.S. Nonequilibrium chemical kinetics and its application. – Moscow: Nauka, 1979. – 248 p.
11. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling [Electron resource]. – <http://airsite.unc.edu/docs/specialdocs.html>
12. Herron J.T., Huie R.E. Rate Constants for the Reaction of Atomic Oxygen O(<sup>3</sup>P) with Organic Compounds in the Gas Phase // J. Phys. and Chem. Ref. Data. – 1973. – V. 2. – № 3. – P. 467–518.
13. Paraskevopoulos G., Cvetanovic R.J. Competitive Reactions of the Excited Oxygen Atoms, O(<sup>1</sup>D) // J. Am. Chem. Soc. – 1969. – V. 91. – № 27. – P. 7572–7577.
14. Kondratiev V.N. Constants of gas-phase reaction rate. – Moscow: Nauka, 1970. – 351 p.
15. Berezin I.V., Denisov E.T., Emanuel N.M. Cyclohexane oxidation. – Moscow: MSU Press, 1962. – 302 p.
16. Denisov E.T. Rate constants of hemolytic liquid-phase reactions. – Moscow: Nauka, 1971. – 712 p.

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