Experimental research and simulation of the process of interaction between a barrier discharge and natural gas

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Abstract: The process of interaction of a dielectric barrier discharge with natural gas in a plasma-chemical reactor was studied experimentally. This process was also simulated. The dependences of methane conversion and the yield of the reaction products on the specific energy input are obtained.

Keywords: dielectric barrier discharge, methane, natural gas, plasma pyrolysis

1. Introduction

There are a large number of reactions, for the initiation of which it is necessary to increase the temperature and/or pressure. However, there is another way – to activate the reaction using an electric discharge. In this work, a barrier discharge was used for this purpose, since it has the following advantages: non-equilibrium plasma ($T_e >> T_i$, so on most of the energy inject in the plasma goes to the acceleration of electrons, which are involved in the initiation and stimulation of chemical reactions), the electrodes are covered with dielectric (thus, the resource increases), the discharge operates at atmospheric pressure (there is no need for expensive vacuum equipment). Pilot studies were conducted first. [1]. In this work, we investigated the interaction of the barrier discharge with natural gas, analyzed the input and output composition of the gas mixture, simulated the process of discharge development and plasma chemical reactions in it. The results of these studies will allow more efficient use of the barrier discharge in relation to plasma chemistry.

2. Experimental setup

In the experiments, a plasma-chemical reactor (PCR) with a coaxial configuration of electrodes was used. The diameter of the internal electrode was 18 mm. The distance between the inner electrode and the dielectric was 1.5 mm. The thickness of the dielectric tube was 2 mm. Borosilicate glass was used as a dielectric. The outer electrode was adjacent to the outside of the dielectric tube. The length of the external electrode – 115 mm. The internal electrode was grounded. Rectangular high-voltage pulses with a frequency of 4 kHz (T = 250 μs), a duration (τ) of 60 μs and an amplitude of 15 kV were applied to the external electrode.

Natural gas was used as feed gas (CH_4 – 93.8 % vol., C_2H_6 – 3.7 % vol., C_3H_8 – 1.1 % vol. and a small amount of impurities). Gas consumption ranged from 0.4 l/min to 18 l/min. The gas composition was analyzed by two methods: using a gas chromatograph and a quadrupole mass spectrometer.

3. Description of the model

The change in parameters was calculated along the r axis (Fig. 1). How the initial data was set: the distance between the grounded electrode and the dielectric (AB = 1.5 mm), dielectric thickness (BC = 2 mm), potential at point A (φ_A = 0, since the internal electrode was grounded), voltage function over time $U_C(t)$ at point C (Fig. 1), initial composition of gas supplied to PCR (same as experiment), pressure P_{PCR} = 1 atm., gas temperature T = 293 K. Reactions that were taken into account in the model are listed in the table 1.

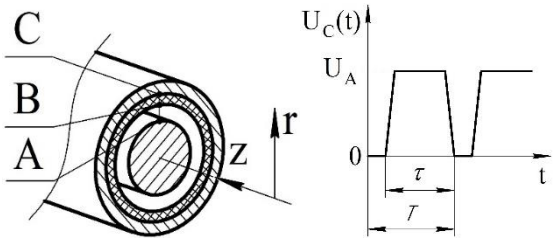

Fig. 1. Cross-section of the discharge gap and the dependence of voltage on time

The dependence of the electron concentration on time and at each point was calculated from the solution of the continuity equation:

$$\frac{\partial n_e}{\partial t} + \nabla \cdot [-n_e(\mu_e \cdot \mathbf{E}) - D_e \nabla n_e] = R_e \qquad (1)$$

here n_e is the electron concentration ($1/m^3$), μ_e is the electron mobility ($m^2/(V \times s)$), E is the electric field strength (V/m), D_e is the electron diffusion coefficient (m^2/s). The second term reflects the movement of electrons under the action of an electric field, the third - the diffusion of electrons from areas with high electron density to low, R_e – a term representing the appearance or absorption of electrons as a result of plasma chemical reactions. The electron energy distribution function was also calculated. Using the distribution function and reference data on cross sections, the rate coefficients of the reactions of interest to us were calculated:

$$k_j = \gamma \int_0^\infty \varepsilon \, \sigma_j(\varepsilon) f(\varepsilon) d\varepsilon \qquad (2)$$

In this equation: $\gamma = (2q_e/m_e)^{0.5}$, q_e – electron charge (C), m_e – electron mass (kg), ε – energy (eV), σ_j – reaction cross section (m^2), f – electron energy distribution function ($eV^{-1.5}$).

4. Experimental and simulation results

As a result of the experiments, the following discharge parameters were obtained: the average power was 75.2 W, the energy in one discharge pulse was 18.8 mJ, the

Table 1. List of reactions

Reaction	Ref.
Elastic	
CH3 + e → CH3 + e CH4 + e → CH4 + e C2H4 + e → C2H4 + e C2H6 + e → C2H6 + e	[2]
Ionization	
CH4 + e → CH4+ + 2e C2H4 + e → C2H4+ + 2e C2H4 + e → C2H3+ + H + 2e C2H6 + e → C2H6+ + 2e C2H6 + e → CH3+ + CH3 + 2e C3H6 + e → C2H4+ + CH2 + 2e C3H6 + e → CH2+ + C2H4 + 2e C3H7 + e → C2H4+ + CH3 + 2e C3H7 + e → CH3+ + C2H4 + 2e	[3, 4]
Dissociation	
CH4 + e → CH3 + H + e CH4 + e → CH2 + H2 + e CH4 + e → CH + H2 + H + e CH4 + e → C + 2H2 + e C2H4 + e → C2H3 + H + e C2H4 + e → C2H2 + H2 + e C2H6 + e → C2H5 + H + e C2H6 + e → C2H4 + H2 + e C3H6 + e → C2H4 + CH2 + e C3H6 + e → C2H3 + CH3 + e C3H6 + e → C2H2 + CH4 + e C3H7 + e → C2H4 + CH3 + e C3H7 + e → C3H6 + H + e	[3, 4]
The interaction of neutral species	
CH + H2 = CH2 + H CH2 + H2 = H + CH3 CH2 + CH4 = CH3 + CH3 CH2 + C2H3 = C2H2 + CH3 CH2 + C2H5 = C2H4 + CH3 CH2 + C3H7 = C3H6 + CH3 CH2 + C3H8 = C3H7 + CH3 CH3 + C2H4 = C2H3 + CH4 CH3 + C3H7 = C3H6 + CH4 C2H4 + H = C2H3 + H2 CH4 + H = CH3 + H2 CH4 + C2H5 = C2H6 + CH3 CH4 + C3H7 = C3H8 + CH3 C2H3 + C3H7 = C3H6 + C2H4 C2H3 + C3H8 = C3H7 + C2H4 C2H4 + H = C2H3 + H2 C2H4 + C2H5 = C2H6 + C2H3 C2H5 + H = CH3 + CH3 C2H5 + H2 = C2H6 + H C2H5 + C2H5 = C2H6 + C2H4 C2H5 + C3H7 = C2H4 + C3H8 C2H5 + C3H7 = C2H6 + C3H6 C2H5 + C3H8 = C3H7 + C2H6 C2H6 + C3H7 = C3H8 + C2H5 C3H7 + C3H7 = C3H6 + C3H8 C3H8 + H = C3H7 + H2 CH3 + CH3 + CH4 = C2H6 + CH4 CH3 + CH4 + C2H3 = C3H6 + CH4 CH3 + CH4 + C2H5 = C3H8 + CH4 CH4 + C2H5 + H = C2H6 + CH4 CH4 + C2H4 + H = C2H5 + CH4 CH4 + C2H2 + H = C2H3 + CH4	[5]
The interaction of neutral species and ions	
CH2+ + CH4 = C2H4+ + H2 CH4+ + C2H4 = C2H5+ + CH3 C2H3+ + C2H6 = C2H5+ + C2H4 C2H3+ + C2H4 = C2H5+ + C2H2	[6, 7]

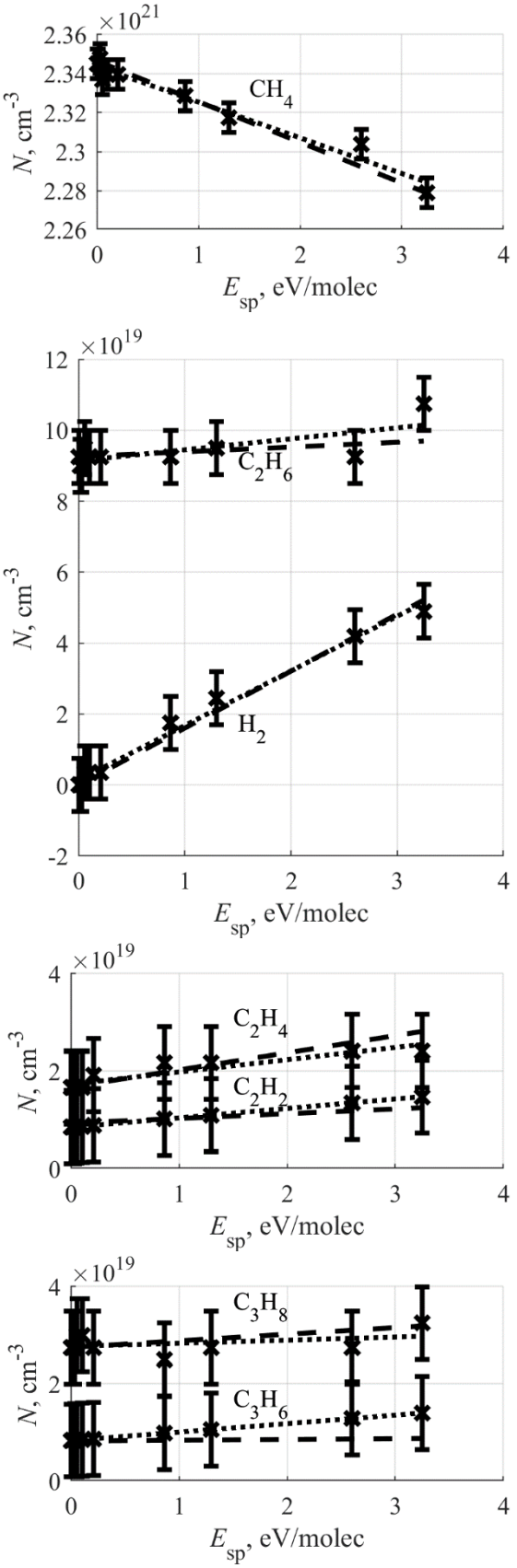

Fig. 2. Concentration dependence on specific energy
x - experimental points; dashed line – simulation; dotted line – experimental approximation.

amplitude of the current pulse was 40 A. The electrical parameters of the discharge supply did not change, but the gas flow rate through the PCR changed, hence the specific energy input changed. In the experiments, it varied from 0 to 3.25 eV/molec. The dependence of the concentration of plasma pyrolysis products on the energy range is shown in Fig. 2.

The simulation results are also presented in Fig. 2 (dashed line). The simulation results are in good agreement with the experimental results. It should be noted that the concentration dependences on the specific energy are linear. It is also necessary to note the fact that when the flow rate changes (because of this, the specific energy input changes) the discharge mode changes. With a low flow rate - the multichannel mode, with a large one, a more homogeneous mode (this phenomenon was studied in more detail in [8]). On this basis, we conclude that the yield of products is clearly independent of the discharg mode.

5. Conclusion

As a result of the interaction of the barrier discharge with natural gas, methane was converted to more complex hydrocarbons. This process has been modeled. The simulation results are in good agreement with the experimental results. This will allow to predict the output composition of the gas when changing external parameters such as: form and amplitude of the supply voltage, flow rate and composition of the source gas, the geometry of the discharge gap, the properties of the dielectric and electrodes.

6. Acknowledgment

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7. References

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