Partial Methane and Nitrogen Oxidation Initiated by Pulsed Electron Beam

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Abstract – In the paper the investigation results of methane oxidation in the mixture with oxygen and hydrogen and nitrogen oxidation in the mixture with oxygen and hydrogen are presented. The process of oxide synthesis was initiated by pulsed electron beam. The analysis of reaction products is carried out by the mass-spectrometer. It is obtained that in the non-equilibrium conditions the mode of partial oxidation is realized. The main reaction products of synthesis are CO and NO + N_2O. The energy imputs for methane and nitrogen conversion are measured.

Introduction

The intensive application of liquid hydrocarbon raw material for automobile fuel production, for application in chemical industry, technical carbon production causes the distortion of natural resources. That is why last years the interest to hydrocarbon gases arises. The main component of the gas is methane. The raw stock of hydrocarbon gases exceeds the oil and condenser resources. Moreover the content of hydrocarbon gases in the earth's crust increases both due to the biological raw stock and other geological processes processing [1].

The methane molecules more chemically stable comparing to other hydrocarbon compositions. That is why for methane conversion different chemical and physical processes are used. Now in the large scale production mainly steam and carbonic acid conversions are used [2]. These two methods require high energy imputs of about 200–250 kJ for 1 mole of methane ignoring the consumptions for initial raw stock heating and for reaction zone heating up to the temperature of 600–1500 °C [2]. The energy source is the combustion reaction (complete oxidation) of methane in the conversion furnace. To generate the required energy in the technology of methane conversion up to 80% of initial raw stock is combusted.

At the partial methane oxidation the additional energy imputs are not required as the oxidation reaction goes with energy liberation. At present the investigations on incomplete (partial) oxidation in the mixture with oxygen and air at the elevated temperature [2], with application of energy installations [3], microwave discharge plasma [4], continuous electron beams [5] are carried out. Under the absence of external influence the process of partial methane oxidation goes at the temperature of more than 450 °C and the pressure more than 7.5 MPa [2]. At the oxygen content in the mixture of more than 10% the reaction velocity of partial oxidation sharply decreases. This limits the conversion degree of raw material for one reaction zone pass.

The high interest is raised by the investigation of methane oxidation process under the non-equilibrium conditions. High degree of process non-equilibrium can decrease the inhibitory influence of oxygen on the partial methane oxidation and provide the methane processing with high selectivity and conversion degree [2]. The non-equilibrium plasmochemical processes go at the low gas temperature what in addition to the significant decrease of power consumptions simplify the task of synthesis product stabilization.

The atmospheric nitrogen oxidation in plasma except for high applied importance is interesting because it can effectively stimulate by oscillatory excitation of reacted molecules [6]. The experimental investigations of NO synthesis in the non-equilibrium plasma were carried out from the beginning of thirties in the glow discharge. The efficiency of nitrogen synthesis left low in these systems. Relatively higher values of energetic effectiveness were carried out at the atmospheric pressure in non-self-maintained discharge supported by high-current beams of relativistic electrons. The boundary energetic effectiveness was 14% (energy imputs 7 eV/mole NO). The highest energetic effectiveness of nitrogen oxide synthesis (~30%, energy imputs are ~3 eV/molecule) was achieved in the non-equilibrium microwave discharge with magnetic field working under the conditions of electron-cyclotron resonance [6].

2. Experimental Set-up

The works were carried out at the specialized electron accelerator TEU-500 [7]. The parameters of the electron beam are the following: electron energy is 450–500 keV, pulse duration at the half-height is 60 ns, energy in pulse is up to 200 J, and beam diameter is 5 cm. The pressure in the reactor and energy imputs of electron beam in gas was controlled by the fast-response differential pressure sensor [8]. The scheme of experimental bench is shown in Fig. 1.

The plasmochemical reactor (PCR) represents a cylindrical closed chamber with the volume of 6.2 liters and inner diameter of 14 cm. The electron beam *4* injection to the plasmochemical reactor *3* was carried out from the face plane of reactor through the anode foil *5*. Before the filling the reactor by the gas mixture the PCR volume was pumped out by the forepump *1*, the pressure was controlled by the standard pressure-gauge *2*. The content of the initial reagent mixture

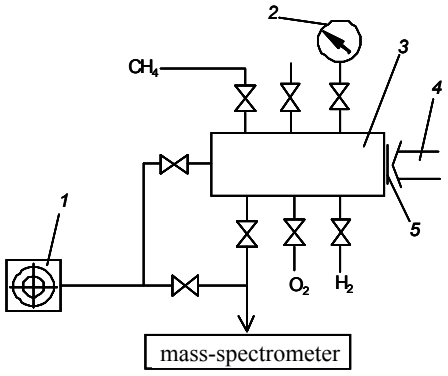

Fig. 1. The experimental bench scheme

and the change of gas mixture content in the reactor under the influence of pulsed electron beam were measured by mass-spectrometer MX-7403. The output signal of mass-spectrometer was transferred to the computer through AZP La-7 (in Russian marked АЦП Ла-7) with galvanic uncoupling. The change of gas mixture component content was evaluated according to the change of the corresponding peak.

3. Partial Methane Oxidation

During the experiment the following mixture was used: 130 Torr of H_2 + 70 Torr of O_2 +CH_4 + 40 Torr of Ar with different content of methane.

At the electron beam injection the hydrogen oxidation took place. The energy liberated in this process was used for methane decomposition. As a calibrating gas for mass-spectrometer the inertial gas argon was used. The complete methane oxidation was executed for 1 pulse of electron beam. Fig. 2 represents the mass-specters of initial gas mixture and reaction products.

Figure 3 shows the dependences of peak area of products of methane decomposition in the mixture with oxygen and hydrogen on the initial partial methane pressure.

The carried out investigations showed that at the increase of initial partial methane pressure in the gas mixture of $H_2 + O_2 + CH_4 + Ar$ and constant oxygen pressure in the final products the part of monoxide of carbon and hydrogen increases.

The methane decomposition under the influence of pulsed electron beam was carried out completely for one pulse of beam influence.

Let us estimate the energy imputs of electron beam for methane decomposition. Suppose that all the energy of electrons is absorbed by the gas mixture and is spent for methane decomposition (upper estimate). Then at the electron beam energy in pulse of 100 J (working mode of the accelerator), at the initial partial methane pressure of 60 Torr and reactor volume of 6.2 liters we will get that the energy imputs of electron beam for methane conversion does not exceed 4.6 kJ/mole.

The process of methane decomposition in our experimental conditions continues after electron beam injection for not more than 5 ms. Fig. 4 shows the

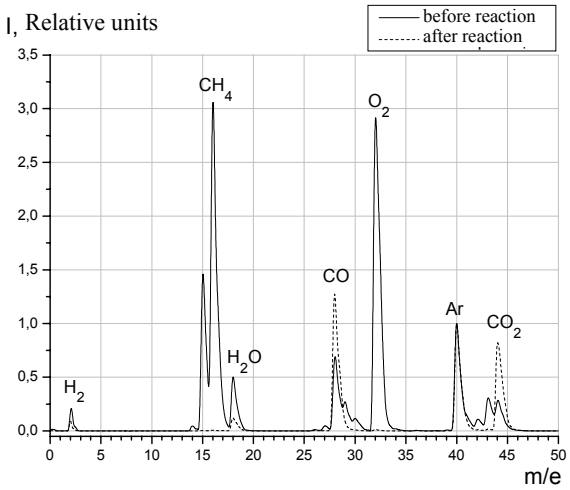

Fig. 2. The mass-specter of gas mixture $H_2 + O_2 + CH_4 + Ar$ before and after the reaction at the initial partial methane mixture of 60 Torr. The peak amplitude is normalized for the argon peak value

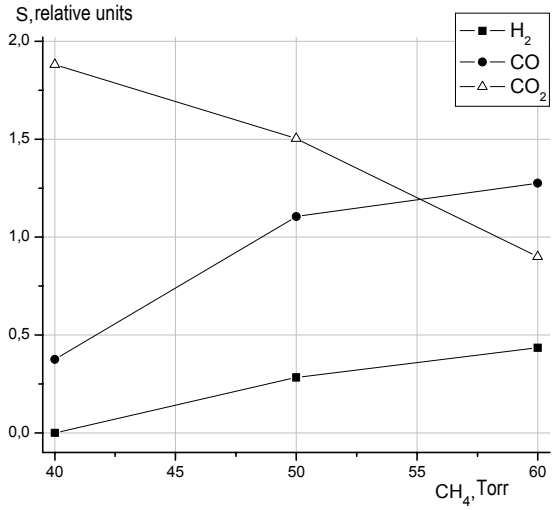

Fig. 3. The dependences of peak area of carbon monoxide, carbonic acid and hydrogen of mass-specter of gas mixtures $H_2 + O_2 + CH_4 + Ar$ after pulsed electron beam influence on the initial partial methane pressure. The value of hydrogen peak area is increased by 10 times

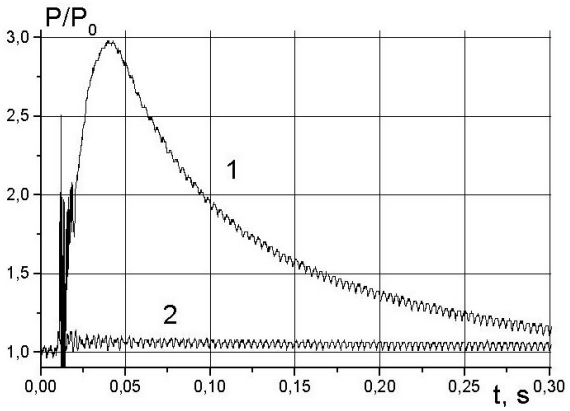

Fig. 4. The pressure change (of normalized to initial) in the reactor after pulse electron beam injection at the mixture ignition (*1*) and incase of reaction absence (*2*)

oscillograms of pressure change in the reactor obtained with the help of fast-response differential sensor of pressure. The pressure increase in the reactor at the methane decomposition reaction going does not exceed triple value. From the equation of state for ideal gas we get that the temperature at that does not exceed 600 °C.

4. Partial Nitrogen Oxidation

In the experiment the following gas mixture was used H_2 (100 Torr) + O_2 (50 Torr) + N_2 (250 Torr). The gas mixture was filled after reactor pumping out to the vacuum to the vacuum of 10^{-1} Torr. As a calibrating gas the argon was used. After the electron beam influence in the reactor the chain reaction of hydrogen oxidation was initiated. The reaction energy was used for nitrogen oxide synthesis. Fig. 5 represents the mass-specters of mixture content before and after electron beam influence at the total beam energy of 100 J. In the presented mass-specters it is clearly seen that after the reaction the hydrogen (mass 2), nitrogen (mass 28) and oxygen (mass 32) peaks decreased and peaks of 30 and 44 mass appeared. The mass 30 corresponds to nitrogen monoxide NO, mass 44 corresponds to nitrogen oxide N_2O (fission ion with $m/e = 30$) [9]. The nitrogen dioxide NO_2 ($m/e = 48$) was not registered in the reaction products.

Figure 6 represents the histograms reflecting the change of mass-specter peak area corresponding to the argon peak area (mass 40) at the pressure of gas mixture of 400 Torr.

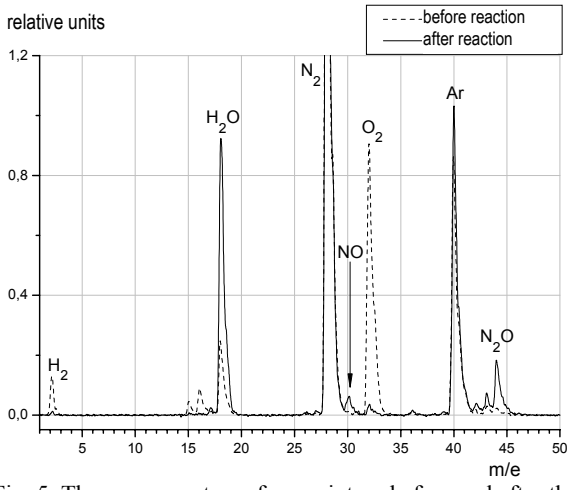

Fig. 5. The mass-specters of gas mixture before and after the reaction at the total mixture pressure of 400 Torr

The nitrogen conversion degree was 11% at the energy imputs of 0.11 eV/molecule.

5. Conclusion

Under the pulsed electron beam influence on the mixture of methane, oxygen and hydrogen the non-equilibrium mode of partial methane oxidation is realized. The non-equilibrium process character of partial

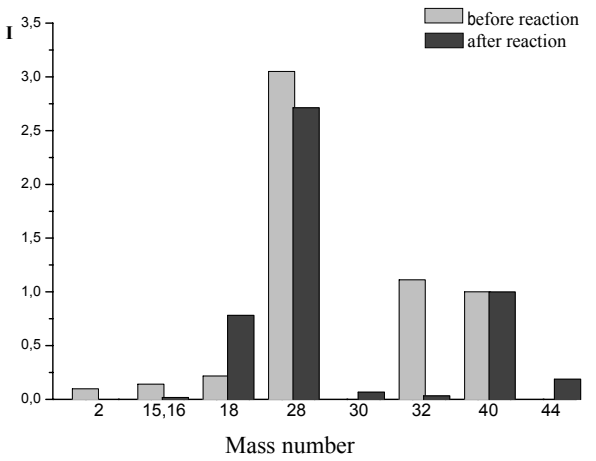

Fig. 6. The histograms of mass-specter peak area before and after the reaction at the total mixture pressure of 400 Torr

methane oxidation in our experimental conditions allows to decrease significantly the temperature and initial pressure in the reactor. The process of incomplete methane oxidation (to CO) goes effectively at a high concentration of oxygen (more than 30%) in the initial mixture. The pulsed electron beam only initiates the methane conversion process and is not the main source of process energy. That is why it is possible to realize the methane conversion in large volumes at the installation with low power consumption.

The carried out experimental investigations showed that under the electron beam influence on the oxygen-nitrogen-hydrogen gas mixture the plasmochemical reaction goes with the formation of nitrogen oxides. The power consumptions for nitrogen oxidation are 0.11 eV/molecule (accelerator efficiency is 40%). This is significantly lower than values achieved by other methods of nitrogen oxide synthesis. Undere the influence of pulsed electron beam the mode of partial nitrogen oxidation is realized (the same as at methane oxidation). The final reaction products ate oxides NO and N_2O.

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