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Processing of Methane in Dielectric-Barrier Discharge

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Dielectric barrier discharge (DBD) is a specific form of electrical discharge [1], which happens under high alternating voltage in the gas space between flat electrodes being separated by means of a dielectric barrier (*e.g.* glass or ceramic plate, Fig. 1). In the presence of the dielectric barrier, limiting the charge carrier movement, the current flows through a number of tinny short-lived sparkles – microdischarge channels randomly distributed in time and in the space of the discharge gap. Thus, the DBD exhibits an inhomogeneous (filamentary) structure with non-equilibrium plasma being generated inside in the microdischarge channels. In the DBD plasma at atmospheric pressure, the average electron energy achieves at least 4–5 eV, whereas in the environment of cool gases the temperature does not exceed several hundred Kelvins. Under conditions of DBD a number of reactions may be conducted, however, those generating non-equilibrium products are of special interest, *e.g.* the ozone synthesis from oxygen. It was found that due to the low average temperature of reactants, even unstable substances can be produced effectively. Under non-equilibrium plasma conditions, the rates of reactions being initiated by the electron impacts are relatively high even at low gas temperatures. Two kinds of DBD arrangement have been developed for the commercial use: 1) that generating the volume discharges as described above, and 2) basing on the action of surface discharges where the microdischarge channels are evolved on the surface of the dielectric. It should be added that the surface discharges can be observed also in the case when the grains of the dielectric material are introduced into the discharge gap of the DBD reactor. It is expected that the surface discharge may be even more efficient than the volume one, especially when the solid surface participates in the chemical transformations.

It is generally expected that methane from natural gas resources will play an increasingly important role in chemicals manufacturing. Taking this into account, a number of investigations were performed on methane processing using non-equilibrium plasma generated in DBDs. The reactions of methane both pure and in mixtures with helium or ethane were examined at ambient temperatures [2]. Considerable methane conversion was observed (over 20% with pure CH_4, and about 30% in mixtures with helium), ethane, ethylene, propane and butane being the reaction products. It is

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to point out that no acetylene formation was observed. Using DBD, the reactions of methane with carbon dioxide were studied [3–7]. At frequencies of 15 to 20 kHz methanol was obtained (up to 0.5%) with traces of CH_3OCH_3 in CH_4+O_2 mixtures and ethane (2%) in CH_4+CO_2 mixture. Various products, such as C_2 hydrocarbons and oxygenated compounds were obtained, depending on the CH_4/CO_2 ratio in the starting mixture [8]. A direct synthesis of methanol from methane and water vapour may proceed in DBD when ultra-short voltage pulses are applied [9,10]. Up till now, the yields of the reactions under investigation mentioned above were not satisfactory. The methane conversion into higher hydrocarbons was examined under DBD conditions using a flow reactor operated at atmospheric pressure and the frequency of 50 Hz [11]. It was made of a quartz-glass tube (being a dielectric barrier) with an inner metal (aluminium) high voltage electrode. Inter-electrode voltage was maintained constant at the 18 kV level and the temperature of the reactor was about 45°C. The methane conversion was examined in the presence of granular quartz-glass and silica gel grains (size of 1–2 mm), and without packing. Those materials did not influence the current-voltage characteristics of the discharge. The mixtures of methane 99.5% and argon 99.999% were used as the inlet gas. The gas compositions were determined using gas chromatography (GC Agilent 6890N).

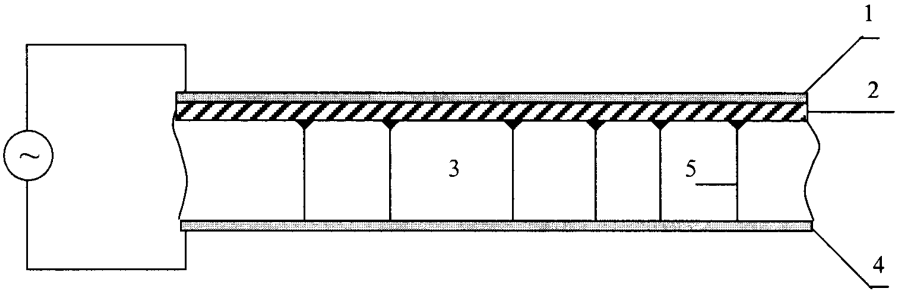

Figure 1. The structure of dielectric-barrier discharge (DBD); 1 and 4 – electrodes, 2 – dielectric barrier, 3 – discharge gap, 5 – microdischarge channel.

The results of experiments with CH_4+Ar mixture of 7.5% methane content, for the gas flow rate 2.7 – 16 Nl/h, are presented (Figs. 2–4) using the following quantities:

W	–	starting flow rate of CH_4+Ar mixture [mmol/h]
$W[CH_4]$	–	starting flow rate of CH_4 [mmol/h]
$W[CH_4]^*$	–	flow rate of CH_4 in the outlet [mmol/h]
P	–	discharge power [W], constant for all the measurements (5 W)

Overall methane conversion $$X = \frac{W[CH_4] - W[CH_4]^*}{W[CH_4]} \cdot 100\%$$

Methane conversion rate $$Y = X\,W[CH_4] \cdot \frac{1}{100} [\text{mmol } CH_4/h]$$

Specific energy per methane unit $$E_R = \frac{3600P}{W[CH_4]} \quad [\text{J/mmol } CH_4]$$

Energy efficiency $$\eta_E = \frac{Y}{3600P} \quad [\text{mmol } CH_4/J]$$

The growth of the overall methane conversion X, methane conversion rate Y, and energy efficiencies η_E were observed using both packing materials quartz-glass and silica gel. The influence of the packing on the methane conversion into C_2H_6 was examined (Table 1) for the flow rate W = 2.7 Nl/h.

Table 1. The influence of the packing on the overall methane conversion and conversion into C_2H_6 for CH_4+Ar mixture (7.5% CH_4) and W = 2.7 Nl/h.

Packing	Overall CH_4 conversion X [%]	CH_4 conversion into C_2H_6 [%]
None	33.8	8.4
Quartz-glass	43.5	9.2
Silica gel	38.9	9.2

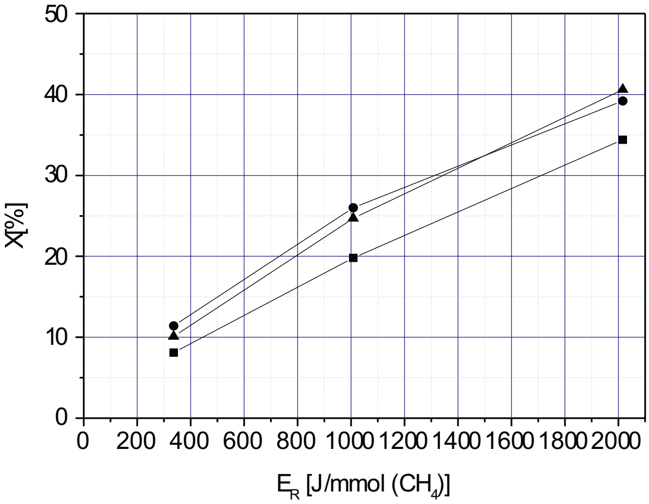

Figure 2. Overall conversion X *vs*. specific energy per CH_4 unit E_R for CH_4+Ar mixture (7.5% CH_4); W = 2.7, 4.9, 15.6 Nl/h; ■ – without packing, • – quartz-glass, ▲ – silica gel.

Under the action of barrier discharges in CH_4+Ar mixtures, ethane and hydrogen were the main gas products with small addition of unsaturated hydrocarbons C_2 (C_2H_2 and C_2H_4). A part of methane was transformed into non-volatile products (not identified). The high selectivity of ethane formation was observed earlier when methane

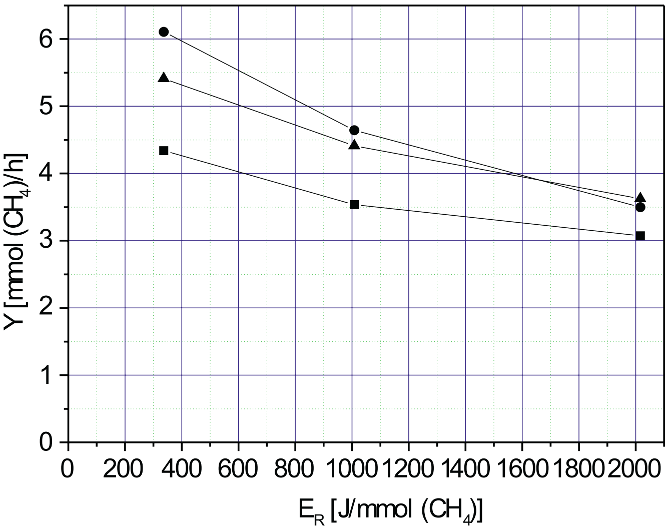

Figure 3. Methane conversion rate Y *vs.* specific energy per CH_4 unit E_R for CH_4+Ar mixture (7.5% CH_4); W = 2.7, 4.9, 15.6 Nl/h; ■ – without packing, ● – quartz-glass, ▲ – silica gel.

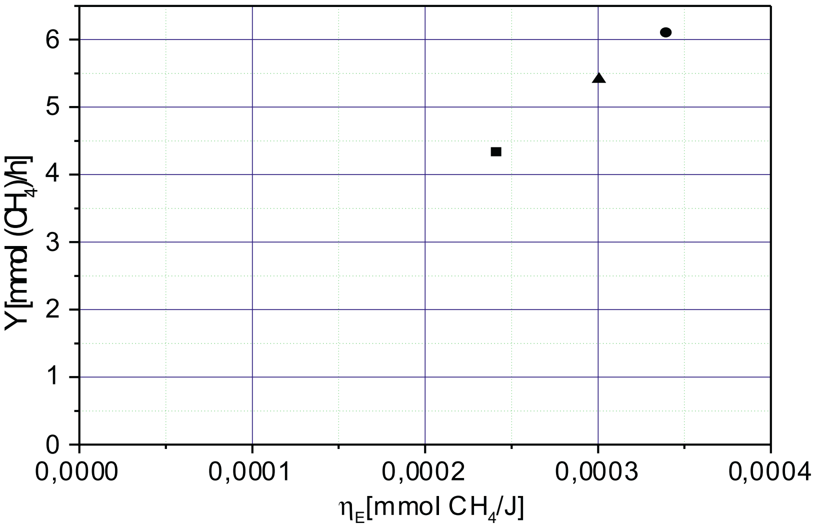

Figure 4. Methane conversion rate Y and energy efficiency η_E for CH_4+Ar mixture (7.5%, CH_4); W = 15.6 Nl/h; E_R = 336 J/mmol CH_4; ■ – without packing, ● – quartz-glass, ▲ – silica gel.

was converted under the conditions of DBD [2,8] and corona discharges [12]. Taking into account the low conversion into unsaturated hydrocarbons, it may be concluded that after the first steps of the chain reaction [11] when methane was converted into ethane, the transformation path was terminated. The filamentary feature of DBD is taken into account as the main reason for that. The chain reaction of methane conversion is started in the short-lived filamentary microdischarge (in several dozens of nanoseconds) and it is stopped shortly after the microdischarge disappears in the surroundings of cool gas. In addition, the solid surfaces of the packing grains may act as chain stoppers, being involved in the deactivation of high-energy particles (radicals, excited molecules). On the other hand, the surface feature of the microdischarges is a favourable circumstance for evolving the heterogeneous reactions of the active species on the grain surfaces. One can conclude that those processes take part in the overall methane transformation.

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