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Direct Plasma-Chemical Conversion of Methane into Gaseous and Liquid products

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Abstract

Research was carried out on non-oxidative conversion of methane and its mixture with water into gaseous and liquid products in the barrier discharge (BD) plasma. The major products of methane conversion are hydrogen (~60 %) and ethane (~29 %), and also gaseous C₃–C₄ hydrocarbons (~10 %) and C₅₊ alkanes (~1 %), of mainly isomeric composition. The conversion of methane is 9.5–9.7 % in both cases, which corresponds to the energy consumption for CH₄ reforming in the order of 46 eV/molecule. The presence of water on plasma-chemical reactor walls makes conditions for the efficient withdrawal of products from the discharge zone and prevents the formation of a deposit on the surface of the electrodes, which is proven by IR spectroscopy data. The paper deals with the redox mechanism of methane conversion in the BD plasma. As demonstrated, there is reaction initiation resulting from the collision of methane molecules with discharge electrons. Methyl and methylene radicals, and also atomic and molecular hydrogen, are mainly generated as a consequence of dissociation of the electron-excited methane molecule. Reaction products are further formed *via* the radical mechanism. The kinetics of transformation of the methane-water vapour-gas mixture into BD was modelled using the effective rate constant of the electron-molecular reaction and a simple expression to assess the value of the former. The expression for assessing the effective rate constant links the actual constant of the electron-molecular reaction rate to key parameters of the BD plasma and allows simplification of the simplification procedure of the modelling of the first. The chemical kinetics model for methane conversion involves 74 reactions. The calculation results are in good agreement with experimental data. As demonstrated by the analysis of reaction sensibility coefficients, there is an increase in the molecular mass of products mainly due to processes with methylene radical involvement.

Key words: methane, discharge barrier, non-oxidative conversion, reaction mechanism

INTRODUCTION

The importance of natural and associated gas for the energy industry and petrochemistry, and also to address environmental tasks is increased year by year. Therefore the development of new efficient methods for the conversion of hydrocarbon gases is one of the crucial scientific areas.

Methods for plasma-chemical conversion of methane, i.e. the major component of natural and associated oil gas, are being extensively considered in addition to thermocatalytic ones.

Researchers extensively deal with the latter in order to produce new petrochemical products.

Modern works on the plasma-chemical conversion of methane are focused on two areas of transformation: conversion to synthesis-gas for the Fischer–Tropsch process [1–9] and direct conversion into liquid products, mainly to methanol [10, 11]. The major causes that hold back the development of plasma-chemical methods for methane conversion are the low selectivity of plasma-chemical processes and the lack of a sufficient amount of data on their kinetics and mechanisms of transformations of organic compounds in electric discharges.

The present research reports experimental results for direct non-oxidative conversion of meth-

ane and its mixture with water into gaseous and liquid products in the barrier discharge (BD) plasma. The addition of water into methane flow prevents the process of deposit formation on the surface of reactor electrodes and makes conditions for the efficient withdrawal of reaction products from the discharge zone. Earlier, the authors successfully deployed the addition of *n*-octane into a flow of a mixture of propylene and oxygen when researching plasma-chemical oxidation of propylene into the BD plasma for similar purposes [12]. In this case, the selection of water is due to its higher resistance towards decomposition when exposed to the BD plasma compared to liquid hydrocarbons. Moreover, reaction products with the BD plasma involvement are easy to identify.

EXPERIMENTAL

Figure 1 lists an experimental setup. The outer wall of the reactor made of quartz glass with a thickness of 1.5 mm acts as a dielectric barrier. The grounded electrode is an aluminium foil fastened onto the surface of the former. The temperature of the outer wall of the reactor (20 °C) was controlled with a thermostat.

The high voltage electrode made of stainless steel is coupled to a quartz dielectric with a connection box; the backlash between them is 1 mm. The length of the discharge zone is 10 cm, the volume of 7 cm³. The amplitude of high-voltage

pulses of voltage, their repetition rate, and the active discharge power were 7.2 kV, 2 kHz, and 9.6 W, respectively, in all experiments. Discharge plasma parameters were recorded using Tektronix TDS 380 dual-channel digital oscilloscope *via* a voltage divisor and a shunt capacitance.

The gaseous reaction products were analysed with HP 6890 GC-MS equipped with a thermal conductivity detector (TCD) and a flame-ionisation detector (FID). Hydrogen content in the products was determined using the TCD and an HP-PLOT Molecular Sieves 5A column. The hydrocarbon fraction was analysed with the FID together with HP-PoraPlot Q and HP-1 columns for the gas and liquid fractions, respectively.

The formation of the deposit on the electrode surface was monitored using IR spectroscopy with Nicolet 5700 FTIR spectrometer and Collector II diffuse reflectance accessory.

RESULTS AND DISCUSSION

Table 1 lists the conversion and composition of gaseous transformation products of methane alone and its mixture with water. The major products of methane conversion are hydrogen (~60 %) and ethane (~29 %), and also C₃-C₄ gases (~10 %) and C₅₊ alkanes (~1 %). Ethylene and propylene were found in small amounts; their total content of ~0.6 %. In addition, there was methanol formation in a small amount (~0.2 %) was observed in ex-

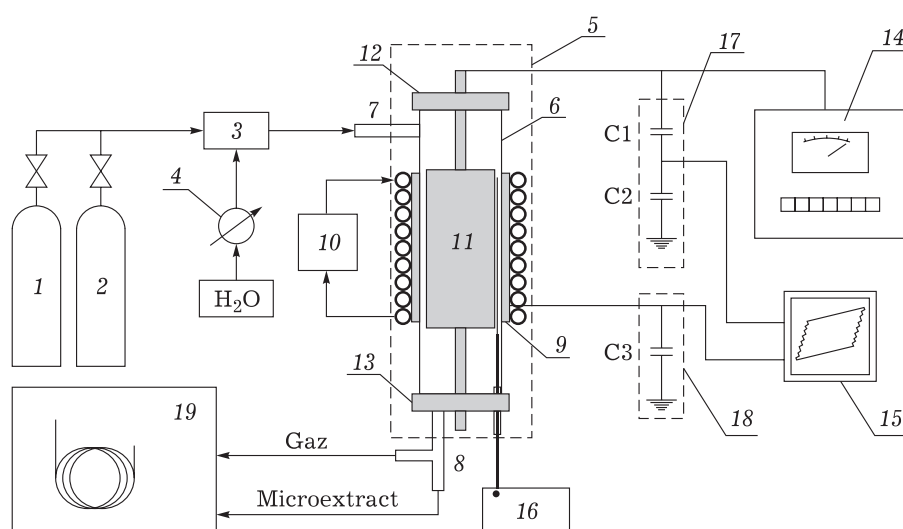


Fig. 1. Setup for direct non-oxidative conversion of methane in the barrier discharge plasma in the presence of water: 1 – methane, 2 – argon, 3 – mixer, 4 – peristaltic pump, 5 – plasma chemical reactor, 6 – quartz dielectric barrier, 7 – inlet fitting, 8 – outlet fitting, 9 – grounded electrode, 10 – thermostat, 11 – high-voltage electrode, 12, 13 – coupling, 14 – high-voltage pulse generator, 15 – digital oscilloscope, 16 – fibre optic spectrometer, 17, 18 – voltage divider and shunt capacitance, respectively, 19 – GC-MS.

periments with water. Methane conversion is 9.5–9.7 % in both cases, which corresponds to the energy consumption for transforming the initial hydrocarbon of the gas – in the order of 46 eV/molecule. The energy consumption for the conversion of methane in the BD is not contradictory to the literature data found in the 38–58 eV/molecule range [13].

The conversion of hydrocarbon gases under the BD exposure is accompanied by the formation of the deposit on the surface of reactor electrodes [14]. The addition of water as a liquid into the reactor prevents this process, which is proven by IR reflection spectra from the surface of the high-voltage electrode (Fig. 2). The spectrum acquired for the conversion of methane alone contains intense vibration bands for CH moieties typical for hydrogenated carbon-based materials [14].

In order to interpret the data acquired, the modelling of the kinetics of the transformation for a mixture of methane and water in the BD was carried out. The conversion involved the following steps: 1) the determination of the BD active power and electric field strength at the discharge gap of the reactor based on the coulombic performance; 2) calculations of the rate constants of electron-molecular reactions, the drift velocity of electrons using BOLSIG⁺ software [15], the effective rate constant of the electron-molecular reaction; 3) the modeling of chemical kinetics using the Kintecus program [16] for the mode of the ideal displacement without considering the dissolution of liquid products in water.

In order to assess the effective rate constant, there was suggested the expression:

TABLE 1

Conversion and composition of gaseous transformation products of methane alone and its mixture with water. Volumetric flow rates of methane and water are 30 cm³/min and 0.1 cm³/min, respectively

Products	Content, %		
	Experiment		Calculation
	CH ₄	CH ₄ -H ₂ O	CH ₄ -H ₂ O
H ₂	60.4	60.6	66.6
C ₂ H ₄	3.3	0.5	–
C ₂ H ₆	24.6	28.9	16.2
C ₃ H ₆	0.5	0.1	–
C ₃ H ₈	7.8	5.5	6.7
<i>i</i> -C ₄ H ₁₀	1.0	1.0	1.1
<i>n</i> -C ₄ H ₁₀	1.6	2.3	3.3
C ₅₊	0.8	0.9	4.6
CH ₃ OH	–	0.2	1.9
Conversion, %	9.7	9.5	6.8

$$k_{\text{eff}} = k_e W_s f / q_e v_e (E/n) n_0 \quad (1)$$

where k_e , W_s , q_e , v_e , E/n , and n_0 are the rate constant of the electron-molecular reaction, the specific energy of BD, the repetition rate of voltage pulses, the elementary charge of the electron, the drift velocity of electrons, the reduced electric field strength, and the Loschmidt constant, respectively.

Expression (1) links the actual rate constants of electron-molecule reactions with BD key parameters (the specific power of discharge, the adduced strain of the electric field, and the drift velocity of electrons) and significantly simplifies calculations.

Initiating the reaction in electric discharges occurs resulting from the collision of molecules with

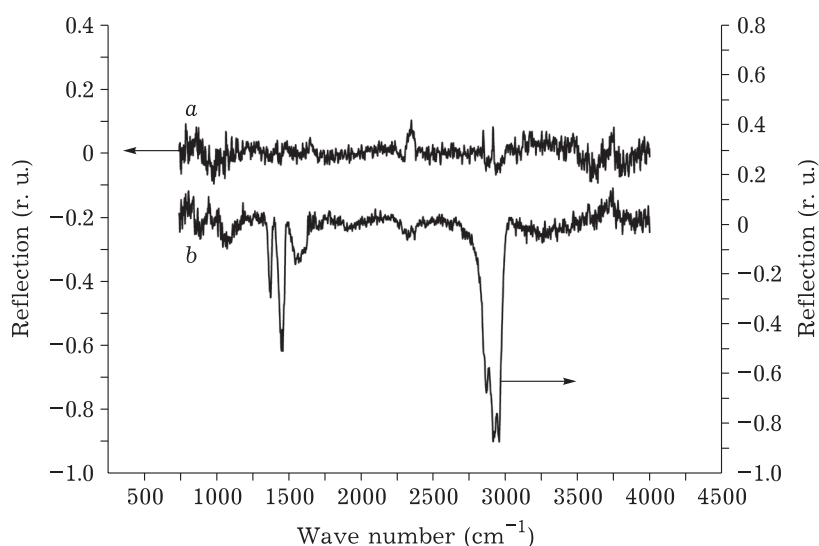
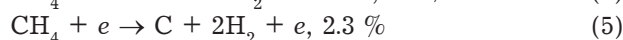
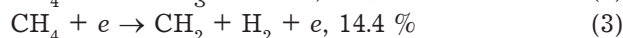
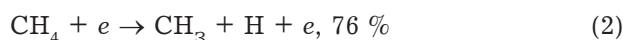


Fig. 2. IR reflection spectra from high-voltage electrode surface: *a* – methane – water mixture, *b* – methane alone.

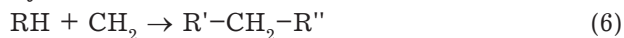
electrons. Paper [17] reports the data regarding the major dissociation channels for the electron-excited methane molecule:



The model of chemical kinetics of methane conversion into BD involves 74 reactions. They are limited by processes with the involvement of pentane. The values for rate constants of chemical reactions are borrowed from the available database [18]. Selecting the most important reactions was made on the basis of the analysis of rate constants of electron-molecular reaction and sensibility coefficients of interactions using Kintecus and Atropos programs [19]. The database [20] provided cross sections for the scattering of electrons by methane molecules.

Table 2 lists a set of reactions and appropriate rate constants. The calculation results are in good agreement with experimental data (see Table 1). The elevated content of C_{5+} alkanes and methanol is related to the fact that the calculations do not consider the solubility of the species in water.

As demonstrated by the analysis of sensibility coefficients of the reactions, C_{3+} hydrocarbons are mainly generated because of the embedding reaction of the CH_2 group into the C–C bond of the hydrocarbon molecule:



Thus, the proposed kinetic model for the process of non-oxidative conversion of methane in the BD in the presence of water explains an increase in the molecular mass of transformation products of methane due to processes with the involvement of the CH_2 group.

CONCLUSION

This paper proposes a novel method for non-oxidative conversion of methane into gaseous and liquid products in the barrier discharge (BD) plasma. The use of water enables to avoid the undesirable formation of the deposit on the surface of the reactor electrodes and increase the selectivity of the process.

The major products of methane conversion are hydrogen (~60 %) and ethane (~29 %), gaseous $\text{C}_3\text{--C}_4$ hydrocarbons (~10 %), and C_{5+} alkanes (~1 %)

TABLE 2

Set of reactions and appropriate rate constants of the model chemical kinetics of non-oxidative conversion of methane in the barrier discharge plasma

Entry	Reaction	Reaction rate constant, $\text{cm}^3 \cdot \text{s}^{-1}$	Reference
1	$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	$9.12 \cdot 10^{-3} \text{ s}^{-1}$	Calculation
2	$\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2$	$1.68 \cdot 10^{-3} \text{ s}^{-1}$	»
3	$\text{CH}_4 \rightarrow \text{CH} + \text{H}_2 + \text{H}$	$8.40 \cdot 10^{-4} \text{ s}^{-1}$	»
4	$2\text{CH}_3 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_4$	$1.56 \cdot 10^{-26} \text{ cm}^6 \cdot \text{molecule}^{-2} \cdot \text{s}^{-1}$	[21]
5	$\text{CH}_4 + \text{CH} \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$2.49 \cdot 10^{-12}$	[22]
6	$2\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	$5.30 \cdot 10^{-11}$	[23]
7	$\text{CH}_3 + \text{H} + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_4$	$5.94 \cdot 10^{-29} \text{ cm}^6 \cdot \text{molecule}^2 \cdot \text{s}^{-1}$	[21]
8	$\text{CH}_2 + \text{H} \rightarrow \text{CH} + \text{H}_2$	$2.01 \cdot 10^{-10}$	[21]
9	$\text{C}_2\text{H}_6 + \text{CH}_2 \rightarrow \text{C}_3\text{H}_8$	$4.80 \cdot 10^{-12}$	[24]
10	$\text{C}_2\text{H}_6 + \text{CH} \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	$1.30 \cdot 10^{-10}$	[25]
11	$\text{C}_3\text{H}_8 + \text{CH}_2 \rightarrow n\text{-C}_4\text{H}_{10}$	$4.42 \cdot 10^{-12}$	[24]
12	$\text{C}_3\text{H}_8 + \text{CH}_2 \rightarrow i\text{-C}_4\text{H}_{10}$	$1.89 \cdot 10^{-12}$	[24]
13	$n\text{-C}_4\text{H}_{10} + \text{CH}_2 \rightarrow \text{C}_5\text{H}_{12}$	$4.30 \cdot 10^{-12}$	[24]
14	$i\text{-C}_4\text{H}_{10} + \text{CH}_2 \rightarrow \text{C}_5\text{H}_{12}$	$6.44 \cdot 10^{-12}$	[24]
15	$\text{C}_5\text{H}_{12} + \text{CH}_2 \rightarrow \text{C}_6\text{H}_{14}$	$6.44 \cdot 10^{-12}$	By analogy with [14]
16	$\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5$	$1.20 \cdot 10^{-12}$	[26]
17	$\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	$3.01 \cdot 10^{-12}$	[26]
18	$\text{C}_3\text{H}_6 + \text{H} \rightarrow \text{C}_3\text{H}_7$	$9.39 \cdot 10^{-14}$	[28]
19	$2\text{C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$	$1.69 \cdot 10^{-11}$	[27]
20	$\text{H}_2\text{O} + \text{CH} \rightarrow \text{CH}_2\text{OH}$	$3.39 \cdot 10^{-11}$	[29]
21	$\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CH}_3\text{OH}$	$2.89 \cdot 10^{-10}$	[30]

of mainly isomeric composition. Methane conversion in the presence of water is ~ 9.5 . That corresponds to the energy consumption for CH_4 reforming in the order of 46 eV/molecule.

The modelling method of chemical kinetics in the BD using the effective rate constant of the electron-molecular reaction and a simple expression to assess the value of the latter significantly simplifying kinetical calculations has been suggested. As demonstrated by an example of modelling the kinetics of methane transformation, an increase in the molecular mass of the products takes place due to processes involving the CH_2 group.

In the long run, gaseous hydrocarbons formed upon the conversion of methane are of interest as raw materials for subsequent catalytic processing, e.g., into aromatic hydrocarbons, and C_{5+} hydrocarbons as synthetic liquid fuel components. Their relatively high energy cost in the latter case may be compensated by the lack of the energy-intensive catalytic gas-to-liquid (GTL) process.

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