

A Kinetic Study on the Conversion of Methane to Higher Hydrocarbons in a Radio-Frequency Discharge

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Abstract—This study investigated methane conversion with direct current discharge at low pressure in a radio frequency. The main gaseous products of the reaction were ethane, ethylene, acetylene and propane. This study was concentrated on the influence of discharge conditions on the conversion of methane to higher hydrocarbons. Reaction temperature, electron density and mean residence time were calculated from experimental data and mathematical relations. The maximum conversion of the methane was about 45% with the pure methane as a reactant. Ethane was the main product when the reaction occurred in the glow discharge. Ethane selectivity decreased with the increase of the gas temperature. The kinetics of reactions was also analyzed from possible reaction equations and various rate constant data. Consequently, the dissociation constant and the density of radicals could be obtained at any experimental conditions.

Key words: Plasma, Methane, Conversion, Radio-frequency Discharge, Kinetics

INTRODUCTION

Natural gas, which contains about 90% methane, can be used as a raw material for the chemical industry. Methane is very stable, so it is very difficult to convert it to other chemicals. This problem has been extensively studied [Kassel, 1932], and there are two ways to solve it: methane pyrolysis and methane conversion by chemical reactions, including catalytic and plasma processes [Cho et al., 1998; Jeong et al., 2001].

The present study is devoted to methane conversion in radio-frequency discharge at low pressure. The previous study in our group was also devoted to the methane dissociation process [Kim et al., 2003; Hwang et al., 2003; Sergey et al., 2003; Na et al., 2002; Savinov et al., 1999, 2002; Lee et al., 2001; Jeong et al., 2001]. In our work the plasma parameters (electron density, mean electron energy, gas temperature in discharge zone etc.) were not necessary for estimating the methane conversion in radio-frequency plasma. It needed only the information about specific energy per one molecule of the feed gas. However, we needed some information about electron density and gas temperature in the discharge zone to understand the higher hydrocarbon formation processes. The present study concentrates on the influence of discharge conditions on the conversion of methane to higher hydrocarbons such as ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2) and propane (C_3H_8).

EXPERIMENTAL

The experimental setup was almost the same as our previous work [Savinov et al., 1999]. A cylindrical continuous-flow reactor was used for capacitively coupled radio-frequency discharge. The plasmachemical reactor was made of a Pyrex (or quartz) tube. Four cop-

per wires located on the outside tube were used as electrodes. The diameter of the wire was $d/10$, where d is inner diameter of the tube. Any two of these were connected to a power supply and the other two were grounded. Methane (or gas mixtures) went through the discharge tube and the product gases were analyzed by mass spectrometer. The radio-frequency plasmachemical reactor and most of experimental equipment were described in detail in our previous work [Savinov et al., 1999]. The main peculiarity of this type of reactor was the very small size of the electron sheathes. Consequently, almost all the discharge tube volume was filled with positive column plasma. This fact enabled us to use the results which were obtained from positive column plasma of direct current glow discharge for the interpretation of experimental data of radio-frequency discharge.

A radio-frequency generator with 13.56 MHz (Auto Electric Co., Model ST-350) and a Matching Network (Auto Electric Co., Model LC-1000) delivered output power from zero to 300 W. The magnitude of reflected power did not exceed 5% of the delivered power. The maximum of unique input power for the reactor was about 7.2 Wcm^{-3} . While measuring the input power, we ignored the energy loss through radiation. Furthermore, we suggested that all input power is absorbed by positive column plasma.

Some experiments were made with direct current glow discharge. A glass water-cooled discharge tube with inner diameter of 1.6 cm and the length of discharge zone of 12.5 cm was used. DC power supply with an ohmic ballast resistance ($R=100\text{--}400 \text{ k}\Omega$) delivered an electrode voltage up to 10 kV and a discharge current up to 50 mA.

Quadrupole mass spectrometer (Balzers, QMS200) with Quadstar software was used for qualitative and quantitative analysis of the gas mixture. Before measurements, we calibrated the mass spectrometer with the data based on the mass spectrum of the binary mixtures. CH_4 , C_2H_6 , C_2H_4 , C_3H_8 and Ar gases with 99.9% purity were used for the calibration.

Some expressions in our previous work [Savinov et al., 1999]

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were used to define the conversion of the initial substance, molecular flow of substance and products. The residence time was considered for the change of the flow rate by chemical reactions.

THEORETICAL BACKGROUND

1. Remarks about Measurements in Chemically Active Flowing Systems

We investigated plasmachemical reactions in a flow system, which meant that the discharge medium in our system might be inhomogeneous. In order to evaluate the inhomogeneity, it is necessary to compare the residence time of molecules in the discharge zone and the diffusion times. The residence time for the system is [Savinov et al., 1999]

$$\tau_R = 0.395 \frac{LS}{\delta_R \hat{V}_0 \bar{T}_R} \frac{P_R}{\bar{T}_R} \quad (1)$$

where L is length of the discharge zone, S is cross section of the discharge tube, $\hat{V}_0$ is total flow rate of a gas at $P_0=760$ torr and $T_0=300$ K, P_R is the gas pressure and $\bar{T}_R$ is the mean gas temperature in the discharge zone. The factor δ_R gives an account of the flow rate change because of chemical reactions. In our experimental conditions, τ_R was from 0.1 sec ($\hat{V}_0=100$ cm³min⁻¹, $P_R=9$ torr and $\bar{T}_R=740$ K) to 1.75 sec ($\hat{V}_0=31$ cm³min⁻¹, $P_R=28$ torr and $\bar{T}_R=480$ K).

Diffusion time towards the tube walls (radial diffusion) is [Raizer, 1991]

$$\tau_1^D = \frac{1}{D} \left(\frac{r}{2.4} \right)^2 \quad (2)$$

Diffusion time along to the axis of the discharge tube (axial diffusion) is [Raizer, 1991]

$$\tau_2^D = \frac{1}{D} \left(\frac{L}{\pi} \right)^2 \quad (3)$$

In Eqs. (2) and (3), D is a mutual diffusion coefficient and r is the radius of discharge tube.

The main components of the gas mixture in the discharge zone are hydrogen and methane [Savinov et al., 1999]. For calculation of mutual (CH_4 and H_2) diffusion it is possible to use the Chapman-Enskog formula for the diffusivity [Bird et al., 1960].

It is possible to show that $\tau_1^D \ll \tau_R$ and $\tau_2^D \gg \tau_R$ for all experimental conditions. For example, $\tau_R=1.75$ sec at $\hat{V}_0=31$ cm³min⁻¹, $P_R=28$ torr and $\bar{T}_R=480$ K. Under these conditions, $D_{\text{CH}_4, \text{H}_2}=1,300/P_R=46.4$ cm²s⁻¹ and $\tau_1^D=3.7 \times 10^{-3}$ sec, $\tau_2^D=5.5$ sec. It means that, in the first approximation, the chemical composition of the gas medium is homogeneous in cross-section of the discharge tube and inhomogeneous along the axis of this tube. Consequently, all the plasma parameters will depend on the axis co-ordinate. When these parameters are defined, they will concern the intermediate cross section of the discharge tube.

2. Estimation of a Gas Temperature in the Discharge Zone

It is known that the radial temperature distribution in a gas discharge tube is parabolic [Raizer, 1991; Brunet and Lavarini, 1969; Ochkin et al., 1989].

$$T(r) = T(0) - [T(0) - T(R)] \frac{r^2}{R^2} = T(0) - \Delta T \frac{r^2}{R^2} \quad (4)$$

It is convenient to use the arithmetic mean value of a gas temperature $\bar{T} = [T(0) - T(R)]/2$.

There are two ways for transport of Joule heat in a flowing gas discharge: thermal conductivity and convective heat transport.

2-1. Transport of Joule Heat by Thermal Conductivity

In a tube without gas flow, the heat is transported to the walls, which can be assumed to be at room temperature. The heat flux density into the wall of the tube is

$$J_R = -k \frac{\partial T}{\partial r} \Big|_{r=R} = \frac{4k(\bar{T} - T_w)}{R} \quad (5)$$

where k is the thermal conductivity and T_w is the temperature of the reactor wall.

The energy loss from 1 cm³ of a gas at each second is

$$w = \frac{2\pi RL}{\pi R^2 L} J_R = \frac{2J_R}{R} = \frac{8k(\bar{T} - T_w)}{R^2} \quad (6)$$

By using the conduction of energy balance, we define

$$\eta \frac{W}{V} = \frac{8k(\bar{T} - T_w)}{R^2} \quad (7)$$

where W is the total input power, V is the volume of discharge zone ($V=\pi R^2 L$), and η is the fraction of total input power transferred to the heat.

Expression for energy loss may be written as follows [Raizer, 1991]:

$$\frac{k(\bar{T} - T_w)}{R^2} = NC_{p1}(\bar{T} - T_w) \nu_T \quad (8)$$

where N is the gas density [cm⁻³], C_{p1} is the heat capacity at constant pressure per one molecule and ν_T is heat removal frequency (the inverse to the time of heat removal from the volume).

The heat removal frequency is [Raizer, 1991]

$$\nu_T = \frac{\chi}{\Lambda^2} \quad (9)$$

where $\chi = k/(NC_{p1})$ is the thermometric conductivity and $\Lambda = R/\sqrt{8}$ is the heat length.

From Eq. (7), we obtain

$$T = T_w + \frac{\eta W}{8\pi k L} \quad (10)$$

For pure gases, k values are known, but thermal conductivity of gas mixtures at low density may be estimated by a method analogous to the semi-empirical formula of Wilke for viscosity [Bird et al., 1960].

2-2. Convective Heat Transport

Another mechanism is possible for transporting heat out of an effluence gas through the reactor. If we talk in terms of temperature averaged over the length L , the rate of heat removal from the discharge volume can be written in the familiar form $NC_{p1}(\bar{T} - T^0)\nu_F$ [Raizer, 1991]. T^0 is the temperature of the gas entering the discharge zone, and ν_F is convective heat output frequency described as follows:

$$\nu_F \approx \frac{2}{\tau_R} \quad (11)$$

where τ_R is the residence time of molecules in the discharge. The factor "2" takes into account that on average, the heat is transported "half the distance." In order to know the main method of heat transport, the frequency of thermal conductivity output and the frequency of convective heat output must be compared.

There is an example to define the mechanism of heat loss. The main components of the gas mixture are methane and hydrogen. At $T_0=300$ K, the thermal conductivity of hydrogen ($k_{H_2}=18.3 \times 10^{-4} \text{ Wcm}^{-1}\text{K}^{-1}$) was greater than the one of methane ($k_{CH_4}=3.42 \times 10^{-4} \text{ Wcm}^{-1}\text{K}^{-1}$) [Arigorev et al., 1991].

From Eqs. (8), (1) and (11), we obtain

$$v_T = \frac{k}{N C_{p1} R^2} \quad (12)$$

$$v_F = 5.06 \frac{\delta_R \hat{V}_0}{N \kappa L S} \quad (13)$$

where $\kappa=1.04 \times 10^{-19} \text{ torr cm}^3 \text{ K}^{-1}$ is Boltzmann's constant.

By using Eq. (12) and (13), we find

$$\frac{v_F}{v_T} = 1.9 \times 10^{18} \frac{\delta_R \hat{V}_0 C_{p1}}{\kappa L} \quad (14)$$

For methane, $C_p=36 \text{ J mol}^{-1}\text{K}^{-1}$, $C_{p1}=C_p/N_A=6 \times 10^{-23} \text{ J K}^{-1}$. In a case of $L=50 \text{ cm}$, $\hat{V}_0=1.67 \text{ cm}^3\text{s}^{-1}$, $k=3.42 \times 10^{-4} \text{ Wcm}^{-1}\text{K}^{-1}$ and $\delta_R \sim 1$, $v_F/v_T=10^{-2} \ll 1$. It means that the main mechanism of the heat transport is only thermal conductivity. For estimation of a gas temperature in the discharge zone, Eq. (10) may be used. It is possible to put $\eta \approx 1$ in Eq. (10). This is true for many types of atomic and molecular gases excluding nitrogen [Raizer, 1991].

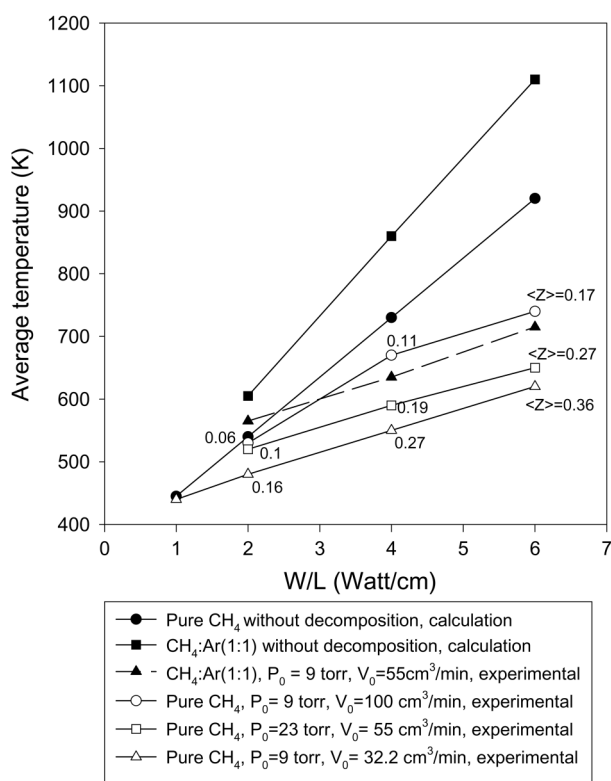


Fig. 1. The dependence of the mean gas temperature in discharge zone on W/L.

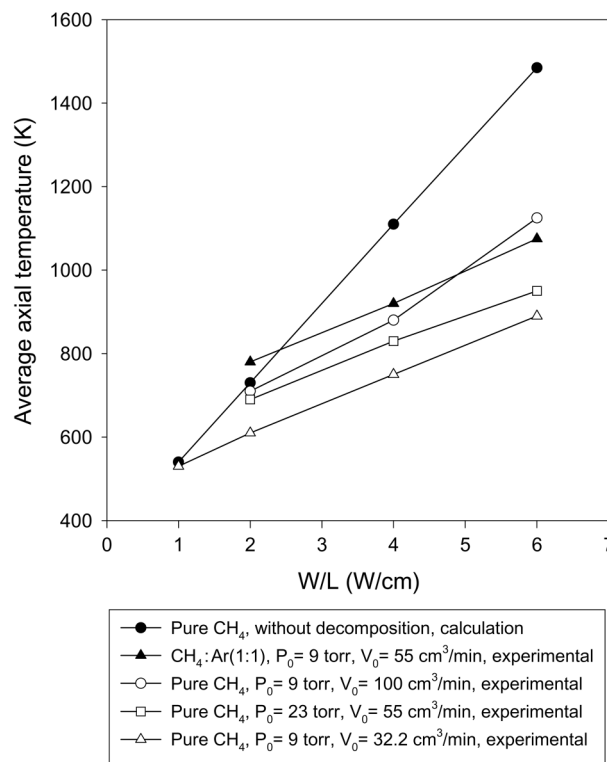


Fig. 2. The dependence of the mean axial temperature in discharge zone on W/L.

RESULTS AND DISCUSSION

We calculated the value of the gas temperature in the discharge zone by taking into account the dissociation of methane. For the experiments with pure CH_4 , we supposed that the gases in the discharge zone were mixtures of CH_4 and H_2 . For the experiments with a mixture of CH_4 and Ar, we supposed that the gases in the discharge zone were the mixtures of CH_4 , Ar and H_2 . That is, we did not take into account the influence of the thermal conductivity of producing higher hydrocarbons. The results of these calculations are shown on Fig. 1 and Fig. 2. Fig. 1 gives us information about the dependence of the mean gas temperature in the discharge zone on W/L, and Fig. 2 about the dependence of the mean axial temperature in the discharge zone on W/L.

It may be seen from these figures that the dissociation of CH_4 very noticeably decreases with the gas temperature, where $\langle Z \rangle$ in Fig. 1 is the mean value of conversion over the length of the discharge tube. This is true both for pure CH_4 and for mixture of CH_4 -Ar(1:1). This temperature decrement was caused by the hydrogen formation in discharge zone and as result the increase of the total thermal conductivity of gas mixture. These results about estimation of the gas temperature in the discharge zone will be used in the next sections of this study.

1. Estimation of an Electron Density

Complicated methane plasma chemistry in discharge begins because of the process of methane dissociation by direct electron impact. For interpretation of processes taking place in gas discharge plasma, it is necessary to have information about electron density, n_e .

1-1. Basic Relation

The mobility of massive ions is hundreds of times less than that of an electron [Raizer, 1991]. As a rule, the contribution of ions to the electric current is small. The current density J in plasma with $n_e \approx n_i^+$ is

$$J = -en_e v_d \quad (15)$$

where e is the electron charge, n_e is the electron density and v_d is the electron drift velocity. The energy related by the current in 1 cm³ of the gas and 1 second is

$$w = \frac{W}{LS} = JE \quad (16)$$

where E is the electric field strength. From Eqs. (15) and (16), we obtain

$$n_e = \frac{W}{LS} \frac{\kappa T_R}{e v_d (E/N) P} \quad (17)$$

where N is the total density of heavy particles (atoms and molecules) in plasma.

The drift velocity depends on the parameter, E/N . v_d of pure gas is a known value [Arigorev et al., 1991]. When drift velocities are evaluated for gas mixtures, the averaging over percentage contents of the components must be carried out not for velocities, but for their inverse values [Raizer, 1991].

$$(v_{d,mix})^{-1} = \sum_i \frac{N_i}{N} (v_{d,i})^{-1} \quad (18)$$

In order to determine n_e by using Eq. (17), we must know input power, gas pressure, gas temperature in discharge zone and parameter, E/N (if we know E/N , we also know the drift velocity).

1-2. Determination of E/N and n_e

For determination of E/N , we used direct current glow discharge in mixtures $\text{CH}_4\text{-H}_2$ and $\text{CH}_4\text{-H}_2\text{-Ar}$ at the conditions which correspond to the conditions in the intermediate cross section of the tube with radio-frequency discharge. The pressure in DC discharge tube was selected by using similarity law [Granovsky, 1952], $P(\text{DC})d(\text{DC}) = P(\text{rf})d(\text{rf})$, where $d(\text{DC})$ is the diameter of the DC discharge tube and $d(\text{rf})$ is one of the radio-frequency discharge tubes.

With help of DC glow discharge, we obtained the dependencies of $E/N = E \kappa T_R / P_R$ on the value of W/L . The temperatures were determined in accordance with the above section. These dependencies were used for the determination of E/N for the radio-frequency discharge. After this, it was possible to find the values of electron density n_e . Fig. 3 shows the dependencies of electron density on input power for discharge in pure CH_4 and in mixture of CH_4 and Ar. In the figure γ is the fraction of gas-phase hydrocarbon product. Initial conditions were: (1) pure CH_4 at $P_0 = 23$ torr, $\hat{V}_0 = 55 \text{ cm}^3 \text{ min}^{-1}$, and (2) Mixture of CH_4 and Ar at $P_0 = 23$ torr, $\hat{V}_{0,\text{CH}_4} = 27.5 \text{ cm}^3 \text{ min}^{-1}$ and $\hat{V}_{0,\text{Ar}} = 27.5 \text{ cm}^3 \text{ min}^{-1}$.

The electron densities of both cases were increased with increasing input power and at the same input power, n_e for the discharge in $\text{CH}_4\text{-Ar}$ mixture was noticeably higher than that for the discharge in pure methane ($n_e(\text{CH}_4\text{-Ar})/n_e(\text{CH}_4) \approx 1.6$).

2. The Mechanism of CH_4 Dissociation and Higher Hydrocarbon Formation in Nonequilibrium Plasma: Analysis of Kinetics

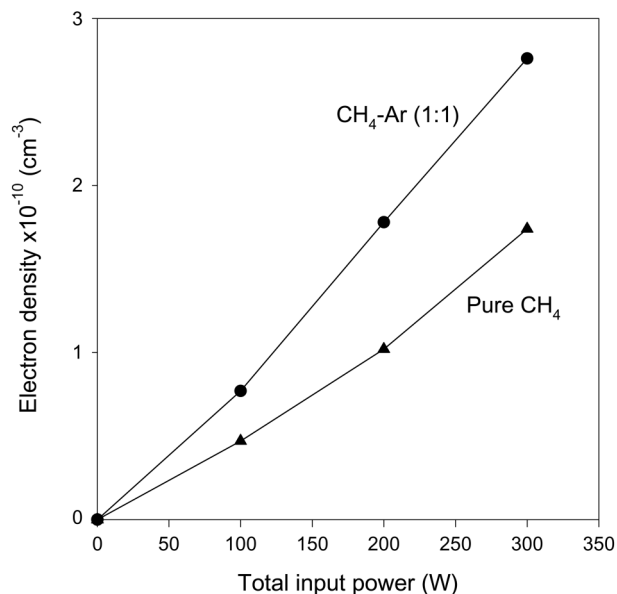


Fig. 3. The dependencies of electron density on the input power for discharge in pure CH_4 and in mixture of CH_4 and Ar.

The total mechanism of methane dissociation and higher hydrocarbon formation is highly complicated. For example, in order to understand detailed kinetic modeling of autocatalysis in methane pyrolysis (the process without discharge), Dean [1990] analyzed 44 gas-phase reactions among 25 species. In nonequilibrium gas discharge, the situation is more complex. We do not know many values of rate constants for reactions in each condition. In this work, we give the approximate description of the plasmachemical processes.

2-1. Gas-phase Reactions

The main objectives of this work were the homogeneous gas-phase plasmachemical reactions. In this paper, we were limited only to the qualitative description.

The main gas-phase products of methane decomposition in gas discharge in our case were ethane, ethylene, acetylene, propane and hydrogen. In order to determine the fraction of gas-phase hydrocarbon products, we used the next relation.

$$\gamma_{\text{gas-phase}} = \frac{2([C_2H_6] + [C_2H_4] + [C_2H_2]) + 3[C_3H_8]}{[CH_4]_{\text{diss}}} \quad (19)$$

where $[]$ is the density of each component, and $[CH_4]_{\text{diss}}$ is the density of the dissociated methane. All of these densities were measured by mass spectrometer. The dependencies of $\gamma_{\text{gas-phase}}$ on specific input power are presented on Fig. 4 for some experimental conditions. From Fig. 4 and Fig. 1, the following phenomena were observed.

(1) The fraction of gas-phase hydrocarbon products was decreased with the increase of specific input power.

(2) The fraction of gas-phase hydrocarbon products was high if the gas pressure was high at the same input power.

(3) The fraction of gas-phase hydrocarbon products was high if the gas temperature in the discharge zone was low at the same gas pressure.

All of these facts can be explained qualitatively by the diffusion phenomenon. The molecular flow on the walls of the discharge was

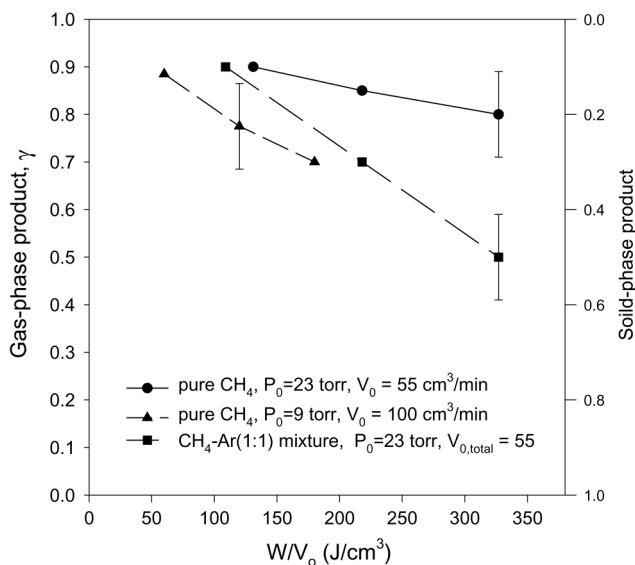


Fig. 4. The fraction of gas-phase products for specific input power.

caused by diffusion. The mean frequency of diffusional removal of particles (radicals, atoms and molecules) was increased with increasing gas temperature, and was decreased with increasing gas pressure. The solid-phase product was increased with increasing the input power. This was related to the increase of the number of active species. The solid-phase material is high molecular hydrocarbons.

2-2. CH₄ Decomposition and Higher Hydrocarbon Formation: The Results of Experiments

Fig. 5 shows the dependencies of methane conversion, Z , on specific input power for the discharge in pure methane ($P_0=23$ torr, $\hat{V}_0=55$ cm³min⁻¹) and in CH₄-Ar(1:1) mixture ($P_0=23$ torr, $\hat{V}_{0,CH_4}=27.5$ cm³min⁻¹ and $\hat{V}_{0,Ar}=27.5$ cm³min⁻¹). As shown in Fig. 5, methane

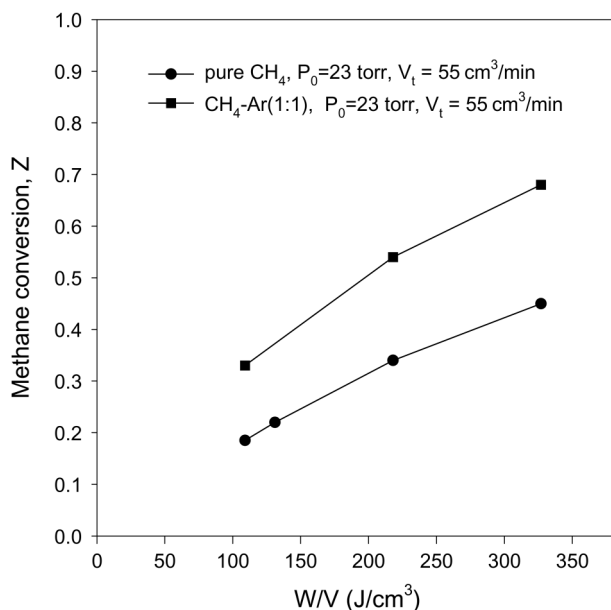


Fig. 5. The dependencies of methane conversion on the specific input power for the discharge in pure methane and CH₄-Ar (1 : 1).

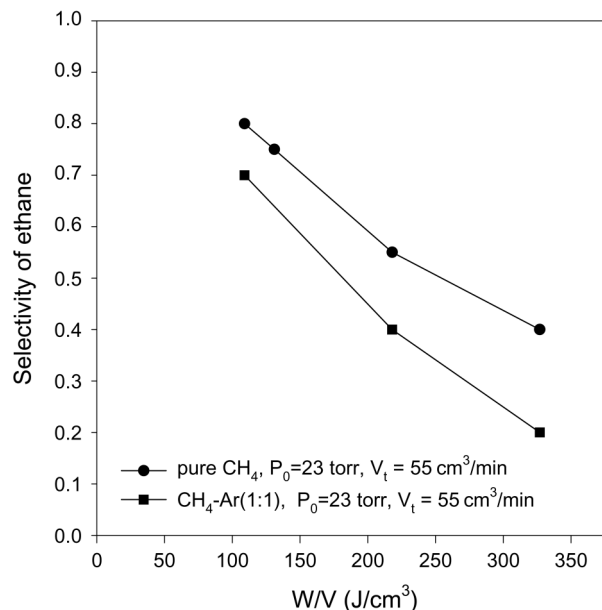


Fig. 6. The dependencies of ethane selectivity on the specific input power for discharges in the pure methane and mixture.

conversion was increased with increasing input power and methane conversion of mixture was higher than that of pure methane.

Fig. 6 shows the dependencies of ethane selectivity γ ($\gamma_{C_2H_6}=2[C_2H_6]/[CH_4]_{diss}$) on specific input power for discharges in the pure methane and mixture. The ethane selectivity was decreased with increasing input power. The ethane selectivity for the discharge in the pure methane was higher than that in the mixture. At small input power, the ethane selectivity is quite high. In our case, at $W \sim 100$ Jcm⁻³, γ is equal to 0.8 for discharge in the pure methane. Fig. 7 represents the dependencies of propane selectivity ($\gamma_{C_3H_8}=3[C_3H_8]/[CH_4]_{diss}$) on

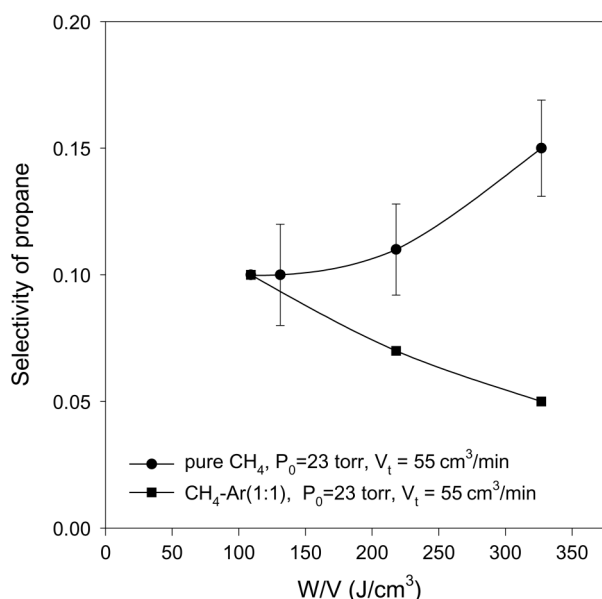


Fig. 7. The dependencies of the propane selectivity on the specific input power for discharges in the pure methane and mixture.

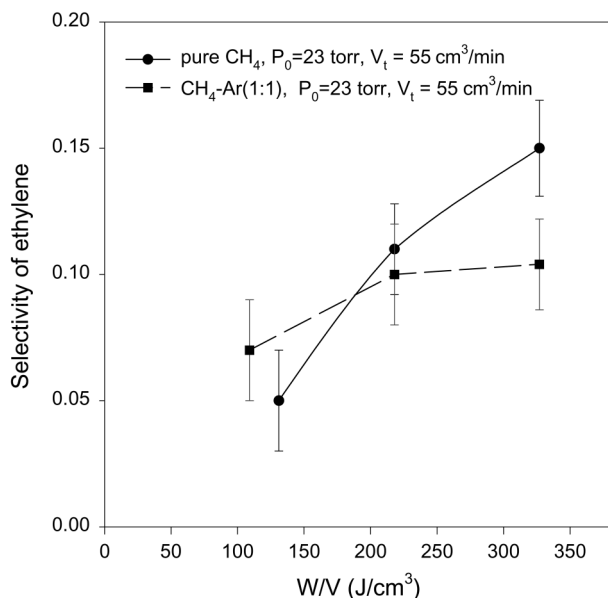


Fig. 8. The dependencies of the ethylene selectivity on the specific input power for discharges in the pure methane and mixture.

specific input power for the above-mentioned conditions. At small specific input power, the propane selectivity for these cases was the same ($\gamma_{C_3H_4} \sim 0.1$), but it was increased for discharge in the pure methane and decreased for the mixture with increasing specific input power. Fig. 8 shows the dependencies of the ethylene selectivity ($\gamma_{C_2H_4} = 2[C_2H_4]/[CH_4]_{diss}$) on specific input power at the same conditions. The ethylene selectivity for the discharge in pure methane increased with increasing input power more sharply than that for the discharge in the mixture. Fig. 9 shows the dependencies of the

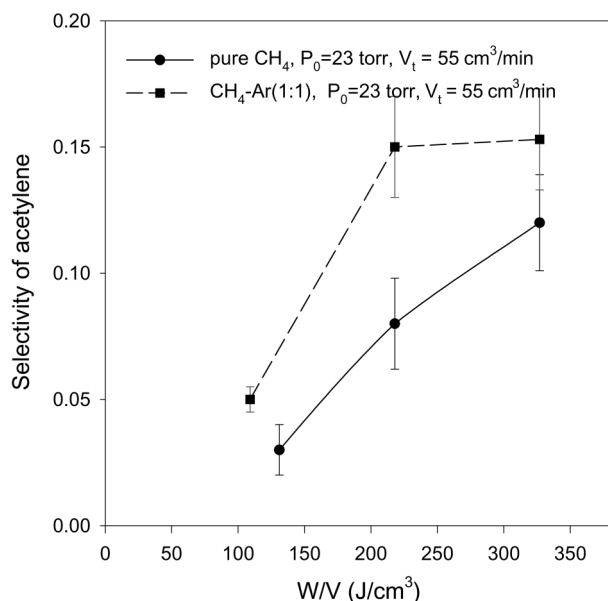


Fig. 9. The dependencies of the acetylene selectivity on the specific input power for discharges in the pure methane and mixture.

acetylene selectivity ($\gamma_{C_2H_2} = 2[C_2H_2]/[CH_4]_{diss}$) on specific input power. The acetylene selectivity for discharge in mixture was higher than one for discharge in the pure methane. When Ar was used as the mixture gas, the concentration of CH₄ was lower than the pure methane. The methane molecule had more chance to be exposed to the plasma energy. Ar molecule acted as the energy transfer medium. When Ar with high energy collided with methane, the energy was transferred to the methane and it was activated.

From all these facts, we can make some conclusions:

- (1) The main products of methane decomposition in radio-frequency discharge were ethane, ethylene, propane and acetylene.
- (2) If the electron density and gas temperature were not so high (when the input power was small), the main product was ethane.
- (3) When the electron density and gas temperature were increased, the ethane selectivity was decreased and other hydrocarbons began to form in noticeable amount.

2-3. Analysis of Kinetics

In order to understand the characteristics of methane decomposition process in gas discharge, let us consider the group of main plasmachemical reactions taking place in our conditions. At the conditions of $\bar{T} \leq 1,000$ K, $\tau_r \leq 1$ s and $P_r \sim 20$ torr, the influence of thermal dissociation of methane was negligibly small. For example, the characteristic time of thermal dissociation at $\bar{T} = 1,038$ K and $P = 0.58$ atm was 4.5×10^6 sec [Dean, 1990].

For the gas discharge plasma, the first stage of all processes is the dissociation of stable molecules by direct electron impact. This stage gives atoms and free radicals, which are chemically active at interaction with each other and stable molecules. The main stable products in our case are CH₄, H₂, C₂H₆, C₂H₄, C₂H₂ and C₃H₈. It is possible to show that the next tabulated gas-phase plasmachemical reactions play the main role in the process of methane conversion in the gas discharge (see the list of the main reactions, Table 1). It is necessary to give some comments to this list. For the estimation of the rate constants of the most part of these reactions, we used the data of Dean [1990]. This work was devoted to the detailed kinetics of methane pyrolysis at $T_0 = 1,038$ K and $P_0 = 0.58$ atm. The number of these data gives the possibility of calculating the rate constants in wide range of temperature. In order to estimate the rate constants for reverse processes, $k^R(T)$, we used the known approximate relation [Lieberman and Lichtenberg, 1994]

$$k^R(T) = k^f(T) \exp\left\{\frac{\Delta G_r(T_0)}{RT_0}\right\} \exp\left\{\frac{\Delta H_r}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right\} \quad (20)$$

where $k^f(T)$ is the rate constant for forward reaction at temperature T , $\Delta G_r(T_0)$ is the standard Gibbs free energy for reaction at $T_0 = 1,038$ K, and ΔH_r is the standard enthalpy for reaction. It was supposed that ΔH_r was independent of the gas temperature ($\Delta H_r \approx \text{constant}$).

The rate constants for dissociation of methane molecules by direct electron impact will be defined later by using our experimental results. The association reactions of free radicals (for example, $CH_3 + H \rightarrow CH_4$, $CH_3 + CH_3 \rightarrow C_2H_6$, ...) can be elementary bimolecular reactions. For complex molecules, the excess of energy is immediately distributed over its vibrational degree of freedoms. On the contrary, the association of H atoms (the reaction (3)') must be three-body reaction. The rate constant for the reaction (3)' is about $8.3 \times 10^{-33} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}$ [Baulch et al., 1972]. It can be shown that this

Table 1. List of the main reactions for methane decomposition in gas discharge plasma

Rate equations	No.	Rate constants
$\text{CH}_4 + e^- \rightarrow \text{CH}_3 + \text{H} + e^- - 4.5 \text{ eV}$	(1)	k_{1f}
$\text{CH}_3 + \text{H} \rightarrow \text{CH}_4 + 4.5 \text{ eV}$	(1)'	k_{1r}
$\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 - 0.03 \text{ eV}$	(2)	k_{2f}
$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} + 0.03 \text{ eV}$	(2)'	k_{2r}
$\text{H}_2 + e^- \rightarrow \text{H} + \text{H} + e^- - 4.5 \text{ eV}$	(3)	k_{3f}
$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} + 4.5 \text{ eV}$	(3)'	k_{3r}
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + 3.9 \text{ eV}$	(4)	k_{4f}
$\text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{CH}_3 - 3.9 \text{ eV}$	(4)'	k_{4r}
$\text{C}_2\text{H}_6 + e^- \rightarrow \text{C}_2\text{H}_5 + \text{H} + e^- - 4.2 \text{ eV}$	(5)	k_5
$\rightarrow \text{CH}_3 + \text{CH}_3 + e^- - 3.9 \text{ eV}$	(6)	k_6
$\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2 + 0.3 \text{ eV}$	(7)	k_{7f}
$\text{C}_2\text{H}_5 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H} - 0.3 \text{ eV}$	(7)'	k_{7r}
$\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_6 + 4.2 \text{ eV}$	(8)	k_8
$\rightarrow \text{CH}_3 + \text{CH}_3 + 0.3 \text{ eV}$	(9)	k_9
$\rightarrow \text{C}_2\text{H}_4 + \text{H}_2 + 2.8 \text{ eV}$	(10)	k_{10}
$\text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_8 + 3.7 \text{ eV}$	(11)	k_{11}
$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 + 2.8 \text{ eV}$	(12)	k_{12}
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10} + 3.5 \text{ eV}$	(13)	k_{13}
$\rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 + 2.5 \text{ eV}$	(14)	k_{14}
$\text{C}_2\text{H}_6 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4 + 0.3 \text{ eV}$	(15)	k_{15f}
$\text{C}_2\text{H}_5 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3 - 0.3 \text{ eV}$	(15)'	k_{15r}
$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H} - 1.7 \text{ eV}$	(16)	k_{16f}
$\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5 + 1.7 \text{ eV}$	(16)'	k_{16r}
$\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2 - 0.06 \text{ eV}$	(17)	k_{17f}
$\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H} + 0.06 \text{ eV}$	(17)'	k_{17r}
$\text{C}_2\text{H}_4 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_3 + \text{CH}_4 - 0.03 \text{ eV}$	(18)	k_{18f}
$\text{C}_2\text{H}_3 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3 + 0.03 \text{ eV}$	(18)'	k_{18r}
$\text{C}_2\text{H}_4 + e^- \rightarrow \text{C}_2\text{H}_3 + \text{H} - 4.6 \text{ eV}$	(19)	k_{19f}
$\text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_4 + 4.6 \text{ eV}$	(19)'	k_{19r}
$\text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + 2.8 \text{ eV}$	(20)	k_{20}
$\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H} - 1.8 \text{ eV}$	(21)	k_{21f}
$\text{C}_2\text{H}_2 + \text{H} \rightarrow \text{C}_2\text{H}_3 + 1.8 \text{ eV}$	(21)'	k_{21r}
$\text{C}_2\text{H}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_4 + 2.8 \text{ eV}$	(22)	k_{22}
$\rightarrow \text{C}_3\text{H}_6 + 4.2 \text{ eV}$	(23)	k_{23}
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_6 + 2.6 \text{ eV}$	(24)	k_{24}
$\rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 + 3.0 \text{ eV}$	(25)	k_{25}
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 + 2.8 \text{ eV}$	(26)	k_{26}
$\rightarrow \text{C}_4\text{H}_6 + 4.6 \text{ eV}$	(27)	k_{27}
$\text{C}_2\text{H}_2 + e^- \rightarrow \text{C}_2\text{H} + \text{H} + e^- - 5.8 \text{ eV}$	(28)	k_{28f}
$\text{C}_2\text{H} + \text{H} \rightarrow \text{C}_2\text{H}_2 + 5.8 \text{ eV}$	(28)'	k_{28r}
$\text{C}_3\text{H}_8 + e^- \rightarrow \text{C}_3\text{H}_7 + \text{H} + e^- - 4.2 \text{ eV}$	(29)	k_{29}
$\rightarrow \text{C}_2\text{H}_5 + \text{CH}_3 - 3.8 \text{ eV}$	(30)	k_{30}
$\text{C}_3\text{H}_8 + \text{H} \rightarrow \text{C}_3\text{H}_7 + \text{H}_2 + 0.2 \text{ eV}$	(31)	k_{31}
$\rightarrow \text{C}_2\text{H}_6 + \text{CH}_3 + 0.55 \text{ eV}$	(32)	k_{32}
$\text{C}_3\text{H}_8 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_7 + \text{CH}_4 + 0.2 \text{ eV}$	(33)	k_{33}
$\rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_6 - 1.32 \text{ eV}$	(34)	k_{34}

reaction is not effective compared to the reactions (2) and (6) at low gas pressure ($P \leq 10 \text{ atm}$). The reaction (4)' (thermal dissociation of C_2H_6) is ineffective at our experimental conditions. For example, at $T_0 = 1,038 \text{ K}$ and $P_0 = 0.58 \text{ atm}$, the characteristic time of C_2H_6 decom-

position is equal to 175 sec [Dean, 1990] (compare this time to the residence time of our system, $\tau_r \leq 1 \text{ sec}$).

The C_2H_5 and C_2H_3 radicals are quite stable at low temperature, but at high temperature, $T \geq 1,000 \text{ K}$, the process of thermal dissociation is quite effective for these radicals (see reactions (16) and (21)). For example, the characteristic time of C_2H_3 decomposition at $T = 600 \text{ K}$ is $4.32 \times 10^3 \text{ sec}$ (radical is stable) and this one at $T = 900 \text{ K}$ is 0.02 sec (radical is unstable).

By using above data, it is possible to obtain a system of kinetic equations for processes of methane decomposition in plasma. Before this, we must do important remark. All values of rate constants were calculated at the equilibrium conditions, when the translational temperature is equal to the vibrational temperature of molecules. However, in the plasma of glow discharge, the vibrational temperatures are higher than the translational temperature. The number of vibrational excited molecules in plasma exceeds the equilibrium value as a rule. The rate constants of endothermic plasmachemical processes for vibrational excited molecules are noticeably higher than those for the molecules in ground vibrational state [Rusanov and Fridman, 1984]. In order to take into account the influence of the nonequilibrium vibrational excitation of molecules, it is necessary to have additional information about the vibrational temperature of molecules and to make new calculations of rate constants. In the frame of this work, we will not do it, and nonequilibrium vibrational excitation will be taken into account qualitatively.

After analysis of the above processes, it is possible to obtain the next kinetic equations for mixture.

$$\frac{d[\text{CH}_4]}{dt} = -(n_e k_{1f} + [\text{H}] k_{2f}) [\text{CH}_4] \quad (21)$$

The solution of Eq. (21) is

$$[\text{CH}_4] = [\text{CH}_4]^0 \exp \{ -(n_e k_{1f} + [\text{H}] k_{2f}) t \} \quad (22)$$

For ethane, ethylene, acetylene and propane (the main stable products in our case), it is possible to obtain such equations.

$$\begin{aligned} \frac{d[\text{C}_2\text{H}_6]}{dt} = & k_{4f} [\text{CH}_3]^2 + k_8 [\text{C}_2\text{H}_5][\text{H}] + k_{24} [\text{C}_2\text{H}_3][\text{C}_2\text{H}_5] \\ & - (n_e k_5 + [\text{H}] k_{7f}) [\text{C}_2\text{H}_6] \end{aligned} \quad (23)$$

$$\begin{aligned} \frac{d[\text{C}_2\text{H}_4]}{dt} = & k_{12} [\text{C}_2\text{H}_5][\text{CH}_3] + k_{10} [\text{C}_2\text{H}_5][\text{H}] + k_{14} [\text{C}_2\text{H}_5]^2 \\ & + k_{25} [\text{C}_2\text{H}_3][\text{C}_2\text{H}_5] + k_{16f} [\text{C}_2\text{H}_5] \\ & - (n_e k_{19f} + [\text{H}] (k_{16r} + k_{17f})) [\text{C}_2\text{H}_4] \end{aligned} \quad (24)$$

$$\frac{d[\text{C}_3\text{H}_8]}{dt} = k_{11} [\text{C}_2\text{H}_5][\text{CH}_3] - (n_e k_{29} + [\text{H}] k_{31}) [\text{C}_3\text{H}_8] \quad (25)$$

$$\begin{aligned} \frac{d[\text{C}_2\text{H}_2]}{dt} = & [\text{C}_2\text{H}_3] (k_{20} [\text{H}] + k_{22} [\text{CH}_3] + k_{24} [\text{C}_2\text{H}_5] + k_{26} [\text{C}_2\text{H}_3]) \\ & + k_{21f} [\text{C}_2\text{H}_3] - (n_e k_{28f} + [\text{H}] k_{21r}) [\text{C}_2\text{H}_2] \end{aligned} \quad (26)$$

It may be shown that the characteristic frequency for stable products (CH_4 , C_2H_6 , ...) is much less than one for radicals. It means that the density of radicals is stationary, that is, $d[\text{H}]/dt \approx d[\text{CH}_3]/dt \approx d[\text{C}_2\text{H}_5]/dt \approx d[\text{C}_2\text{H}_3]/dt \approx 0$, and for radicals, it is possible to use the balance equations:

$$\begin{aligned} n_e k^d ([\text{CH}_4]^0 + [\text{H}_2]) + [\text{C}_2\text{H}_5] k_{16f} + [\text{C}_2\text{H}_3] k_{21f} \\ = ([\text{CH}_4] k_{2f} + [\text{C}_2\text{H}_6] k_{7f} + [\text{C}_2\text{H}_4] (k_{16r} + k_{17f})) \end{aligned}$$

$$+[\text{C}_2\text{H}_2]\text{k}_{21r} + [\text{C}_3\text{H}_8]\text{k}_{31r}[\text{H}] + ([\text{CH}_3]\text{k}_{1r} + [\text{C}_2\text{H}_5](\text{k}_8 + \text{k}_9 + \text{k}_{10}) + [\text{C}_2\text{H}_3](\text{k}_{19r} + \text{k}_{20}))[\text{H}] \quad (27)$$

$$(\text{n}_e\text{k}_{1f} + [\text{H}]\text{k}_{2f})[\text{CH}_4] + 2\text{n}_e\text{k}_6[\text{C}_2\text{H}_6] + 2[\text{C}_2\text{H}_5][\text{H}]\text{k}_9 \\ = ([\text{H}](\text{k}_{1r} + 2[\text{CH}_3]\text{k}_{4f} + [\text{C}_2\text{H}_5](\text{k}_{11} + \text{k}_{12}) + [\text{C}_2\text{H}_3](\text{k}_{22} + \text{k}_{23}))[\text{CH}_3] \quad (28)$$

$$(\text{n}_e\text{k}_5 + [\text{H}]\text{k}_{7f})[\text{C}_2\text{H}_6] + [\text{C}_2\text{H}_4][\text{H}]\text{k}_{16r} \\ = ([\text{H}](\text{k}_8 + \text{k}_9 + \text{k}_{10}) + [\text{CH}_3](\text{k}_{11} + \text{k}_{12}) + 2[\text{C}_2\text{H}_5](\text{k}_{13} + \text{k}_{14}) + [\text{C}_2\text{H}_3](\text{k}_{24} + \text{k}_{25}))[\text{C}_2\text{H}_5] + [\text{C}_2\text{H}_5]\text{k}_{16f} \quad (29)$$

$$(\text{n}_e\text{k}_{19f} + [\text{H}]\text{k}_{17f})[\text{C}_2\text{H}_4] + [\text{C}_2\text{H}_2][\text{H}]\text{k}_{21r} \\ = ([\text{H}](\text{k}_{19r} + \text{k}_{20}) + [\text{CH}_3](\text{k}_{22} + \text{k}_{23}) + [\text{C}_2\text{H}_5](\text{k}_{24} + \text{k}_{25}) + 2[\text{C}_2\text{H}_3](\text{k}_{26} + \text{k}_{27}))[\text{C}_2\text{H}_3] + [\text{C}_2\text{H}_3]\text{k}_{21f} \quad (30)$$

In obtaining of these equations, we supposed that $[\text{CH}_4]^0 \approx [\text{CH}_4] + [\text{C}_2\text{H}_6] + [\text{C}_2\text{H}_4] + [\text{C}_3\text{H}_8] + [\text{H}_2]$, and the dissociation rate of stable compounds are all the same, that is, $k^d = k_{\text{CH}_4}^d \approx k_{\text{C}_2\text{H}_6}^d \approx k_{\text{C}_2\text{H}_4}^d \approx k_{\text{C}_2\text{H}_2}^d \approx k_{\text{C}_3\text{H}_8}^d$, where $k_{\text{CH}_4}^d = k_{1f}$, $k_{\text{C}_2\text{H}_6}^d = k_5$, $k_{\text{C}_2\text{H}_4}^d = k_{19f}$, $k_{\text{C}_2\text{H}_2}^d = k_{28f}$, and $k_{\text{C}_3\text{H}_8}^d = k_{29}$, respectively. We can assume this because the heat of reaction is very

close from Table 1.

For analysis of the kinetics of CH_4 conversion with help of these equations, we used the next way. First, we found the radical densities $[\text{H}]$, $[\text{CH}_3]$, $[\text{C}_2\text{H}_5]$ and $[\text{C}_2\text{H}_3]$ and the value of k^d from the Eqs. (27) to (30) with value of stable product densities obtained from experiments. The constant k^d was found from Eq. (22) by using experimental values of $[\text{CH}_4]_{\text{exp}}$, n_e , τ_R and calculation value of $[\text{H}]_{\text{calc.}}$. After then, we used Eqs. (22) to (26) to obtain the values of stable product densities ($[\text{C}_2\text{H}_6]_{\text{calc.}}$, $[\text{C}_2\text{H}_4]_{\text{calc.}}$, $[\text{C}_2\text{H}_2]_{\text{calc.}}$ and $[\text{C}_3\text{H}_8]_{\text{calc.}}$). The last stage of this way was a comparison of the results of calculations and measurements. The results of this method for analysis of kinetics are shown in Tables 2 and 3. In these tables, all values of the same conditions are the results of using the same experimental data. Consequently, from the above analysis, the dissociation constant k^d and density of radicals such as $[\text{H}]$, $[\text{CH}_3]$, $[\text{C}_2\text{H}_5]$ and $[\text{C}_2\text{H}_3]$ can be obtained by experimental results at any experimental conditions.

CONCLUSIONS

Table 2. Calculation results of the radical densities and k^d

Run	Rate constant			Concentration $[\text{cm}^{-3}]$			
	$\text{k}_{16f} [\text{s}^{-1}]$	$\text{k}_{21f} [\text{s}^{-1}]$	$\text{k}^d [\text{cm}^3\text{s}^{-1}]$	$[\text{H}]_{\text{calc.}}$	$[\text{CH}_3]_{\text{calc.}}$	$[\text{C}_2\text{H}_5]_{\text{calc.}}$	$[\text{C}_2\text{H}_3]_{\text{calc.}}$
First	0	0	5.52×10^{-11}	3.1×10^{13}	4.8×10^{13}	2.6×10^{13}	2.8×10^{12}
Final	2,000	2,500	5.23×10^{-11}	4.2×10^{13}	4.8×10^{13}	2.0×10^{13}	1.7×10^{12}

Conditions: initial CH_4 flowrate $55 \text{ cm}^3\text{min}^{-1}$, pressure 23 torr, applied input power 100 W; $\bar{T} = 530 \text{ K}$, $\text{n}_e = 0.48 \times 10^{10} \text{ cm}^{-3}$, $[\text{CH}_4]^0 = 4.27 \times 10^{17} \text{ cm}^{-3}$, $\tau_R = 0.72 \text{ sec}$

Run	Rate constant			Concentration $[\text{cm}^{-3}]$			
	$\text{k}_{16f} [\text{s}^{-1}]$	$\text{k}_{21f} [\text{s}^{-1}]$	$\text{k}^d [\text{cm}^3\text{s}^{-1}]$	$[\text{H}]_{\text{calc.}}$	$[\text{CH}_3]_{\text{calc.}}$	$[\text{C}_2\text{H}_5]_{\text{calc.}}$	$[\text{C}_2\text{H}_3]_{\text{calc.}}$
First	0	0	4.77×10^{-11}	2.3×10^{13}	3.2×10^{13}	5.1×10^{13}	2.2×10^{13}
Final	1.5×10^4	6.0×10^3	3.67×10^{-11}	4.1×10^{13}	3.6×10^{13}	2.9×10^{13}	1.8×10^{13}

Conditions: initial CH_4 flowrate $55 \text{ cm}^3\text{min}^{-1}$, pressure 23 torr, applied input power 300 W; $\bar{T} = 650 \text{ K}$, $\text{n}_e = 1.73 \times 10^{10} \text{ cm}^{-3}$, $[\text{CH}_4]^0 = 4.2 \times 10^{17} \text{ cm}^{-3}$, $\tau_R = 0.62 \text{ sec}$

Table 3. Calculation results of the stable product densities

Run	Rate constant $[\text{s}^{-1}]$		Concentration $[\text{cm}^{-3}]$				
	k_{16f}	k_{21f}		$[\text{C}_2\text{H}_6]$	$[\text{C}_2\text{H}_4]$	$[\text{C}_3\text{H}_8]$	$[\text{C}_2\text{H}_2]$
First	0	0	Exp.	3.5×10^{16}	2.4×10^{15}	3.1×10^{15}	1.4×10^{15}
			Calc.	3.3×10^{16}	5.6×10^{14}	1.3×10^{16}	2.6×10^{14}
Final	2000	2500	Exp.	3.5×10^{16}	2.4×10^{15}	3.1×10^{15}	1.4×10^{15}
			Calc.	3.1×10^{16}	2.3×10^{15}	9.1×10^{15}	1.3×10^{15}

Conditions: initial CH_4 flowrate $55 \text{ cm}^3\text{min}^{-1}$, pressure 23 torr, applied input power 100 W; $\bar{T} = 530 \text{ K}$, $\text{n}_e = 0.48 \times 10^{10} \text{ cm}^{-3}$, $[\text{CH}_4]^0 = 4.27 \times 10^{17} \text{ cm}^{-3}$, $\tau_R = 0.72 \text{ sec}$

Run	Rate constant $[\text{s}^{-1}]$		Concentration $[\text{cm}^{-3}]$				
	k_{16f}	k_{21f}		$[\text{C}_2\text{H}_6]$	$[\text{C}_2\text{H}_4]$	$[\text{C}_3\text{H}_8]$	$[\text{C}_2\text{H}_2]$
First	0	0	Exp.	3.8×10^{16}	1.5×10^{16}	9.8×10^{15}	1.2×10^{16}
			Calc.	2.3×10^{16}	9.2×10^{14}	1.7×10^{16}	8.7×10^{14}
Final	1.5×10^4	6.0×10^3	Exp.	3.8×10^{16}	1.5×10^{16}	9.8×10^{15}	1.2×10^{16}
			Calc.	1.8×10^{16}	1.6×10^{16}	7.8×10^{15}	1.0×10^{16}

Conditions: initial CH_4 flowrate $55 \text{ cm}^3\text{min}^{-1}$, pressure 23 torr, applied input power 300 W; $\bar{T} = 650 \text{ K}$, $\text{n}_e = 1.73 \times 10^{10} \text{ cm}^{-3}$, $[\text{CH}_4]^0 = 4.2 \times 10^{17} \text{ cm}^{-3}$, $\tau_R = 0.62 \text{ sec}$

This study investigated methane conversion with direct current discharge at low pressure in a radio frequency. The main gaseous products of the reaction were ethane, ethylene, acetylene and propane. This study was concentrated on the influence of discharge conditions on the conversion of methane to higher hydrocarbons. Reaction temperature, electron density and mean residence time were calculated from experimental data and mathematical relations.

The fraction of gas-phase hydrocarbon products was decreased with the increase of specific input power. The fraction of gas-phase hydrocarbon products was high if the gas pressure was high at the same input power. The fraction of gas-phase hydrocarbon products was high if the gas temperature in discharge zone was low at the same gas pressure. All of these facts can be explained qualitatively by the diffusion phenomenon. The molecular flow on the walls of the discharge was caused by diffusion. The mean frequency of diffusional removal of particles is increased with increasing gas temperature, and is decreased with increasing gas pressure.

The maximum conversion of the methane was about 45% with the pure methane as a reactant. Ethane was the main product when the reaction occurred in the glow discharge. Ethane selectivity decreased with the increase of the gas temperature. The kinetics of reactions was also analyzed from possible reaction equations and various rate constant data. Consequently, the dissociation constant and the density of radicals could be obtained at any experimental conditions.

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NOMENCLATURE

C_{p1}	: heat capacity at constant pressure per one molecule [JK^{-1}]
d	: inner diameter of plasmachemical reactor [cm]
D	: diffusivity [cm^2s^{-1}]
e	: electron charge [1.602×10^{-19} C]
E	: strength of the electric field [Vcm^{-1}]
J	: discharge current density [Acm^{-2}]
J_R	: heat flux density [Wcm^{-2}]
k	: thermal conductivity [$\text{Wcm}^{-1}\text{K}^{-1}$], and rate constant [s^{-1}]
L	: length of plasmachemical reactor [cm]
n	: particle density [cm^{-3}]
n_e	: electron density [cm^{-3}]
N	: total density of particle [cm^{-3}]
P	: pressure [torr]
R	: radius of discharge reactor [cm]
S	: area of cross section of plasmachemical reactor [cm^2]
T	: temperature [K]
$\bar{T}$	: mean temperature [K]
v_d	: electron drift velocity [cm s^{-1}]
V	: volume of discharge zone [cm^3]
$\hat{V}$	: flowrate of gases [cm^3s^{-1}]
w	: specific energy [Wcm^{-3}]
W	: total input power [W]
Z	: methane conversion

Greek Letters

δ_r	: factor for calibrating flowrate change by chemical reaction
χ	: thermometric conductivity [cm^2s^{-1}]
γ	: fraction of gas-phase hydrocarbon product
η	: fraction of total input power transferred to the heat
κ	: Boltzmann's constant, 1.381×10^{-23} J/K
ν_e	: collision frequency [s^{-1}]
ν_r	: heat removal frequency [s^{-1}]
ν_F	: convective heat output frequency [s^{-1}]
Λ	: heat length [cm]
τ_r	: resident time [s]
τ_1^D	: radial diffusion time [s]
τ_2^D	: axial diffusion time [s]

Superscripts

f	: forward reaction
R	: backward reaction

Subscripts

i	: component
w	: wall
0	: initial state
R	: reaction section

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