Methane Conversion in the Microwave Pulse Discharge.

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INTRODUCTION

The experimental results of methane conversion in pulse microwave discharge and
theoretical model for their explanation are presented in this work. It was shown in [1-2], small
addition of microwave energy (up to 20 % from a thermal energy) resulted in significant
increase of methane conversion degree and sharp decrease of conversion energy cost up to
thermodynamic limit ∆H = 0.8 eV/CH4 molecule. This fact was explained as the result of ion
chain reactions: CnH_n+ + CnH_n = Cn+ + mlH_{n+2} + H_2 [5], which take place in methane plasma
and resulted in significant increase of methane conversion efficiency (so-called plasma
catalysis effect). The kinetic model of methane conversion was developed based on basic
physical parameters of microwave discharge obtained from experimental measurements and
derived from theoretical models of microwave streamer.

PAPER BODY

Basic physical parameters of microwave streamer discharge were determined both
from experimental spectroscopic measurements and from theoretical models of streamer
evolution. Experimental values of electric field intensities in the streamer channel were
obtained from Stark broadening of I_n and I_N spectral lines [7]. The value of field intensity
was derived from the best fitting of theoretical spectral line contour to experimental one. The
shape of line contour was calculated taking into account line splitting in the electric field,
monochromator contour, Doppler shift and line broadening due to electron impacts [3]. The
experimental and calculated shapes of I_n line in methane are shown in the Fig. 1 (for the sake
of clearness the heights of two contour are different). The similar picture was obtained for I_N
spectral line. The line contours were measured in course of time interval 50-200
ns after discharge ignition. At late time moments the shape of line contour was
determined by electron and ion broadening due to the rapid increase of electron
concentration in the streamer channel. During the first 50 ns the radiation flux
from the streamer was too weak to obtain reliable measurement of spectral line
shape.

Electric field values in the streamer body were also calculated based on

Fig. 1. Hα contour in MW field 20kV/cm.
1 – experimental contour
2 – calculated contour in CH₄
streamer propagation velocity in frame of streamer head model. Since microwave wavelength is larger than streamer head radius we used quasi-electrostatic approach for streamer head modelling. Moreover, as increase of electron concentration occurs on distances smaller than streamer head size, the one-dimensional diffusion model of propagation was applied. (Microwave amplitude decrement caused by streamer head curvature was neglected). Effects of ionisation and electron diffusion restricted by ambipolar electric field and electron-ion recombination determine streamer propagation velocity. The Kolmogorov-Petrovsky-Piskunov equation can be derived from supposition of uniform wave propagation and quasi neutrality requirement:

\[
\frac{d}{dz} D_e \frac{d}{dz} n_e + \gamma_1 - K_e n_e^2 = V \frac{d}{dz} n_e,
\]

where \( n_e \) – electron concentration, \( \gamma_1 \) – ionisation frequency, \( D_e \) – ambipolar diffusion coefficient, \( K_e \) – electron – ion recombination rate constant, \( V \) - streamer propagation velocity.

The streamer propagation velocity can be determined from asymptotic solution of (1):

\[
V = 2\sqrt{D_e (F_{\text{max}})} \frac{\gamma_1 (F_{\text{max}})}{n_e},
\]

The electron concentration in plasma channel body is grown rapidly up to stationary value, which depends on electric field intensity inside plasma. On the other hand, electrostatic assumption allows us to determine electric field intensity in streamer body as function of maximum field value on the channel head and electron concentration inside it. Thus, the set of parameters of streamer head (electron concentration and microwave intensity at the streamer surface and inside plasma body) can be determined as implicit function of measurable streamer propagation velocity (1.3 10^6 cm/s in methane, 2.8 10^6 cm/s in hydrogen). Electric field intensities in the channel (H_2 - 100 Td, CH_4 - 90 Td) derived from the plane ionization wave theory and quasi-stationary assumption are in good agreement with experimental measurements both in hydrogen (=30 kV) and methane (≈20 kV) for normal conditions. The deviation in case of hydrogen plasma can be due to impurities in the bulk gas, such as 1% H_2O. Electron temperatures, corresponding to these field intensities are about 2 eV.

Alternative way to determine these temperatures is analysis of population of hydrogen excited states, based on lines intensities [7]. To perform these studies kinetic model of hydrogen levels population taking into account impact excitation and deexcitation, spontaneous radiation and ionization processes was developed including the plane front wave results and calculation of electron energy distribution function (EEDF) [4]. The model has shown that population of excited hydrogen levels is strongly non-equilibrium with respect to electron temperature: \( T_e \) were about 0.3–0.4 eV for desired levels while \( T_e \) was about 2 eV. These results are in good agreement with experimental observation \( T_e \) about 0.3 eV and coincide with previous kinetic calculations in hydrogen.

After the first stage of streamer channel evolution (250 ns in methane and 400 ns in hydrogen) the width of \( I_a \) and \( I_b \) spectral lines increased significantly due to the growth of electron concentration [7]. The line shape was controlled by ion quasi-static and electron impact broadening. The value of quasi-static ionic electric field was about 50 kV/cm and exceeded microwave field intensity. Electron concentration was derived from the electron broadening of the central component of \( I_a \) line. Obtained separately electron and ion concentrations were quite close to each other. At earlier time moments (less than 250 ns for methane) electron concentration in the streamer body was estimated based on microwave energy adsorption by the discharge. This method gives electron concentration \( 1 \sim 10^{15} \) 1/cm² for the “cold” stage of streamer channel evolution. The evolution of electron concentration in the streamer channel is shown in the Fig. 2.
The neutral gas temperature was determined from the measurement of $C2$ rotating specter. Derived rotational temperatures are also displayed in the Fig. 2. (see line 5). One can see abrupt temperature growth up to $5000^\circ K$ after 200 ns in methane.

The rate of gas heating in plasma can determine the beginning of quasi-equilibrium stage due to ionization-heat instability in the streamer channel. The rate of gas heating was determined from the solution of kinetic equation for EEDF and finding contribution of each elementary process in gas heating taking into account energy conservation in some degrees of freedom. For example, one should expect that vibrational energy is stored without relaxation to translational and rotational degrees of freedom at least at low temperatures. Simulation gives temperature increase about 100 K in course of first 100 ns. This value is enough to initiate ionization-heating instability in the channel if pressure relaxation occurs quite rapid. The characteristic hydrodynamic time is about 100 ns for hydrogen and somewhat larger for methane. Thus ionization instability in the streamer channel seems to be responsible for channel thermalization in about 200 ns in hydrogen, since experiment data show strong rise of gas temperature and electron concentration after about 200 ns in hydrogen and 400 ns in methane. As one can expect, electron concentration in quasi-equilibrium stage is determined from condition that the thickness of skin layer is about streamer radius. This assumption produces electron concentration about $10^{10} \frac{1}{cm^3}$, which is in reasonable agreement with experimental value about $5*10^{10} \frac{1}{cm^3}$. The gas temperature from the experiment (about 5000 K in methane) is slightly lower than equilibrium temperature for this electron concentration (about 6000 K), and thus prove quasi-equilibrium state of the plasma in the channel.

Based on obtained above parameters of the streamer channel we made estimations of methane conversion energy cost in the microwave discharge. Since the dominant fraction of methane conversion occurs at the stage of plasma channel decay, the model of streamer decay was developed. The electron-ion recombination is a primary process at first stage of channel decay [6]. If we assume that recombination is the primary process of active species losses, the number of conversion acts induced by charged particles (per unit of plasma volume) can be evaluated:

$$N_{conversion} = \frac{K_{conversion}}{K_e} \frac{N}{N_e} \ln \left( K_e \frac{I_{ion}}{I_{rad,io}} \right),$$

where $N$ – concentration of methane (background gas), $K_{conversion}$ – conversion rate constant, $N_e$ – initial electron concentration and decay time is estimated as diffusion expansion time.
(t\text{decay}\sim 10^{-4}\text{ s}). This formula gives quite high energy cost of methane conversion ~500 eV per methane molecule. Thus the diffusion process can strongly decrease electron and ion recombination losses. The equation of channel decay taking into account recombination processes and diffusion looks like:

\[
\frac{d n_e(t,r)}{dt} = D_e \frac{1}{r} \frac{d}{dr} \left( r \frac{d n_e(t,r)}{dr} \right) - K_e n_e^2(t,r) n_e(t,r), \quad \left| r = R \right. = 0,
\]

where R - radius of reaction chamber. At the final stage of channel decay the main process of active particle losses is diffusion and recombination at the boundary of the reaction chamber. The condition of switching between these two stages may be estimated from:

\[
K_e n_e^2 = D_e \left| \frac{\partial n_e}{\partial r} \right| \left| r = r^* \right|, \quad \text{or} \quad n_e(r, t=0) = \frac{D_e}{r^2 K_e} = 3 \cdot 10^{11} \text{ m}^{-3}
\]

The time duration of the first stage, in which recombination processes are the dominant, can be estimated as \( t_{\text{streamer}} = \frac{1}{\gamma_e} \left( \gamma_{n_e} - \gamma_{n_e} \right) \approx \frac{1}{\gamma_e} \) (about \( 10^{-4} - 10^{-5}\text{ s}, as used up). In assumption of boundary recombination as the only mechanism of ions losses, the active particle lifetime can be estimated: \( t_{\text{streamer}} = \frac{K_e}{4 D_e} \approx 0.3 s \). Finally energy cost of methane conversion (including correction on diffusion expansion at recombination time) can be obtained as:

\[
p = 4 r^2 \frac{K_e}{R^2} C \frac{1}{\ln \left( \frac{n_e(\text{start})}{n_e(\text{end})} \right)} \approx 0.1 - 1.0 \text{ eV},
\]

where C is energy input per molecule of streamer (~5eV). This result is in reasonable agreement with experimental results (~0.25 eV per molecule).

The main ambiguity in the previous result concerns with three next reasons: error of methane conversion rate constant, neglecting of hydrodynamic expansion and rough description of recombination decay - diffusion decay transition. Last two sources of errors can be avoided in frame of numerical model of streamer channel decay.

The numerical model of streamer decay included recombination of active particles, multicomponent diffusion, ions drift in self-consistent ambipolar electric field, hydrodynamic expansion (including shock wave formation), thermoconductivity and energy losses due to the chemical reactions. Electron concentration was obtained from quasi neutrality equation. Since plasma thermalisation time is small enough (~2-4 \( 10^{-7}\) s) assumption of temperature equilibrium was used to obtain ambipolar field intensity:

\[
E_a n_e = k_b T_e, \quad \sum n_e z_i = n_e,
\]

where \( E_a \) - ambipolar electric field, \( z_i \) - charges of species, \( n_e \) - their concentrations. As gas temperature in the center of plasma channel is high enough, shock wave formation length is comparable with initial channel radius. Therefore hydrodynamic equations with \( V \) energy correction was used:

\[
\frac{d}{dt} \left( E + \frac{\rho V^2}{2} \right) + \nabla \left( \left( E + \frac{\rho V^2}{2} \right) \frac{V}{\rho} + \rho \frac{\partial V}{\partial t} \right) + \sum W_j H_j = 0,
\]

\[
\rho \left( \frac{dV}{dt} + (\nabla V) V \right) + \nabla P = 0,
\]

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$$\frac{d}{dt} \bar{n}_i + \nabla \bar{S}_i + \nabla \left( \bar{V} \bar{n}_i \right) + \sum_j W_j \alpha_{ij} = 0,$$

(10)

where $S_i$ are diffusion fluxes, $W_j$ – reaction rates, $\alpha_{ij}$ – steechiometry numbers.

Due to presence of particles with varying masses and cross-sections, multicomponent diffusions model was used. It also included drift of particles under ambipolar electric field and electron-ion friction:

$$\kappa \nabla \left( T n_i \right) + z n_i e \bar{E} + \sum_j \left( n_i \bar{S}_j - n_j \bar{S}_i \right) \frac{v_{ij}}{1/m_i + 1/m_j} - n_i \bar{G} = 0, \sum_i \bar{S}_i = 0,$$

(11)

where $i_{ij}$ – collision frequencies.

As it was shown by numerical computations shock wave formation completed at the distance 0.3 – 0.4 cm from the center of plasma channel (radius of plasma channel was about ~0.1cm, see Fig. 3). Thus hydrodynamic motions did not produce significant shifts in active particles distribution, but resulted in loss of about 0.25% of input microwave energy in shock wave formation. The characteristic time of shock wave formation was about $10^{-5}$s, after it no sound-scale hydrodynamic motions was found inside streamer channel and simplified hydrodynamic model could be used. Resulted electron and ion (active particles) distributions at the final stage (shown in the Fig. 4) were used to improve analytical model of the channel decay (6).

Conclusions

New experimental results on microwave streamer evolution are presented in this work. In particular, electric field intensities and electron concentrations in the streamer channel were measured by spectral methods and obtained from theoretical model based on streamer propagation velocity. Moreover kinetic model of methane conversion in streamer microwave discharge based on experimental theoretically derived parameter gave reasonable explanation of observed high efficient methane conversion in the given system.
Fig. 4. Distribution of electrons evaluation in ethane caviers corresponding to times: t = 0.2, 1.2, 2.2, 3.2 $\mu$s.

References


