METHANE DECOMPOSITION UNDER LOW TEMPERATURE PLASMA FLOW CONDITIONS

I.L.Epstein, M.B.Grinchak, A.A. Ovsyannikhov, L.S.Polak
Institute of Petrochemical Synthesis, Leninsky prospect, 29,
Moscow, USSR

ABSTRACT

Experiments and calculations are carried out on methane decomposition in a plasma turbulent flow. The results of calculations using Navier-Stokes equations model agree satisfactorily to data measured provided one of the model empirical coefficients is corrected and gas temperature fluctuations and effects of the sample quenching in the probe are accounted for.

1. INTRODUCTION

At least two important problems are to be solved when chemical reaction under plasma conditions are studied. First, traditional mechanisms of chemical reactions may alter under temperatures of 2 - 5 kK characteristic for plasma - chemical processes (at pressure ≈ 1 atm). Secondly, the characteristic time τ_c for many chemical reactions approach that τ_t for heat and mass transfer e.g. Damköhler number $D_a = \tau_t / \tau_c \gtrsim 1$ and, as a result, the latters influence strongly the reactions kinetics. The aim of the present work was to study methane decomposition kinetics under a plasma-chemical reactor conditions ($p \approx 1$ atm, temperature $T \approx 2\text{-}3{,}5$ kK) at $Da \gtrsim 10$.

2. EXPERIMENTAL

The sketch of the plasma-chemical reactor used is shown in the Fig.1. The axial injection of the reagents jet was applied to facilitate diagnostics and data processing as well as mathematical modelling. The main quantities measured and respective errors are shown in the Table 1. The full and static pressure in the flow were measured with a Pitot tube and through small hole in the reactor wall, respectively. The pressure turbulent fluctuations were measured up to 4 kHz. The temperature turbulent fluctuations were measured using the electrostatic probe (the pure argon instead of the reagent jet being injected into the plasma flow). The composition of the gas sample was measured cromotographically.

3. MODELLING

The model used included Navier-Stokes, chemical kinetics ones and those for turbulent energy q and the rate of the latter dissipation ε . Axisymmetric, stationary, subsonic flow was considered of viscous compressible gas using Gosman et al [1]

approach:

$$a_\varphi\left\{\frac{\partial}{\partial z}\left(\varphi\frac{\partial\psi}{\partial z}\right)-\frac{\partial}{\partial z}\left(\varphi\frac{\partial\psi}{\partial z}\right)\right\}-\left\{\frac{\partial}{\partial z}\left(b_{1\varphi}\frac{\partial}{\partial z}\left(c_\varphi\varphi\right)\right)+\frac{\partial}{\partial z}\left(b_{2\varphi}\frac{\partial}{\partial z}\left(c_\varphi\varphi\right)\right)\right\}+d_\varphi=0\quad(1)$$

Here Ψ - stream function, φ - any of the following functions: H-stagnation enthalpy, n_i - relative mass density of the i-component, expressions for a_φ, b_φ, c_φ, d_φ are given in the Ref. [1].

Turbulent and molecular transfer processes were accounted for to the model. The latter one being described with Stefan-Maxwell equations. The mechanism of methane decomposition is shown in the Table 2. The model and numerical procedure are described in more detail in the Refs. [2,3].

4. RESULTS

In order to correct the values of empirical coefficients of the model a study was carried out of turbulent mixing of chemically inert gases (Ar, H_2 + Ne, He + Ne) with the plasma flow. Calculated ratios H_2 / Ne and He / Ne depend on the value of turbulent energy q_o at the reactor inlet. Turbulent diffusion is increased as q_o^2 compared to the molecular transfer when q_o is increased, while turbulence integral scale L_o influence the transfer processes in a significanty less extent. Numerical solutions of the Navier-Stokes equations show a recirculation zone to exist in the case of an argon jet mixing with the argon plasma flow. This agrees well to experimental observations. In the case of (H_2 + Ne)- jet mixing with the same plasma flow any recirculation does not exist in agreement with the experiment and with the estimation of the Craya-Curtet number which exceed one.

Radial and axial profiles of methane, ethane, ethylene and acetylene were obtained experimentally as well as those of temperature, pressure and their fluctuations (see, for example, the Fig.2). In order to reach an agreement between calculated and measured profiles one of the model empirical coefficients was decreased about 20 percent (that implies the decrease of the turbulent dissipation rate). The effect of temperature fluctuations was accounted for effective reaction activation energics being used which depend on the temperature root-mean-square fluctuating [4]. As a result a satisfactory agreement was obtained for the temperature and component concentrations profiles except for ethane (see the Figs. 3-5). Methyl radicals concentration is seen from the calculations to be high. Thus taking into consideration their recombination under quenching process in the probe improves an agreement between calculated and measured ethane profiles.

Due to that Damköhler number for the present reactor is rather high ($\gtrsim 10$) any of the flow turbulence parameters influence methane conversion noticeably. For example, at external modulation of the plasma flow (at the plasmotrone) at audio frequences (level not more that 5 percent) leads to sharp decrease in the conversion (see the Fig. 6) at a frequence which is about the audio resonance frequency for the reactor duct cavity. This effect is caused by the increase in the heat transfer from

plasma flow to the reactor walls due to an additional turbulization of the flow.

REFERENCES

(1) A.D. Gosman, W.M. Pun, A.K. Runchal, D.B. Spalding, M. Wolfstein, "Heat and Mass Transfer in Recirculating Flows" (Acad. Press, London, 1969).

(2) V.Z. Kompaniets, A.A. Konstantinov, L.S.Polak, M.Ya. Zimbalyuk, I.L. Eps-tein, "Numerical Modelling of Plasma-Chemical Processes" in " Chemical Reactions under Low Temperature Conditions", edited by L.S. Polak (Nauka, Moscow, 1977).

(3) M.B. Grinchak, Ch. Keszei, V.Z. Kompaniets, A.A. Ovsyannikhov, L.S. Polak, I.L. Epstein,"Methane Conversion under Low Temperature Plasma Turbulent Flow Conditions: Experiment and Numerical Modelling" in "Synthesis in Low Temperature Plasma", edited by L.S. Polak (Nauka, Moscow, 1980).

(4) S. Tsugé and K. Sagara, Combustion Science and Technology, 18, 179 (1978).

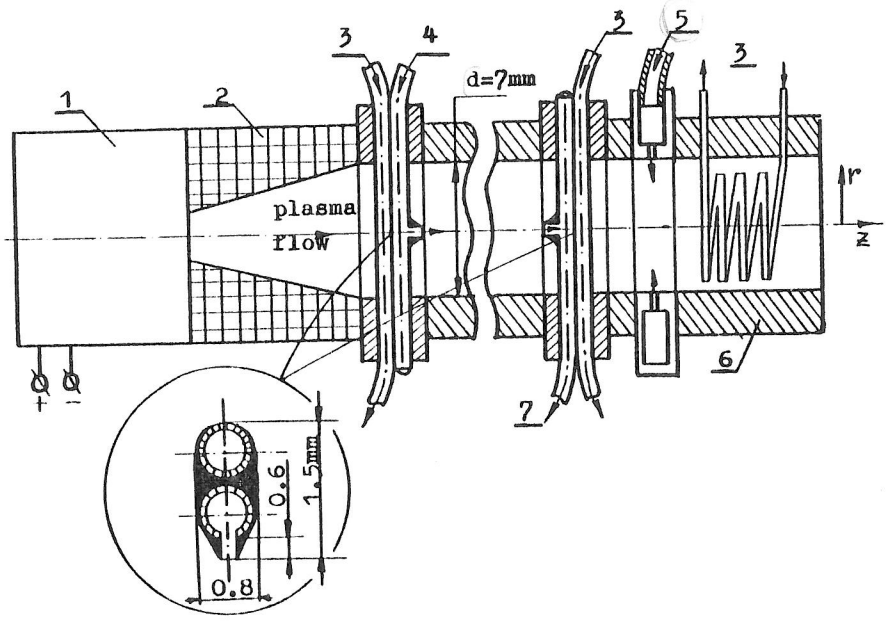


Fig. 1 Plasma - chemical reactor and probe
1-plasmotrone, 2-thermal insulation, 3-cooling water in, 4-reagent injection, 5- quenching gas in, 6-calorimeter, 7-gas sampling Pitot tube and calorimetric probe

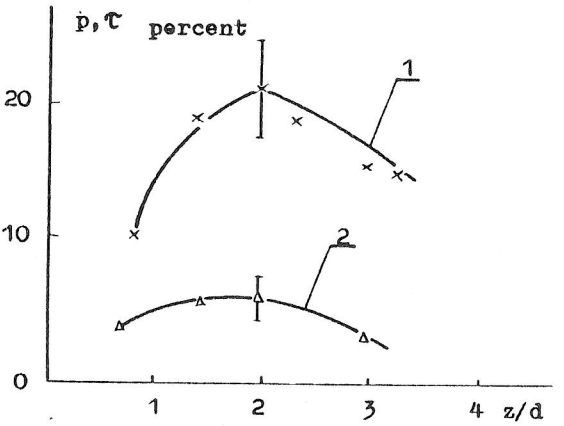
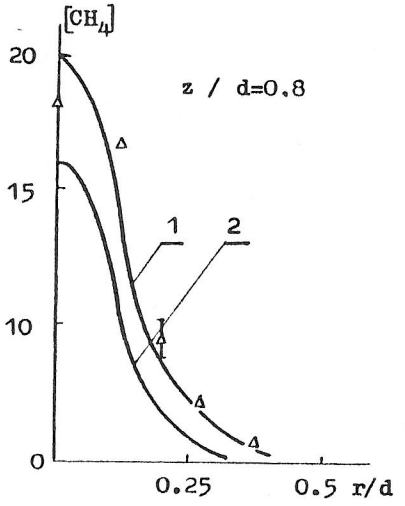


Fig. 2. Axial profiles of relative rms fluctuations of dynamic pressure (1) and temperature (2) in the reactor



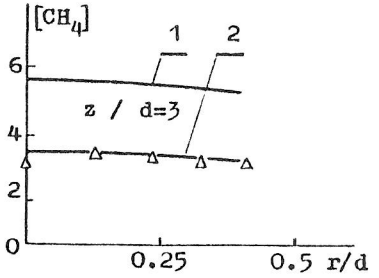
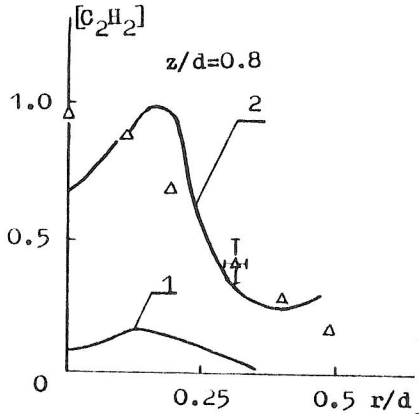


Fig. 3. Radial profiles of methane (vol. percents). Curves are calculated with (2) and without (1) accounting for the temperature fluctuations; $\sqrt{\overline{T'^2}}/\sqrt{\overline{T}} = 0,1$, Δ - measured values



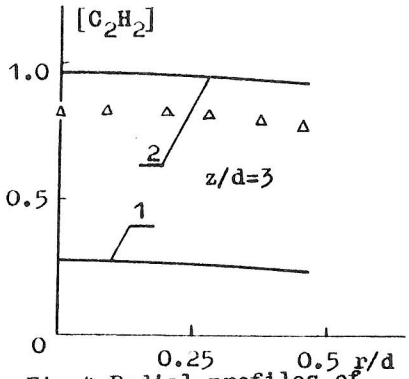


Fig.4 Radial profiles of acetylene (vol. percent). Curves are calculated with (2) and without (1) accounting for the temperature fluctuations; $\sqrt{\overline{T'^2}} / \overline{T} = 0,1$
△ - measured values

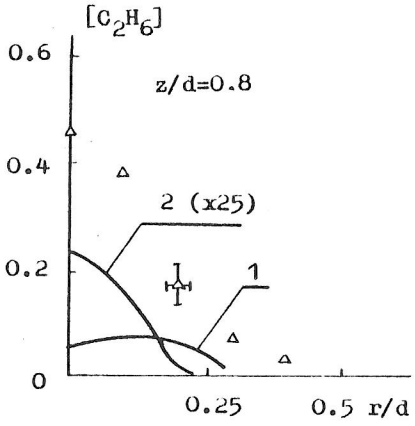


Fig.5 Radial profiles of ethane (vol. percents). Curves are calculated,
△ -measured values, 2-calculated assuming all methyl radicals to recombine into ethane

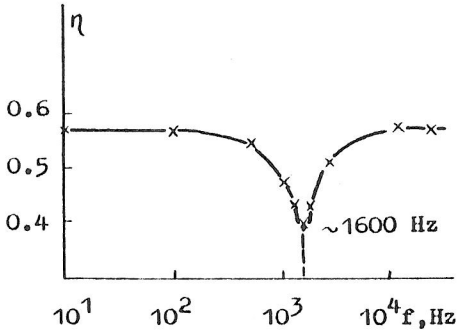


Fig.6 Methane conversion vs. the frequency (Hz) of modulation of the plasmotrone arc current (square wave with amplitude of 2.5 a, the current averaged value being ~50 a)

Table 1

Quantity measured	Units	Range	± Error percent
Gas composition	relative units	0-1	3-5
Local time averaged temperature in mixing and reaction zone	kK	1.5-4.0	20
Temperature relative rms fluctuations	percent	5-20	30
Time averaged dynamic pressure	Pa	$0-2\cdot10^4$	5-7
Dynamic pressure rms fluctuations	Pa	0-150	20-50
Methane conversion	percent	0-90	7-10

Table 2

No	Reaction	lg(A)	E, kcal/mole
1	$CH_4 \longrightarrow CH_3 + H$	13.7	93.0
2	$CH_4 + H \longrightarrow CH_3 + H_2$	13.7	12.9
3	$CH_3 + CH_3 \longrightarrow C_2H_6$	12.9	0
4	$C_2H_6 \longrightarrow CH_3 + CH_3$	14.7	79.3
5	$C_2H_6 \longrightarrow C_2H_4 + H_2$	13.9	69.0
6	$C_2H_4 \longrightarrow C_2H_2 + H_2$	8.5	40.0
7	$C_2H_2 \longrightarrow 2C + H_2$	6.2	30.0