acta phys. slov. 38 (1988), No. 4

EFFECT OF ENERGETIC PARAMETERS OF THE REACTION CHAMBER ON THE PYROLYSIS OF METHANE IN DC HYDROGEN PLASMA JET. PART II. EFFECT OF HYDROGEN ON THE YIELD OF METHANE CONVERSION

SZYMAŃSKI, A.,[1] OPALIŃSKA, T.,[1] Warsaw

The effect of hydrogen as a plasma gas on the reaction of acetylene synthesis was studied on the basis of a model of methane plasma pyrolysis, developed earlier [1].

The experimental results were compared with model calculations. The efficiency of pyrolysis in the range of energetic parameters characterized the process and, related to the minimum unit energy consumptions, was not affected by the dilution of methane by hydrogen applied as a plasma gas.

I. INTRODUCTION

The energy source in a plasma chemical reactor is a hot plasma gas (hydrogen) flowing from the nozzle of a plasma torch. In the forepart of the reaction chamber the plasma gas is mixed with a cold reactant (methane). Thus, the hydrogen temperature is reduced. The temperature of the reacting gases is further reduced owing to the chemical reaction taking place in the reaction chamber as well as the colloing effects. The reaction should be interrupted at that moment when the required methane-to-acetylene conversion degree is attained by quenching the gases at the rate of 10 K/s. At that moment the gases are characterized by a temperature called the quenching temperatur Such assumptions were helpful in the construction of a model of methane plasma pyrolysis, described in the first part of the work [1].

Methane pyrolysis to acetylene in a plasma jet proceeds according to the "brutto" reaction:

$$2\,CH_4 = C_2H_2 + 3\,H_2. \qquad (1)$$

[1]) Department of Chemistry, Warsaw University, Pasteura 1, 02-093 WARSAW, Poland

Hydrogen is one of its products. The use of hydrogen as a plasma gas causes its excess in the reaction medium, which should shift the reaction equilibrium. In consequence, the concentration of the acetylene formed can decrease.

It was assumed in the first part of the work that the plasma gas (hydrogen) did not affect the reaction equilibrium and behaved as an inert diluting gas. In the present work the effect of hydrogen on the reaction equilibrium is taken into consideration. This makes it possible to check whether and how much the change in the process model will affect the conclusions concerning the optimum conditions of the process, determined earlier [1].

II. MODEL CALCULATIONS

The definition of the basis parameters such as the methane conversion degree (u), the methane-to-acetylene conversion degree (u_p), the unit energy consumption (Z), the specific energy of plasma gas (E_g), and the specific energy of methane (E_r) were given before [1]. The fundamental assumption of the model was then given as well. According to them the reaction (1) is the only one taking place in the reaction chamber. In that case the effect of hydrogen as plasma gas modifies the formula for the reaction equilibrium constant (K_p) as follows:

$$K_p = 0.5\,u(1.5\,u + k)^3(1 - u)^{-2}(1 + u + k)^{-2} \qquad (2)$$

where k is the molar ratio of the plasma gas to methane.

The remaining equations, used in calculations, remain unchanged in relation to those given earlier [1].

For a better comparison of the calculations results, the method of calculations presented in the first part of our study is called variant I whereas that presented in this paper is called variant II.

The dependence of parameters characterizing the process on the specific energy of methane was given for various, fixed specific energies of hydrogen (Fig. 1a, 2a, 3a). Also, the relation between the process parameters and the specific energy of hydrogen was found for various fixed specific energies of the reactant (Fig. 1b, 2b, 3b).

The hydrogen slightly decreases the conversion degree, in agreement with the result obtained by other authors [2, 3]. The effect of hydrogene on the methane conversion degree decreases with the increasing specific energy of methane and the plasma gas. For $E_g \geqslant 14.4\,MJ/m^3$ and $E_r \geqslant 14.4\,MJ/m^3$ the differences in the conversion degrees are practically negligible.

The range of the methane specific energy, in which the unit energy consumption is the lowest, is the same for the two calculation variants. The unit energy consumptions, calculated according to variant I for the methane specific energy $12.6\,MJ/m^3$ and $14.4\,MJ/m^3$ differs slightly, whereas for variant II they are

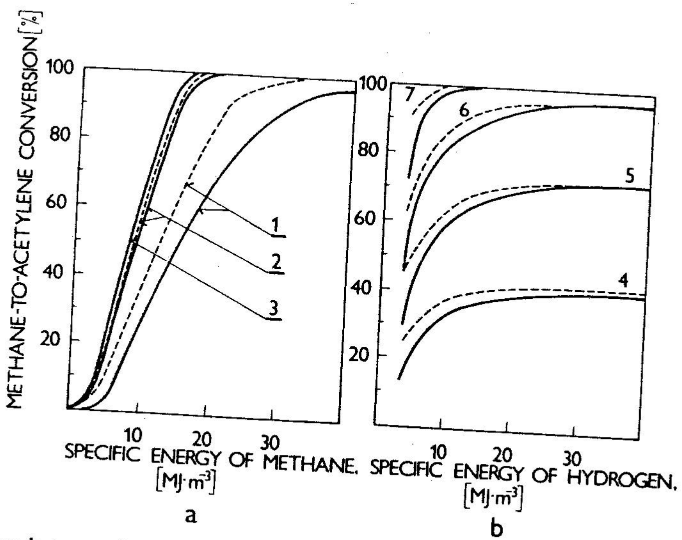

Fig. 1. Relation between the methane conversion degree and: a) the specific energy of methane for fixed values of the specific energy of hydrogen: 1 — 3.6; 2 — 14.4; 3 — 28.8 MJ/m^3, b) the specific energy of the plasma gas for fixed values of the specific energy of methane: 4 — 7.2; 5 — 10.8; 6 — 14.4; 7 — 21.6 MJ/m^3. Broken line — variant I; solid line — variant II.

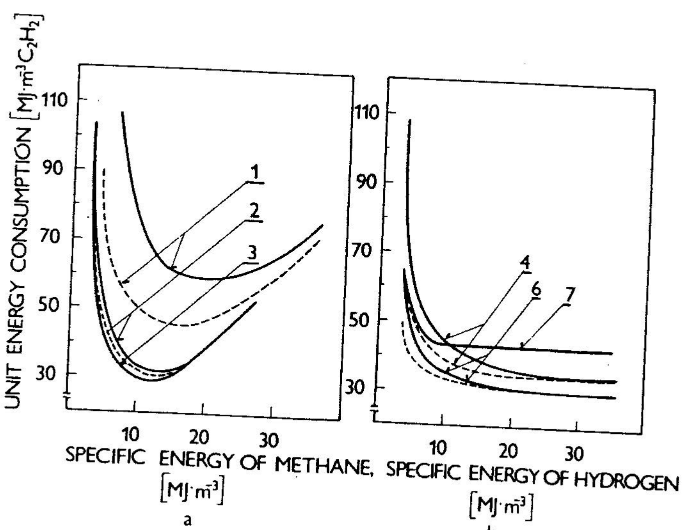

Fig. 2. Relation between the unit energy consumption and: a) the specific energy of methane for fixed values of the specific energy of hydrogen: 1 — 3.6; 2 — 14.4; 3 — 28.8 MJ/m^3, b) the specific energy of plasma gas for fixed values of the specific energy of methane: 4 — 7.2; 6 — 14.4; 7 — 21.6 MJ/m^3. Broken line — variant I; solid line — variant II.

almost identical (for the hydrogen specific energy equal to or higher than 14.4 MJ/m^3). The same conclusions can be drawn from the relation regarding the C_2H_2 concentration (in vol. %) in the off-gases on the specific energy of methane and hydrogen. There is practically no difference between the calculations according to the two variants for E_g = 14.4 MJ/m^3. Only for variant II, the maximum concentration, as dependent on the specific energy of the reactant is shifted towards E_r = 16.2 MJ/m^3. The differences between the acetylene concentration for the reactant specific energy 14.4 MJ/m^3 and 16.2 MJ/m^3 are negligible (<0.1%).

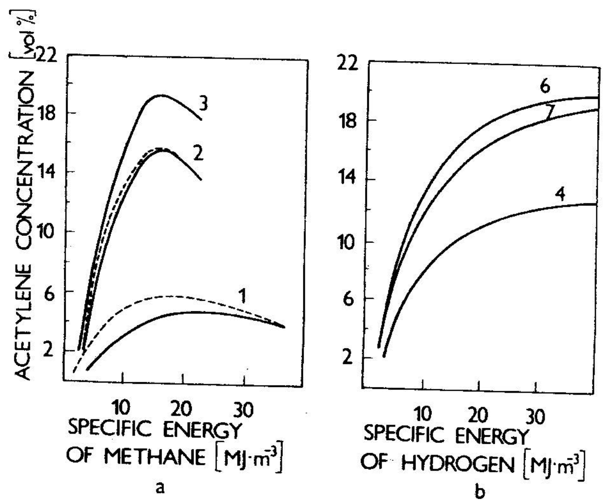

Fig. 3. Relation between the concentration of acetylene and: a) the specific energy of methane for fixed values of the specific energy of hydrogen: 1 — 3.6; 2 — 14.4; 3 — 28.8 MJ/m^3, b) the specific energy of hydrogen for fixed values of the specific energy of methane: 4 — 7.2; 6 — 14.4; 7 — 21.6 MJ/m^3. Broken line — variant I; solid line — variant II.

Gulyayev and Polak [4] have found for the initial composition corresponding to $k = 0.5$ the energy consumption equal to 31.0 MJ/m^3 for methane and the hydrogen specific energies 14.4 MJ/m^3 and 28.1 MJ/m^3, respectively. The unit energy consumption, obtained in the present study, is slightly lower (E_g = 28.8 MJ/m^3, E_r = 14.4 MJ/m^3, Z = 29.9 MJ/m^3), because the acetylene decomposition has not been taken into consideration.

Suris and Shorin [2] have obtained in their calculations the maximum conversion degree for the methane specific energy equal to 15.8 MJ/m^3 and the lowest unit energy consumption for the methane specific energy 12.6 MJ/m^3. The results are close to those obtained in the present work.

III. EXPERIMENTAL

The experiments were performed in a chemical plasma reactor (d.c. plasma jet). Gas containing 95.5 vol. % of methane was the reactant while the hydrogen was the plasma gas. The characteristics of the reactor, the method for the analysis of off-gases and the calculation of the material-energy balance were described earlier [5].

A series of experiments was carried out for $E_g = (9.25 + 0.70)$ MJ/m^3 using an arc discharge power equal to $(101.2 + 1.4)$ MJ/m^3.

IV. COMPARISON OF THE RESULTS OF CALCULATIONS WITH EXPERIMENTAL DATA

The comparison of the experimental and the calculated results according to variant II was carried out as before with respect to the calculations for variant I.

A comparison of the experimental data with the results of calculations is given in Table I.

Table I

Comparison of the experimental and the calculated data of the final parameters of the methane-to-acetylene conversion process: variant II (E_g = (9.25 + 0.70 MJ/m^3))

Specific energy E_r MJ/m^3	Total methane conversion* u %			Methane-to--acetylene conversion* u_p %			Quenching temperature* T_f K			Unit energy* Z MJ/m^3			n
	1	2	3	1	2	3	1	2	3	1	2	3	
10.0	61	56	1.09	55	51	1.08	1460	1462	1.00	36.4	35.6	1.02	4
12.0	73	69	1.07	65	63	1.03	1510	1517	1.00	37.1	34.7	1.07	4
16.7	91	92	0.98	84	72	1.18	1750	1759	1.00	39.2	35.7	1.09	4
22.5	97	99	0.98	91	78	1.16	1830	2015	0.91	49.3	45.4	1.09	1
27.9	99	100	0.99	93	68	1.39	2400	2306	1.05	62.6	55.4	1.09	3
38.9	99	100	1.00	89	—	—	2570	—	—	87.5	—	—	3

* 1 — experimental data; 2 — calculated data; 3 — ratio between experimental and calculated data; n — number of measurements.

No essential differences between the results of calculations and the experimental data have been observed. The total methane conversion degrees calculated according to variant II are slightly lower than those according to variant I (see Tab. I in [1]). This results from the increase of U_p, which causes the decrease of Z. Thus, the correlation between the calculated and the experimental data is by a few percent better for variant II.

However, it does not change the general conclusion concerning the range of the specific energy values of methane and hydrogen for the lowest Z values.

The comparison of the results obtained in the present work with those of other authors is difficult due to the lack of data concerning the reactor energetic efficiency. At best the plasma torch efficiency is reported only. In order to compare the results, the reactor efficiency should be evaluated on the basis of the data given in the cited papers and, thus, to calculate the specific energies of methane and hydrogen. Kozlov et al. [6] have obtained the lowest experimental energy consumption for the specific energy of hydrogen and methane equal to 22.9 and 14.4 MJ/m^3, respectively. These results are close to the results of calculation given in this paper.

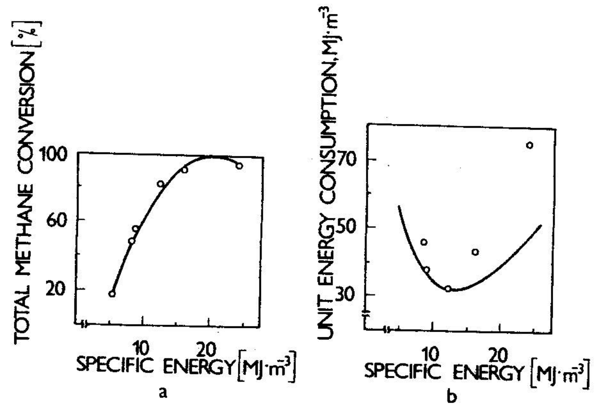

Fig. 4. Relation between: a) the total methane conversion degree and the specific energy of methane, b) the unit energy consumption and the specific energy of methane, ∘ — experimental data by Ganz et al. [7], ——— calculated data (present work). The explanation is in the text.

The experimental results published by Ganz et al. [7] are presented in Fig. 4 for the specific energy of hydrogen 24.0 MJ/m^3. These results were close to those calculated in the present study for variant II and the specific energy of hydrogen 14.4 MJ/m^3, because the differences between the values of the process parameters for the specific energy of hydrogen 14.4 and 28.8 MJ/m^3 are practically negligible (see Fig. 1a, 1b, 2a, 2b). The experimental total methane conversion degrees are placed on the curve calculated in the present paper. The lowest experimental energy consumptions are close enough to the calculated ones. This shows the applicability of the model for the determination of the range of the specific energies of methane and hydrogen, in which the lowest energy consumption should be expected.

V. CONCLUSIONS

The results of calculations presented in this paper indicate that the lowest energy consumption can be expected for $E_g \geqslant 14.4\,MJ/m^3$ for the methane specific energy range from 10.8 to $14.4\,MJ/m^3$. The influence of hydrogen as a plasma gas on the chemical process did not change the conditions given above.

The number of experiments, necessary to determine the optimum energetistic conditions for the methane pyrolysis in any plasma chemical reactor, can be considerably reduced if the range of the hydrogen and methane specific energies corresponding to the lowest unit energy consumption is chosen above.

Studies of improving the process, e.g. the construction, feeding and quenching techniques, should be carried out for the optimum energy conditions found above.

REFERENCES

[1] Opalińska, T.: Acta Phys. Slov.: *this issue.*
[2] Suris, A. L., Shorin, S. N.: Khim. Vys. Energ. *3* (1969), 99, 105.
[3] Gershuni, S. Sh., Suris, A. L., Shorin, S. N.: Khim. Vys. Energ. *9* (1975), 528.
[4] Gulyayev, G. V., Polak, L. S.: *Kinetika a termodinamika khimitscheskikh reakcyi v nizkotemperaturnoy plazme.* Ed. Nauka, Moskva 1965.
[5] Szymański, A.: 3me Symp. Intern. Chimie Plasmas, IUPAC, Limoges 1977, Ref. G.1.13.
[6] Kozlov, I. I., Khudyakov, G. N., Kobozev, Iu. N., Platonova, A. I.: Int. Chem. Eng. *8* (1968), 289.
[7] Ganz, S. N., Melnik, A. P., Parkhomienko, V. D.: Plazma v khimitscheskoy tekhnologii. Ed. Kiev, Kiev 1969.

Received August 6th, 1986
Revised version received January 22nd, 1988
Accepted for publication February 22nd, 1988

ВЛИЯНИЕ ВОДОРОДА НА ЭФФЕКТИВНОСТЬ ПЛАЗМЕННОГО ПИРОЛИЗА МЕТАНА

На основе модели процесса плазменного пиролиза метана, выдвинутой в работе I, исследовано влияние водорода в роли рабочего газа на реакцию синтеза ацетилена. Экспериментальные данные были сравнены с рассчетами в рамках предложенной модели. Установлено, что на эффективность пиролиза в пределе энергетических параметров, характеризующих процесс и отвечающих минимальному единичному расходу энергии, не влияет разбавление метана водородом.