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# INFLUENCE OF PROCESS PARAMETERS ON THE PLASMA PYROLYSIS OF METHANE TO ACETYLENE[1)]

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The influence of the reaction temperature, the $H_2/CH_4$ molar ratio and the thermal efficiency of plasmatrons on the course of the acetylene synthesis from methane in a hydrogen plasma jet was studied. The optimal ranges of the process parameters yielding the lowest energy consumption were found.

## I. INTRODUCTION

The search for effective methods of the acetylene production continues. It seems that such methods are: thermal pyrolysis [1], electrocracking [2—4], plasma pyrolysis of hydrocarbons [2, 5—7] and plasma pyrolysis of coals [8—10]. The present work deals with acetylene synthesis from methane in a hydrogen plasma jet generated in a d.c. arc discharge.

Considering the plasma pyrolysis of methane and the natural gas one can say that the yield of the process is characterized by unit energy consumption $EC$ (calculated relative to the arc energy) and both the methane to acetylene $U_{ac}$ and the total methane $U_t$ conversion degrees depend on many parameters [7, 11—17]. Among them we have chosen the initial reaction temperature ($T_r$), the hydrogen to methane ratio, $X$, as well as the thermal efficiency of plasmatrons ($\eta$). The aim of our investigations was to determine the influence of these parameters on the yield of the process.

The initial reaction temperature, $T_r$, is defined as the meanmass temperature calculated from the energy balance equation of the reaction chamber input

$$E_{pj} = E\eta = V_h \int_{T0}^{T_r} C_p(h)\,\mathrm{d}T + V_m \int_{T0}^{T_r} C_p(m)\,\mathrm{d}T, \qquad (1)$$

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where:
$E_{pj}$, $E$ is the energy of the plasma jet and the arc, respectively, $\eta$ is the thermal efficiency of the plasmatron, $V_h$, $V_m$ is the volume of hydrogen and methane, respectively. According to the equation the plasma jet energy is equal to the sum of the hydrogen and the methane energies at the initial temperature of the reaction

$$E_{pj} = V_h \,.\, \Delta H_h(T_r) + V_m \,.\, \Delta H_m(T_r). \qquad (2)$$

The hydrogen to methane molar ratio, $X$, which is equivalent to the ratio of the reagents flow rates, was calculated from the formula

$$X = V_h/V_m. \qquad (3)$$

The thermal efficiency of plasmatrons, $\eta$, which characterizes the relation between the arc energy $E$ and the energy of the flowing out plasma jet, $E_{pj}$, was calculated from the formula

$$\eta = E_{pj}/E = (E - Q_{cat} - E_a)/E, \qquad (4)$$

where $E_{cat}$, $E_a$ is the energy of the water cooling the cathode and anode, respetively.

## II. EXPERIMENTAL

The experiments were carried out on a laboratory scale (arc power discharge 10—40 kW) as well as on a larger scale reactor of the arc power of 50—100 kW at the Nitrogen Plant at Tarnów [18]. The experiments were performed in an apparatus system (Fig. 1) whose main part is a chemical plasma reactor. It includes a d.c. arc plasmatron with arc stabilization by the magnetic field, a reaction chamber in the shape of a cylinder, a freezing chamber consisting of a heat exchanger of the "tube in tube" type.

In experiments with the reactor of the arc power discharge up to 40 kW anodes of 6.5 or 100 mm diameters and a reactor chamber of a diameter of 10 mm and a length of 52 mm were employed. In experiments carried out at a power of the arc discharge of 50—100 kW, anodes of 16 or 18 mm diameters and reaction chambers of 18 or 20 mm diameters and 54 mm long were used.

The composition of off-gases was determined by gas chromatography. The flow rate of reactants ($V_{pr}$) was calculated on the basis of the content of an inert gas (nitrogen or argon), intentionally added to the post-reaction gas. The flow rate of the inert gas was measured by a rotameter. The content of the components $V_i$ in the post-reaction mixture was calculated from the formula:

$$V_i = (V_{in}/A_{in})\, A_i = V_{pr} A_i, \qquad (5)$$

where $V_i$ is the amount of the inert gas, $A_m$ is the contents of the inert gas, $A_i$ is the contents of the $i$th component in the post-reaction mixture, $V_{pr}$ is the flow rate of the post-reaction gases.

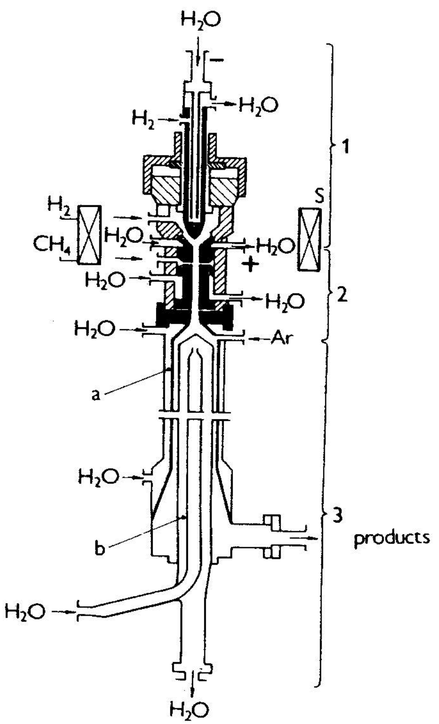


Fig. 1. Diagram of chemical plasma reactor, 1 — plasmatron, 2 — reaction chamber, 3 — freezing chamber, a, b — external, internal cooler, s — solenoid.

## III. RESULTS AND DISCUSSION

From the results of laboratory studies performed earlier [13], the effect of the initial reaction temperature on the energy consumption and the methane conversion degree the total $U$ and to acetylene $U_{ac}$ was determined. The experiments were carried out at $X = 2$. The methane flow rate reached 2.3 $m^3/h$. The reaction temperature varied in the range of 1700—4000 K due to a change of the arc power from 10 to 40 kW. The results of these experiments are presented in Fig. 2.

It is evident from Fig. 2 that there exists and optimum range of initial reaction temperature 2900—3600 K in which the energy consumption $EC$ attains a minimum value of 110—130 $MJ/m^3$ $C_2H_2$. In this temperature range the conversion degree of the substrate to acetylene amounts to 62—83 %. Above 3400 K the total methane conversion degree exceeds 90 %. As can be seen also from Fig. 2, an increase of the reaction temperature caused a decrease of

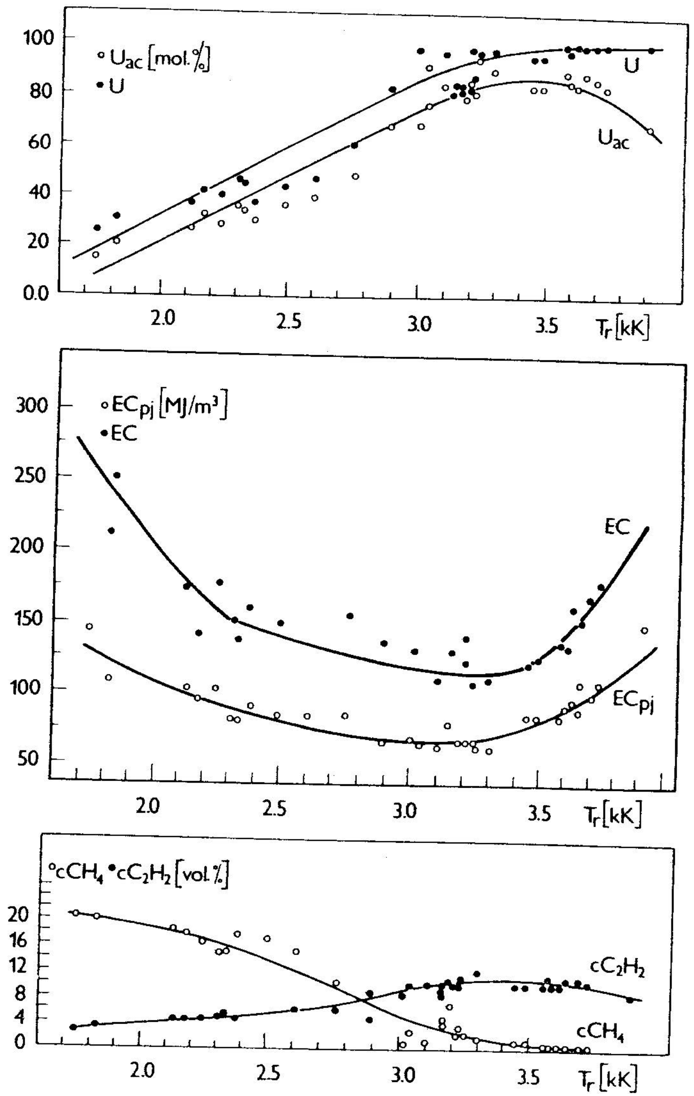


Fig. 2. Effect of initial reaction temperature $T_r$ on the effectiveness of the process.

methane and an increase of acetylene contents in the post-reaction mixture. In the optimal range of the reaction temperature the $C_2H_2$ contents exceeds 8 vol. % and $CH_4$ decreases below 3 vol. %.

In some cases the interpretation of results is made easier by introducing the parameter called "effective energy consumption" $EC_{pj}$, i.e. energy consumption calculated in relation to the effective energy of the plasma jet [11, 13, 17]. Formula

$$EC_{pj} = EC \, . \, \eta, \tag{6}$$

where $\eta$ is the thermal efficiency of a plasmatron, represents its connection with the energy consumption $EC$.

It follows from formula (6) that

$$EC = EC_{pj}/\eta. \tag{7}$$

It is worthwhile to notice that at $\eta \to 1$, $EC \to EC_{pj}$ [17].

The use of $EC_{pj}$ makes it possible to eliminate the effect of thermal efficiency of the plasmatron on the energy consumption $EC$ and, therefore, to compare values obtained in the reactors of different thermal efficiency.

It is evident from Fig. 2 that in the optimum reaction temperature range the energy consumption $EC_{pj}$ also obtains a minimum value of 60—70 MJ/m$^3$ $C_2H_2$.

In the second stage of the laboratory work the effect of the composition of the reaction mixture (defined by $X$) on the yield of the acetylene production from methane was studied. The results of experiments performed in the optimum range of reaction temperatures are given in Table 1.

It results from p. 1—4, Table 1, that the reduced hydrogen content inmixtures with methane, which is equivalent to a decrease of $X$, favours a decrease of the energy consumption $EC$.

Comparison of experiments 4 and 5 shows that at similar $EC_{pj}$ and $X$ a higher plasmatron efficiency, $\eta$, corresponds to a decidedly lower energy consumption of $EC$. This is evident from formula (7).

Table 1

Experimental parameters (a laboratory-scale reactor)

| Parameters | Units | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| $P$ | kW | 28.5 | 22.5 | 28.5 | 26.0 | 30.6 |
| $T_r$ | K | 3 240 | 2 940 | 3 250 | 3 030 | 3 040 |
| $X$ | l | 2.11 | 1.90 | 1.48 | 1.05 | 0.93 |
| $\eta$ | % | 55.3 | 59.3 | 58.4 | 66.4 | 45.9 |
| $EC$ | MJ/m$^3$ | 118 | 95.9 | 92.4 | 86 | 121 |
| $EC_{pj}$ | MJ/m$^3$ | 65.1 | 61.6 | 53.9 | 57.1 | 55.6 |
| $U_t$ | % | 97.3 | 71.1 | 85.6 | 65.4 | 61.2 |
| $U_{ac}$ | % | 87.3 | 70.7 | 80.2 | 57.8 | 55.1 |



Table 2

Experimental parameters (a large-scale plasmatron)

| Parameters | Units | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| $P$ | kW | 61.2 | 64.3 | 96.7 | 99.8 |
| $V_r$ | m$^3$/per hl | 10 | 12 | 18 | 18 |
| $T_r$ | K | 3 090 | 3 330 | 3 260 | 3 300 |
| $X$ | l | 0.83 | 1.33 | 1.2 | 1.2 |
| $\eta$ | % | 84.6 | 88.3 | 88.4 | 87.4 |
| $EC$ | MJ/m$^3$ | 63.4 | 67.6 | 67.5 | 69.1 |
| $EC_{pj}$ | MJ/m$^3$ | 53.6 | 59.7 | 59.7 | 60.4 |
| $U_t$ | % | 64.8 | 76.5 | 69.8 | 69.5 |
| $U_{ac}$ | % | 58 | 76.1 | 68.7 | 69.3 |

It follows from laboratory studies that a reaction temperature in the range of 2800—3400 K a hydrogen/methane molar ratio lower than 1.5 and a plasmatron efficiency above 60 % favour low energy consumption in the production of acetylene from methane.

The above-mentioned conclusions are used in studies performed in an experimental plasma installation of the arc power of 100 kW, at the Nitrogen Plant at Tarnów. The results of measurements are represented in Table 2.

The data from Table 2 show that a low energy consumption $EC$, below 70 MJ/m$^3$ $C_2H_2$ is obtained owing to the use of a high-efficiency plasmatrons. The thermal efficiency of the reaction chamber [15, 19] attained values of 75—80 %. This value approaches those obtained by Jasko and Laktuszyn [20] in a reactor of 1 MW power, with the freezing of the reaction product with a water spray. It results from literature data [2, 5, 8] and our studies [18, 21] that a fast quench of the reaction mixture (during the $C_2H_2$ synthesis from gaseous hydrocarbons) by a liquid hydrocarbons spray instead of diaphragm freezing results in a further decrease of energy consumption. To perform such a task, an additional chamber of 10 mm diameter and 37 mm long has been added to the main reaction chamber.

In the laboratory reactor of a 50 % efficiency an arc power of 35 kW and a hydrogen/methane ratio 2 and the reaction temperature 3700 K, due to an application of *n*-hexane freezing the $C_2H_2$ concentration was increased from 10.5 to 15.0, that of $C_2H_4$ from 1 to 7.5 vol. %, and the energy consumption $EC$ decreased from 115 to 65 MJ/m$^3$ $C_2H_2$. Also, a decrease in the energy consumption in the production of the $C_2H_2 + C_2H_4$ mixture from 110 to 43 MJ/m$^3$ was observed. The energy consumption $EC_{pj}$, calculated in relation to the plasma jet energy, was equal to 58—33 MJ/m$^3$ $C_2H_2$ and 55—21 MJ/m$^3$ $C_2H_2 + C_2H_4$, respectively.

It can be assumed that the application of high-efficiency plasmatron and reaction chambers can result in a further decrease of energy consumption.

In Hüls Co., gaseous hydrocarbons were, pyrolysed in the reactor of 10 MW arc power and a plasmatron efficiency exceeding 80 % [2, 8]. Energy consumption of up to 30—35 MJ/m$^3$ $C_2H_2 + C_2H_4$ was obtained by freezing the reaction products with liquid hydrocarbons.

An analysis of these and other literature data [1, 10] suggests that plasma technology is competitive with other techniques of $C_2H_2$ production such as the carbide method and natural gas partial-combustion.

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## ВЛИЯНИЕ РАБОЧИХ ПАРАМЕТРОВ ПРОЦЕССА НА ЭФФЕКТИВНОСТЬ ПЛАЗМЕННОГО ПИРОЛИЗА МЕТАНА ДО АЦЕТИЛЕНА


Исследовано воздействие начальной температуры реакции, молярного отношения $H_2$: $CH_4$ и термического к.п.д. плазматрона на эффективность синтеза $C_2H_2$ из $CH_4$ в струе водородной плазмы. Определено оптимальные величины параметров процесса для которых расход энергии достигает самых низких величин.