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INFLUENCE OF ENERGETIC REACTOR PARAMETERS ON THE YIELD OF ACETYLENE SYNTHESIS FROM METHANE[1)]

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The effect of specific energy of methane on the yield of acetylene synthesis from methane in a hydrogen plasma jet and the optimum energy range were determined by quasiequilibrium calculations and experiments.

I. INTRODUCTION

Acetylene synthesis from methane has been the object of many experimental and model studies [1–10]. Among thermodynamic models, the quasiequilibrium models are of great importance [1–3, 6–10]. They are based on the fact that reagents remain in the reaction chamber of a plasma reactor only for the time of an order of 10^{-4}s; in so short a time, only reactions of the gaseous phase can take place.

The aim of this paper is to determine the effect of methane specific energy on the yield of C_2H_2 synthesis from methane based on the quasiequilibrium model of the process elaborated earlier [7,10]. This model makes it possible to predict the process yield on the basis of the reaction initial temperature, the ratio of hydrogen to methane flow rates as well as the thermal efficiencies of the plasmatron and the reaction chamber.

II. MODEL

The starting point of the present considerations consists of the energy balance equation of the process at the reaction chamber input, which describes the initial conditions of the synthesis:

$$E_{pj} = E\eta = V_h \int_{T_0}^{T_r} C_p(h)\mathrm{d}T + V_m \int_{T_0}^{T_r} C_p(m)\mathrm{d}T \qquad (1)$$

where E_{pj}, E - is the energy of the plasma jet and arc, respectively, η is the plasmatron efficiency, V_h, V_m - are the volume of hydrogen and methane, respectively, $C_p(h)$, $C_p(m)$ - the specific heat of hydrogen and methane, respectively [11].

For the given initial conditions of the process, of the sum of energies of the reactions products (at the quenching chamber input) plus C_2H_2 formation energy at the quenching temperature $\Delta H^0_{Tq}(\mathrm{C_2H_2})$, plus the energy taken up by water cooling the reaction chamber E_{rch}, represents the plasma jet energy:

$$\begin{aligned} E_{pj} &= 0.5U_{ac}V_m\Delta H_a(T_q) + (1 - U_{ac})V_m\Delta H_m(T_q) \\ &+ 1.5U_{ac}V_m\Delta H_h(T_q) + V_h\Delta H_h(T_q) + 0.5U_{ac}V_m\Delta H^0_{Tq}(\mathrm{C_2H_2}) \qquad (2) \\ &+ E_{rch}, \end{aligned}$$

where U_{ac} - is the methane - to acetylene conversion degree, $\Delta H_a(T_q), \Delta H_m(T_q)$, $\Delta H_h(T_q)$ - are the enthalpy changes of acetylene, methane and hydrogen from the quenching temperature to the standard temperature, $\Delta H^0_{Tq}(\mathrm{C_2H_2})$ is the enthalpy acetylene synthesis from methane at quenching temperature.

If the volume ratio of hydrogen to methane is denoted by X and the eq. (1) is divided by V_m, then a generalized energy balance equation results, which defines the initial conditions of the process as a function of temperature T_r and of the initial composition of the reactants expressed as well X as specific energy of methane E_m.

$$E_m = E_{pj}/V_m = X\Delta H_h(T_r) + \Delta H_m(T_r), \qquad (3)$$

where $\Delta H_h(T_r)$, $\Delta H_m(T_r)$ - are enthalpy changes of hydrogen and methane from the initial temperature of reaction to standard temperature, respectively, E_m - is the specific energy of methane. According to this approach the specific energy of methane determines the initial reaction temperature.

The relationship between the specific energy of methane and the initial temperature of the reaction for various hydrogen/methane volume ratio X is given in Fig. 1.

The specific energy of the substrate is one of the most frequently used parameters influencing the plasmochemical process yield [12]. In the case of the feeding of the reactor with the substrate only, e.g. when methane is electrocraced ($X = 0$), the specific energy is a parameter independent of the reactor power.

For the given initial conditions of the process and or a calculated or assumed reaction chamber efficiency η_{rch}, which to a high degree depends on the reaction

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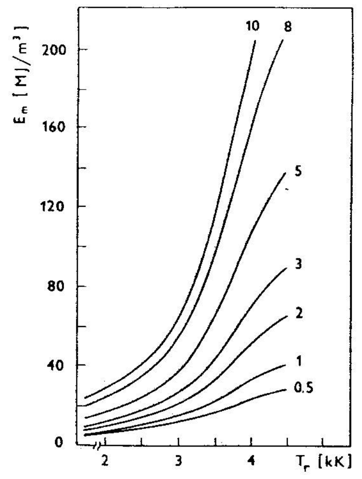

Fig. 1. The relationship between the specific energy of methane E_m and the initial temperature of the reaction T_r for various H_2/CH_4 volume ratios X.

temperature and the specific energy of methane [13], the generalized equation which characterizes the final conditions of the process - acquires the form

$$E_m = E_m(1 - \eta_{rch}) + 0.5U_{ac}\Delta H^0_{T_q}(C_2H_2) + X\Delta H_h(T_q) + \Delta H_m(T_q), \quad (4)$$

where η_{rch} is the reaction chamber efficiency.

It was assumed, similarly as in other works [2,6,8], that the desired reaction is the only one taking place in the system, hydrogen supplying the plasmatron is regarded as an inert energy carrier, i.e. a diluent of the reaction products [1,3,8], and that it attains an equilibrium at quenching temperature. As a consequence it can be concluded that the methane - to - acetylene conversion degree calculated from the energy balance equation

$$U_{ac} = \frac{E_m\eta_{rch} - X\Delta H_h(T_q) - \Delta H_m(T_q)}{0.5\Delta H^0_{T_q}(C_2H_2)} \quad (5)$$

should be equal to that computed from the equilibrium constant K expressed by pressures

$$U_{ac} = \frac{\sqrt{X^2 + 4\left[\left(\sqrt{K} + 1.299\right)/\sqrt{K}\right](1 - X)} - X}{2\left[\sqrt{K} + 1.299/\sqrt{K}\right]} \quad (6)$$

The final conditions of the process can be determined by solving the equation system (5) and (6) with respect to T_q and U_{ac}.

Effective energy consumption EC_{pj}, calculated relative to the plasma jet energy, defined as the ratio of E_{pj} to the volume of acetylene, is expressed by the formula

$$EC_{pj} = \frac{2E_m}{U_{ac}} \quad (7)$$

Taking into account the definition of plasmatron efficiency [4], we obtain an expression defining unit energy consumption EC, calculated relative to the arc energy

$$EC = \frac{EC_{pj}}{\eta} = \frac{2E_m}{U_{ac}\eta} \quad (8)$$

The above method yields the minimum, thermodynamically justifiable value of unit energy consumption.

The relationship between equilibrium conversion degrees and effective energy consumption EC_{pj} and specific energy of methane for various compositions of the H_2-CH_4 mixture is given in Fig. 2. The reaction chamber efficiency was assumed to be 80%.

It results from Fig. 2 that there exists optimum specific energy of methane ranges for which energy consumption attains minimal values dependent on X. Energy consumption is lowest at the highest methane content in its mixture with hydrogen (low value of X). It is evident from the dependences given in Fig. 2 that the specific energy of methane determines essentially the degree of conversion U_{ac} and the effective energy consumption EC_{pj}, possible to achieve.

The use of EC_{pj} makes is 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 efficiencies plasmatrons η. It is worthy of notice that at $\eta \to 1$ $EC \to EC_{pj}$.

III. EXPERIMENTAL

The experiments were carried out in a laboratory scale (arc power discharge 10–40 kW) [14] as well as in a larger scale reactor of the arc power of 50–100 kW at the Nitrogen Plant Tarnow [15]. The experiments were performed in an apparatus system [10,16] whose main part is a chemical plasma reactor. It included d.c. arc plasmatron with arc stabilization by the magnetic field, a reaction chamber in the shape of a cylinder, a quenching 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 10 mm of diameters and a reactor chamber of 10 mm of diameter and 52

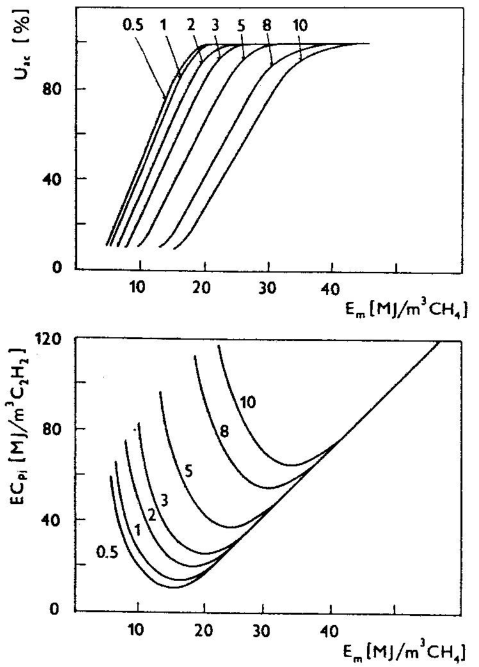

Fig. 2. Dependence of the methane - to - acetylene conversion degree U_{ac} and effective energy consumption EC_{pj} on the specific energy of methane E_m for various H_2/CH_4 volume ratios X.

mm of length were employed. In experiments carried out at the power of the arc discharge of 50–100 kW anodes of 16 or 18 mm of diameters and reaction chambers of 18 or 20 mm of diameters and 54 mm long were used.

The methodology of experiments has been described earlier [14,16]. The specific energy of methane was calculated by the formula:

$$E_m = E\eta/V_m = E_{pj}/V_m. \tag{9}$$

IV. RESULTS AND DISCUSSION

From the results of an analysis of laboratory studies performed earlier [14] the effect of the specific energy of methane on the energy consumption and methane conversion degree: total U_t and to acetylene U'_{ac} was determined.

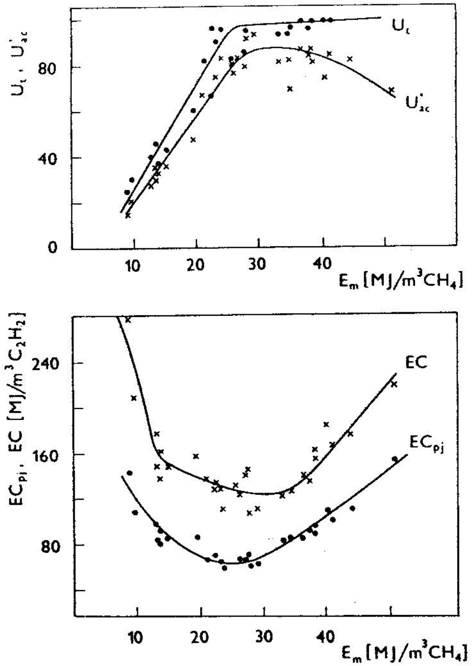

Fig. 3. Effect of the specific energy of methane E_m on the yield of the process.

The experiments were performed at constant hydrogen 4.4 m^3/h and methane 2.2 m^3/h volume fluxes, i.e. at a constant initial composition of reagents, X=2.

Specific energy of methane was varied within the range of 9–52 MJ/m^3 by changing the power of arc from 10 to 40 kW. The results of these experiments are presented in Fig. 3. It results from Fig. 3 that there exists an optimum range of 20–35 MJ/m^3 for which the effective energy consumption EC_{pj} attains a minimum of 60–70 MJ/m^3 C_2H_2. For this energy range the conversion degree of the substrate to acetylene U'_{ac} amounts to 55–85%. Above 22 MJ/m^3 the total methane conversion degree U exceeds 90%. It is evident from Fig. 3 that for the optimum specific energy range the energy consumption EC also attains a minimum 110–130 MJ/m^3 C_2H_2. With a rise of specific energy of methane above 38 MJ/m^3, U'_{ac} decreases. The difference between U_t and U'_{ac} indicates that a side reaction takes place.

It follows from Fig. 2 that a reduction of the volume of hydrogen in mixtures with methane, which is equivalent to a decrease in X, results in a decrease in energy consumption EC_{pj}. Furthemore, it follows from formula (8) that a higher plasma-

Table 1

Experimental results obtained using a reactor on a large laboratory scale.

Parameters	Units	1	2	3	4	5	6
$P^{*)}$	kW	61.2	64.3	66.4	74.8	96.7	99.8
η	%	84.6	88.3	87.5	87.5	88.4	87.4
V_m	m^3/per 1h	12.0	9.0	14.7	13.5	15.0	15.0
X	1	0.83	1.33	0.81	0.88	1.2	1.2
E_m	MJ/m^3CH_4	15.5	22.4	14.2	17.2	20.5	20.9
EC_{pj}	MJ/$m^3C_2H_2$	53.6	59.7	52.1	52.3	59.6	60.4
EC	MJ/$m^3C_2H_2$	63.3	67.6	59.6	59.8	67.5	69.1
U'_{ac}	%	58.0	76.1	54.6	66.7	68.7	69.3

*) power of arc discharge

tron efficiency corresponds to a lower energy consumption EC. The above mentioned conclusions were utilized in studies performed in an experimental plasma installation with an arc power of 50–100 kW, at the Nitrogen Plant Tarnow [10,15,16]. The results of measurements are presented in the Table 1.

It seems that the presented calculation model illustrates well the experimentally found relatioships between the degree of methane conversion into acetylene and energy consumption, on the one hand and the specific energy of methane on the other. Subsequently it was attempted to calculate the parameters of the process carried out on a large laboratory scale in a reactor with the arc power of 1 MW, with efficiencies of the plasmatron and the reaction chamber of 83% and 80%, respectively. Under the above conditions at $V_m = 169m^3/h$, $X = 0.96$ and the specific energy of methane 18 MJ/m^3 the energy EC_{pj} and EC ought to be 39.6 and 47.7 MJ/m^3 C_2H_2, respectively. The degree of conversion methane-to-acetylene ought to be 91%. These values approach those obtained by Zubkova [17] and Laktiushin [18] in a reactor 0.8–1 MW at the specific energy of methane 15–17 MJ/m^3 with the freezing of the reaction products by means of a water spray.

It seems that in the case of the quasiequilibrium C_2H_2 synthesis from methane the proposed method can be useful for predicting the synthesis yield.

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ВЛИЯНИЕ ЭНЕРГЕТИЧЕСКИХ ПАРАМЕТРОВ РЕАКТОРА НА ВЫХОД АЦЕТИЛЕНА ПРИ СИНТЕЗЕ МЕТАНА

С применением квазиравновесных расчетов и экспериментов определено влияние характерной энергии метана на выход ацетилена при синтезе метана в струе водородной плазмы. Установлен также энергетический оптимум.