acta phys. slov. 37 (1987), No. 2

SIMPLE THERMODYNAMIC MODELS OF ACETYLENE SYNTHESIS IN A HYDROGEN PLASMA JET[1])

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

I. INTRODUCTION

Acetylene synthesis from methane has been the object of many experimental and model studies [1—11]. Among thermodynamic models, the quasiequilibrium models are of great importance [1—3]. 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 the present studies was to evaluate the usefulness of the quasiequilibrium model for calculating the energy consumption during the synthesis of C_2H_2 from CH_4 as well as the usefulness of the degree of methane conversion into acetylene, on the ground of the initial temperature of the reaction of the hydrogen-methane molar ratio and the thermal efficiency of the plasmotron and 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

$$E_{pj} = E\eta = V_h \Delta H_h(T_r) + V_m \Delta H_m(T_r) \qquad (1)$$

where E_{pj}, E is the energy of the plasma jet and arc, η is the plasmotron efficiency, V_h, V_m are the volume of hydrogen and methane, $\Delta H_h(T_r)$, $\Delta H_m(T_r)$ are the enthalpy changes of hydrogen and methane from the initial temperature of the reaction to standard temperature (298 K).

For the given initial conditions of the process, the sum of energies of the reactions products (at the quenching chamber input) plus the C_2H_2 formation energy at the standard temperature $\Delta H^0_{298}(C_2H_2)$, plus the energy taken up by water cooling the reaction chamber E_{rch}, represents the plasma jet energy. If the volumes of reagents are expressed as a function of V_m and U_{ac}, the plasma jet energy is determined by the formula

$$E_{pj} = 0.5U_{ac}V_m\Delta H_a(T_q) + (1 - U_{ac})V_m\Delta H_m(T_q) + 1.5U_{ac}V_m\Delta H_h(T_q + \\ + V_h\Delta H_h(T_q) + 0.5U_{ac}V_m\Delta H^0_{298}(C_2H_2) + E_{rch} \qquad (2)$$

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 entalphy changes of acetylene, methane and hydrogen upon the transition from the quenching temperature and the standard 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 X

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

where E_m is the effective specific energy of methane [8].

For the given initial conditions of the process and for a calculated or assumed reaction chamber efficiency η_{rch}, which to a high degree depends on the reaction temperature and on the specific energy of methane [8], the generalized equation (for $V_m = 1$) which characterizes the final conditions of the process — at the quenching chamber input — acquires the form

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

where $\Delta H^0_{Tq}(C_2H_2)$ is the enthalpy of the acetylene synthesis from methane at quenching temperature.

It was assumed, similarly as in other works [2, 7, 11], that the desired reaction is the only one taking place in the system, hydrogen supplying the plasmotron is regarded as an inert energy carrier, i.e. a diluent of the reaction products [1, 3, 11], and thata the process 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

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

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[1]) Contribution presented at the 6th Symposium on elementary Processes and Chemical Reactions in Low Temperature Plasma, JELŠAVA-HRÁDOK, June 9—13, 1986.

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should be equal to that computed from the equilibrium constant K expressed by pressures [7]

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

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

$$EC_{pj} = \frac{E_{pj}}{0.5U_{ac}V_{rt}} = \frac{2E_{m}}{U_{ac}} = \frac{2[X\Delta H_h(T_r) + \Delta H_m(T_r)]}{U_{ac}}. \qquad (7)$$

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

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

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} for various compositions of the H_2—CH_4 mixture is given in Fig. 1. The reaction chamber efficiency was assumed to be 80%.

It results from Fig. 1 that there are exist optimum temperature ranges for which energy consumption attains minimal values dependent on X. Energy consumption is lowest at the highest methane contents in its mixture with hydrogen (low value of X).

III. EXPERIMENTAL

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, $X = 2$ [10]. Reaction temperature varied within the range of 1700—4000 K by changing the power of the arc from 10 to 40 kW. The apparatus and the methodology of experiments have been described earlier [10]. The initial temperature of the reaction was calculated by the formula (1).

IV. RESULTS AND DISCUSSION

The results of an analysis of our earlier work [10] are presented in Fig. 2. It results from Fig. 2 that there exists an optimum range of initial reaction temperature (2600—3300 K) for which the effective energy consumption EC_{pj} obtains a minimum of 60—70 MJ/m^3 C_2H_2. For this temperature range, the conversion degree of the substrate to acetylene U'_{ac} reaches 54—85%. Above 3000 K the total methane conversion degree U exceeds 90%. It is evident from Fig. 2 that for the optimum reaction temperature range the energy consumption EC also attains a minimum 110—130 MJ/m^3 C_2H_2. With an rise of temperature above 3500 K, U'_{ac} decreases. The difference between U and U'_{ac} indicates that a side reaction take place.

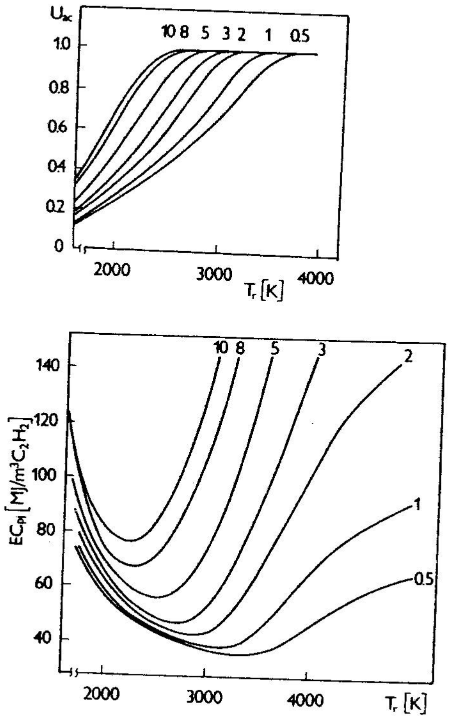

Fig. 1. Dependence of U_{ac} and EC_{pj} on the initial reaction temperature T_r for various H_2/CH_4 molar ratios X.

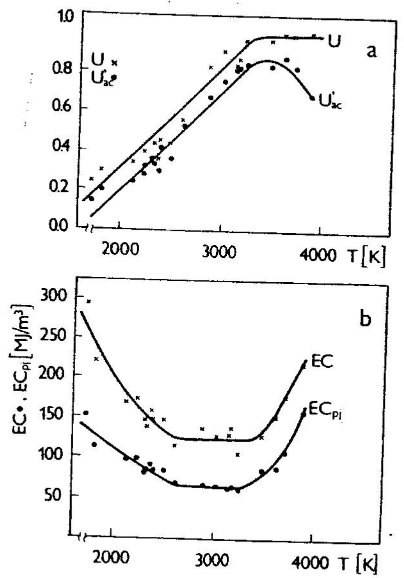

Fig. 2. Effect of initial reaction temperature T_r on the effectiveness of the process.

It follows from Fig. 1 that a decrease of the content of hydrogen in the mixture with methane, which is equivalent to a decrease of X, results in a decrease in energy consumtion EC_{pj}. Furthermore, it follows from formula 8 that a higher plasmotron efficiency corresponds to a lower energy consumption EC. The above mentioned conclusions were utilized in studies performed in an experimental plasma installation with and arc power of 50—100 kW at the Nitrogen Plant Tarnów [6, 9]. The results of measurements are presented in the Table 1.

Table 1

Measurement results obtained using a high-efficiency plasmotron on a large laboratory scale.

Parameters	Units	1	2	3	4	5	6
P	kW	61.2	63.4	66.4	74.8	96.7	99.8
V_m	m^3/per 1 h/	12	9	14.7	13.5	15	15
X	1	0.83	1.33	0.81	0.89	1.2	1.2
η	%	84.6	88.3	87.5	87.5	88.4	87.4
T_r	K	3100	3300	3400	3200	3300	3300
EC_{pl}	$MJ/m^3C_2H_2$	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

It seems that the presented calculation model illustrates well experimentally found relationships between the degree of methane conversion into acetylene and energy consumption on the one hand and the initial temperature of the reaction 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 plasmotron and the reaction chamber of 83 and 80%, respectively, and with plasma jet temperature of 4000 K. Under the above conditions at $V_h = 162\ m^3/h$, $T_r = 3200$ K and $X = 0.96$ the unit energy consumption ought to be 58 MJ/m^3 C_2H_2 and degree conversion methane-to-acetylene 92%. This value approaches to those obtained by Jasko and Laktushin [12] in a reactor of 1 MW power, with the freezing of the reaction products with a water spray.

ACKNOWLEDGEMENTS

I wish to thank Professor Andrzej Szymanski for stimulating discussions and remarks.

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Received August 6th, 1986

ПРОСТАЯ ТЕРМОДИНАМИЧЕСКАЯ МОДЕЛЬ ПРОЦЕССА СИНТЕЗА АЦЕТИЛЕНА В СТРУЕ ВОДОРОДНОЙ ПЛАЗМЫ

В работе определено влияние начальной температуры реакции на эффективность процесса синтеза ацетилена из метана в струе водородной плазмы на основе расчетов равновесия и экспериментов.