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INFLUENCE OF ENERGETICS PLASMATRON PARAMETERS ON THE YIELD OF ACETYLENE SYNTHESIS FROM METHANE[1]

PŁOTCZYK, W. W.,[2] Warsaw

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

INTRODUCTION

As a result of plasma pyrolysis of methane, acetylene was obtained in high yields. Acetylene synthesis from methane is the subject of many papers, both theoretical and experimental.

The aim of the theoretical papers is to predict the process yields (methane-to-acetylene conversion degree, energy consumption in C_2H_2 production) on the basis of kinetic [1—3] or thermodynamic [1, 2, 4—10] models properly formulated. Among thermodynamic models, the quasiequilibrium models are of great importance [1, 2, 4—10]. They are based on the fact that reagents remain in the reaction chamber of a plasma reactor only some time of an order of 10^{-4} s; in so short a time, only reactions of a gaseous phase can take place.

The aim of this paper is to determine the effect of hydrogen specific energy, i.e., the gas stabilizing arc discharge in the plasmatron, on the yield of C_2H_2 synthesis from methane based on the quasiequilibrium model of the process, elaborated earlier [9]. This model makes it possible to predict the process yield on the basis of the initial temperature of the reaction, the ratio of hydrogen to the methane flow rates as well as the thermal efficiencies of the plasmatron and the reaction chamber.

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

II. MODEL

In a plasmatron the energy introduced into an arc discharge is converted into the thermal energy of a plasma jet. The plasma jet can be characterized, from the energetic point of view, by the specific energy of the plasma gas E_h, defined as the reaction of the plasmatron effective power to the hydrogen flow rate. This energy corresponds univocally to the mean-mas temperature of the hydrogen plasma [11].

After the introduction of the reaction substrate-methane into the plasma jet and an instantenous, as it is assumed [12], mixing of gases a mixture of reagents is obtained, which can be characterized by the composition and the initial mean mass temperature of the reaction T_r. The initial temperature of the reaction is calculated by solving the energy balance equation at the reaction chamber input

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

where E_{pj}, E is the energy of plasma jet and arc, respectively, η the thermal plasmatron efficiency, V_h, V_m the volume of hydrogen and methane, respectively, $C_p(h)$, $C_p(m)$ the specific heat of hydrogen and methane, respectively [13].

According to this equation the plasma jet energy is equal to the sum of the hydrogen and methane enthalpies at the initial temperature of the reaction

$$E_{pj} = E\eta = V_h \Delta H_h(T_r) + V_m \Delta H_m(T_r), \tag{2}$$

where $\Delta H_h(T_r)$, $\Delta H_m(T_r)$ are the enthalpy changes of hydrogen and methane from the initial temperature of the reaction to the standard temperature [13].

If the volume ratio of methane to hydrogen is denoted by Y and the eq. (2) is divided by V_h, then a generalized energy balance equation results, it defines the initial conditions of the process as a function of temperature (T_r) and of the initial composition of the reactants expressed as Y

$$E_h = E_{pj}/V_h = \Delta H_h(T_r) + Y\Delta H_m(T_r), \tag{3}$$

where E_h is the effective specific energy of hydrogen [8].

It results from equation (3) that the effective specific energy of hydrogen is equal to the energy contained in 1 m^3 of the plasma jet, indispensable for methane heating by mixing with hydrogen in the volume ratio 1 Y up to the initial temperature of the reaction T_r.

Next, conversion of CH_4 into C_2H_2 takes place in the reaction chamber. The reagents temperature decreases owing to the endothermic chemical process as well as the heat exchange through the chamber wall E_{rch}. The process in the reaction chamber reaches its final state, which can be characterized by means of the quenching temperature T_q and the methane-to-acetylene conversion degree U_{ac}.

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

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

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 entalphy changes of acetylene, methane and hydrogen from quenching temperature to standard temperature [13].

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 [14, 15], the generalized equation (for $V_h = 1$), which characterizes the final conditions of the process, at the quenching chamber input acquires the form

$$E_h = E_h(1 - \eta_{rch}) + 0.5\,YU_{ac}\Delta H^\circ_{Tq}(C_2H_2) + \Delta H_h(T_q) + Y\Delta H_m(T_q), \tag{5}$$

where $\Delta H^\circ_{Tq}(C_2H_2)$ is the enthalpy of the C_2H_2 synthesis from CH_4 at the quenching temperature.

In the above formula E_{rch} is also presented in a generalized form. It results from the definition of the reaction chamber efficiency [14], described by the formula

$$\eta_{\mathrm{rch}} = (E_{pj} - E_{rch})/E_{pj} \tag{6}$$

where

$$E_{rch} = E_{pj}(1 - \eta_{rch}). \tag{7}$$

The parameter Y depends on the parameter X, which was earlier used [9], in the formula

$$Y = 1/X \tag{8}$$

It was assumed, similarly as in other works [2, 8, 10] 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, 2, 7—10], and the process attains an equilibrium at quenching temperature. As

It is evident from Fig. 2 that the optimum specific energies of hydrogen correspond to the optimum temperature of the hydrogen plasma. Thus, e.g. to $E_h = 17\,\mathrm{MJ/m^3}$ at $Y = 1$ there correspond $T_h = 3920\,\mathrm{K}$ and for $E_h = 5\,\mathrm{MJ/m^3}$ at $Y = 0.1$ $T_h = 2950\,\mathrm{K}$.

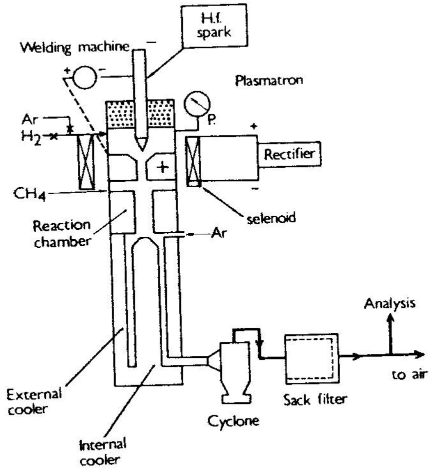

Fig. 2. Experimental set-up.

III. EXPERIMENTAL

The experiments were performed at constant hydrogen ($4.4\,\mathrm{m^3/h}$) and methane ($2.2\,\mathrm{m^3/h}$) volume fluxes, i.e. at a constant initial composition of reagents, with $Y = 0.5$ [16]. The specific energy of hydrogen varied within the range of 1700—4000 K by changing the power of the arc from 10 to 40 kW. The apparatus is in Fig. 2. The methodology of the experiments was described earlier [16].

IV. RESULTS AND DISSCUSION

On the basis of laboratory studies [16], performed earlier, the effect of specific of hydrogen on the yield of the acetylene synthesis from methane at $Y = 0.5$ was determined.

It results from Fig. 3 that there exists an optimum range of specific energy hydrogen 11—15 $\mathrm{MJ/m^3H_2}$ for which the effective energy consumption (EC_{pj}) attains a minimum of 58—70 $\mathrm{MJ/m^3}$ C_2H_2. For this specific energy range, the conversion degree of the substrate to acetylene (U_{ac}) reaches 63—85 %. Above 11 $\mathrm{MJ/m^3H_2}$ the total methane conversion degree (U) exceeds 90 %. It is evident from Fig. 3 that for the optimum energy of the hydrogen range the energy consumption EC also attains a minimum of 110—130 $\mathrm{MJ/m^3}$ C_2H_2. With a rise of the specific energy above 17 $\mathrm{MJ/m^3H_2}$, U_{ac} decreases. The difference between U and U_{ac} indicates that a side reaction take place.

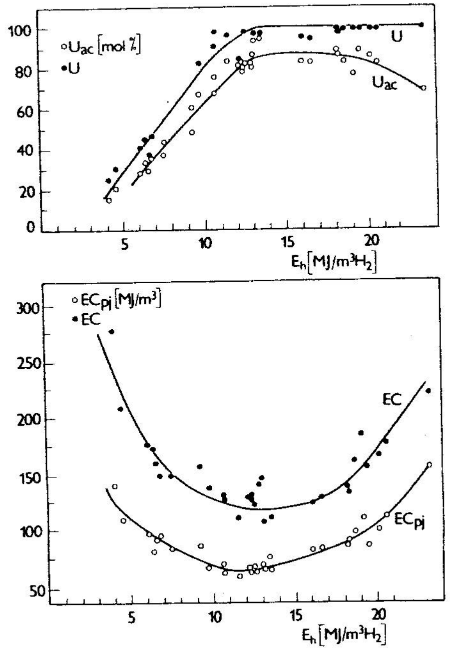

Fig. 3. Effect of the specific energy of hydrogen E_h on the effectiveness of the process.

It follows from Fig. 3 that decreasing the contents of hydrogen in the mixtures with methane, which is equivalent to an increase of Y, results in a decrease in the energy consumption EC_{pj}. Furthemore, it follows from formula (15) that to a higher plasmotron efficiency there corresponds 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, (situated) at the Nitrogen Plant Tarnów [7, 17]. The results of measurements are presented in the Table. The dates in the Table show that a low energy consumption EC, below 60 $\mathrm{MJ/m^3}$ C_2H_2, are obtained to the of a high — efficiency plasmatron as well as a reaction chamber.

It seems that the presented calculation model well illustrates the experimentally found relationships between the degree of the methane conversion into

Table 1

Measurement results obtained using a high-efficiency plasmatron on a lerge 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_h	m^3(per 1 h)	10	12	12	12	18	18
V_m	m^3(per 1 h)	12	9	14.7	13.5	15	15
Y	1	1.2	0.75	1.22	1.11	0.83	0.83
η	%	84.6	88.3	87.5	87.5	88.4	87.4
E_h	MJ/m^3H_2	18.6	16.2	17.4	19.6	17.1	17.4
T_h	K	4050	3900	3950	4100	3900	3950
T_r	K	3100	3300	3400	3200	3330	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	59.4	59.8	67.5	69.1
U_{ac}	%	58.0	76.1	54.6	66.7	68.7	69.3

acetylene and energy consumption, on the one hand, and the specific energy of hydrogen on the other.

Subsequently it was attempted to calculate the parameters of the process production of acetylene in a hydrogen plasma jet carried out on a semi-commercial scale. The operating conditions of this reactor of an arc power of 1 MW with the diaphragm quenching of the reaction products were calculated earlier [9] for the plasmatron and the reaction chamber efficiencies equal to 83 and 80 %, respectively, and the hydrogen plasma jet temperature 4000 K. Under these conditions the hydrogen specific energy is 18.4 MJ/m^3, the hydrogen flow rate 162 m^3/h, the methane flow rate 168.8 m^3/m the energy consumption should be 58 $MJ/m^3C_2H_2$ and the acetylene to methane conversion degree 92 %.

Next, the process with gasoline freezing of the methane pyrolysis products was calculated based on earlier studies [18]. It was assumed that both in the laboratory and on a semi-commercial scale investigations at the same effective specific energy of gasoline (7 MJ/kg), the same additional amounts of 0.25 m^3 of C_2H_2 and 0.5 m^3 of C_2H_4 per 1 kg of the raw material introduced are obtained. It is expected that, after the introduction of 94.8 kg of gasoline into a reactor of 1 MW arc power the energy consumption decreases in the production of C_2H_2 and $C_2H_2 + C_2H_4$ down to 42 and 27 MJ/m^3, respectively. These values are close to those obtained in a modified industrial installation of Hüls Co. [19, 20].

On the basis of the results of laboratory studies, quasi-equilibrium calculations and industry experiments one can say that a specific energy of hydrogen higher that 15 MJ/m^3H_2, a methane/hydrogen molar ratio higher than 0.7, high plasmatron and reaction chamber efficiencies and quenching products pyrolysis of methane by means of liquid hydrocarbons favour low energy consumption in the production of C_2H_2 form CH_4 (or the natural gas).

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ВЛИЯНИЕ ЭНЕРГЕТИЧЕСКИХ ПАРАМЕТРОВ ПЛАЗМАТРОНА НА ЭФФЕКТИВНОСТЬ ПРОЦЕССА СИНТЕЗА АЦЕТИЛЕНА ИЗ МЕТАНА

Процесс проведено в струе водородной плазмы генерерированной в дуге постоянного тока. Воздействие удельной энергии водорода, термического кпд. плазмотрона и молярного отношения метан/водород на эффективность процесса определено так при помощи квазиравновесных расчётов как и при помощи экспериментов.