

EFFECT OF ENERGETIC PARAMETERS OF THE REACTION CHAMBER ON THE PYROLYSIS OF METHANE IN A DC HYDROGEN PLASMA JET

PART I

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The process of methane-to-acetylene pyrolysis in a low temperature hydrogen plasma jet was studied. The specific energies of methane and hydrogen were selected as parameters characterizing the chemical process in the reaction chamber. These parameters were applied in a model description of the process. Test experiments were performed in order to verify the reliability of theoretical considerations. The efficiency of the process, found on the basis of the model, is in agreement with the experimental data within the limits of 10%.

I. INTRODUCTION

Studies on plasma pyrolysis of gaseous aliphatic hydrocarbons show that the final effect of the process depends on numerous parameters, e.g. reaction and quenching temperature, molar ratio of gaseous reagents, residence time in the reaction chamber, quenching rate and technique applied. Hence the difficulties in a general process description, particularly regarding its effectiveness prediction [1—3].

The present studies were undertaken to determine the optimal values of energetic parameters characterizing the reaction chamber in the synthesis of acetylene from methane (reactant) in hydrogen plasma jet. Specific energy of the plasma gas and the reagent, defined and interpreted differently than by other authors [4—7], were selected as the essential parameters.

II. MODEL CONSIDERATIONS

The energy carried to the plasma torch (E_0) is imparted to the plasma gas by an electric discharge. One part of the energy is lost for cooling the elements of

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the plasma torch (E_r) and the reaction chamber (E_c) itself. Hence, the energy which is available in the reaction chamber (E_u) is:

$$E_u = E_a - (E_r + E_c). \quad (1)$$

The ratio of the E_u to E_a defines the energetic efficiency of the chemical plasma reactor (η_r):

$$\eta_r = E_u/E_a; \quad E_u = E_a \eta_r. \quad (2)$$

Thus, the E_u value represents the part of the energy which can be utilized for carrying out the chemical process. Therefore, in the present studies, the specific energy of the reagent (E_r) was defined as the ratio of the E_u value to the volume of the reagent introduced into the reactor (V_r):

$$E_r = E_u/V_r. \quad (3)$$

The specific energy of the plasma gas (E_g), e.g., was defined analogically:

$$E_g = E_u/V_g \quad (4)$$

where V_g is the volume of the plasma gas.

The present reasoning was supported by the results of experiments involving different efficiencies of the chemical plasma reactor [8]. For the same values of the initial temperature and molar ratio of the plasma gas to the reagent (k), due to an increase in the reactor efficiency degrees have been obtained; this was Therefore, in this case the specific energy of the reagent seems to be a dominant parameter in the process description.

Acetylene, formed in the reaction $2\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{H}_2$ is the main product of methane pyrolysis.

One should mention that a part of the reacting methane yielded, except C_2H_2 , other by-products as well (e.g. soot). Thus, in order to describe the process, the total methane conversion degree (u) and the methane-to-acetylene conversion degree (u_p) were introduced.

The total methane conversion degree is defined as the ratio of the methane amount, which undergoes pyrolysis, to that of the methane introduced into the reactor.

The methane-to-acetylene conversion degree is defined as the ratio of the methane amount, which is converted to C_2H_2 , to that of the methane introduced into the reactor.

The two conversion degrees are expressed in per cent.

The amount of acetylene formed in the process, taking into account these definitions, can be described by the formula:

$$n = 0.5 U_p V_r. \quad (5)$$

The utilization of E_u in a synthesis of C_2H_2 is characterized by the unit energy consumption (Z):

$$Z = E_u/n = 2 E_u/(U_p V_r) = 2 E_r/U_p. \quad (6)$$

On the basis of a general model of the process taking place in the reactor [9], three equations balancing E_u can be formulated.

The equation balancing the usable energy before the mixing of the plasma gas with the reagent is represented by:

$$E_u = V_g \int_{T_0}^T c_p^g dT \quad (7)$$

where c_p^g is the specific heat of the plasma gas,

T_0 , T is the standard temperature and the plasma gas temperature, respectively.

Because of the elimination of heat losses through the reaction chamber walls, it was assumed that in the initial phase of the process an immediate loss of heat takes place [10]. At the same time it was assumed that the mixing of the substrate and the plasma gas proceeds instantly. In this case, the total enthalpy of the gaseous mixture in the initial part of the reaction chamber, before the reaction runs, is equal to the usable energy:

$$E_u = V_r \int_{T_0}^{T_m} c_p dT + V_g \int_{T_0}^{T_m} c_p^g dT \quad (8)$$

where T_m is the mean reaction temperature (the mass-mean temperature of the gas mixture),

c_p is the specific heat of the reagent.

On the other hand, E_u can be balanced in the final part of the reaction chamber at the beginning of the quenching stage when the chemical reaction is interrupted. It was assumed that the acetylene synthesis is the only reaction taking place. It means that $u = u_p$. The volume of the products formed is expressed using the conversion degree and the volume of the substrate introduced. In this case

$$E_u = 0.5 u \Delta H^0 V_r + 0.5 u V_r \int_{T_0}^{T_f} c_p^g dT + \\ + (1-u) V_r \int_{T_0}^{T_f} c_p^r dT + (1.5u+k) V_r \int_{T_0}^{T_f} c_p^g dT \quad (9)$$

where ΔH_0 is the enthalpy of the reaction $2\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{H}_2$ at standard temperature.

c_p^a is the specific heat of acetylene,
 T_f is the quenching temperature.

Therefore, the unit plasma energy which can be utilized in the chemical process (according to equation (4)) is determined by the specific energy of the plasma gas, which is represented by

$$E_s = \int_{T_0}^T c_p^s dT. \quad (10)$$

The specific energy of methane, according to equations (5) and (6) can be expressed by

$$E_r = \int_{T_0}^{T_m} c_p^r dT + k \int_{T_0}^{T_m} c_p^s dT \quad (11)$$

$$E_r = 0.5 u \Delta H^0 + 0.5 u \int_{T_0}^{T_f} c_p^a dT + (1-u) \int_{T_0}^{T_f} c_p^r dT + (1.5+k) \int_{T_0}^{T_f} c_p^s dT. \quad (12)$$

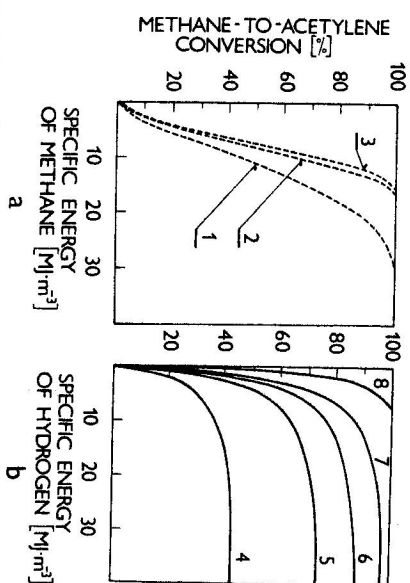
According to this approach the specific energy of methane determines the mean reaction temperature, the quenching temperature and the conversion degree for a given k value. It is independent of the energetic efficiency of the plasma torch and the chemical plasma reactor, as well as of the initial parameters of the process, e.g. the arc discharge energy and the reagent and the plasma gas volumes introduced into the reactor. Therefore, the specific energy in the reactor of various types as well as in their scaling-up.

Next, it was assumed that: 1) the process runs under isobaric conditions at 1 atm pressure; 2) all gases are considered to be ideal; 3) the quenching process begins after the thermodynamic equilibrium is achieved in the system; 4) no temperature corresponds to the quenching system. In this case the equilibrium corresponds to the methane-to-acetylene conversion degree (u) $u = u_p = u_r$.

The equilibrium conversion degree and the temperature related to it are, on the one hand, expressed by equation (9), and on the other hand, by the formula for the reaction equilibrium constant (K_p). The plasma is considered to be an inert diluting gas

$$K_p = 27 u^4 / (16 (1-u)^2 (1+u+k)^2). \quad (13)$$

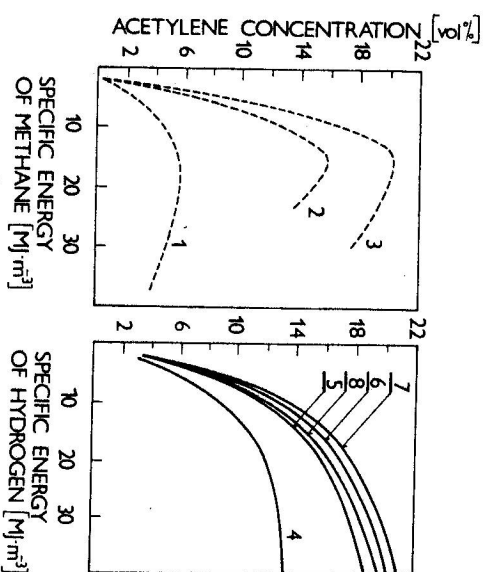
The values of u and T_f for a priori selected specific energies of methane and hydrogen are calculated on the basis of multinomials describing the value of the equilibrium constant as a function of temperature ($\Delta G/RT = \ln K_p$) and on the basis of equation (9). The unit energy consumption is calculated from



a

b

Fig. 1. Relationship between the methane-to-acetylene conversion degree and: a) the specific energy of methane for fixed values of the specific energy of plasma gas: 1 — 3.6; 2 — 14.4; 3 — 36.0 MJ/m³; b) the specific energy of plasma gas for fixed values of the specific energy of methane: 4 — 7.2; 5 — 10.8; 6 — 12.6; 7 — 14.4; 8 — 21.6 MJ/m³.



a

b

Fig. 2. Relationship between the concentration of acetylene and: a) the specific energy of methane for fixed values of the specific energy of plasma gas: 1 — 3.6; 2 — 14.4; 3 — 36.0 MJ/m³; b) the specific energy of plasma gas for fixed values of the specific energy of methane: 4 — 7.2; 5 — 10.8; 6 — 12.6; 7 — 14.4; 8 — 21.6 MJ/m³.

equation (6). The results of the calculation are presented in Figs. 1—3. The relationship between the process parameters and the specific energy of methane is illustrated in Figs. 1a, 2a, 3 for given values of the specific energy of hydrogen. Likewise, the relationship between the above parameters and the specific energy of hydrogen are given for different unchanging values of the specific energy of methane (see Figs. 1b, 2b, 3).

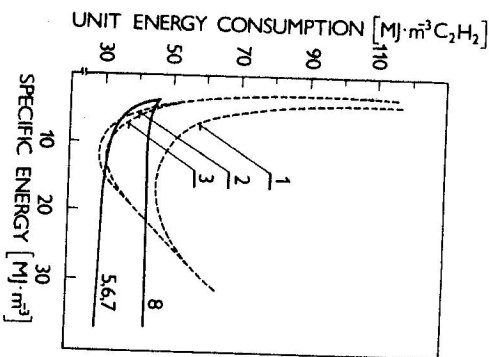


Fig. 3. Relationship between the unit energy consumption and: — the specific energy of methane for fixed values of the specific energy of plasma gas: 1 — 3.6; 2 — 14.4; 3 — 36.0 MJ/m³. — the specific energy of plasma gas for fixed values of the specific energy of methane: 5 — 10.8; 6 — 12.6; 7 — 14.4; 8 — 21.6 MJ/m³.

The methane-to-acetylene conversion is complete for the specific energy of methane exceeding 16.0 MJ m⁻³ and the specific energy of hydrogen exceeding 14.4 MJ m⁻³. The concentration of C₂H₂ in off-gases attains a maximum for $E_g = 14.4 \text{ MJ m}^{-3}$. A rise of the specific energy of hydrogen from 14.4 to 28.8 MJ m⁻³ results in the C₂H₂ concentration increase by nearly 4%. A further consumption is the lowest for $E_g = 10.8\text{--}14.4 \text{ MJ m}^{-3}$ (for the specific energy of hydrogen 14.4 MJ m⁻³). The reaction temperatures of 2800—3200 K and the quenching temperatures of 1600—1800 K correspond to these conditions. Calculations performed by other authors [4], including reaction kinetics, have shown that the results are best for $k = 0.5$; a decrease of this ratio results in a decomposition of C₂H₂. According to the present calculations, $k = 0.5$ corresponds to $E_g = 25.2 \text{ MJ m}^{-3}$. This value can be considered to be the upper limit of the specific energy of plasma gas.

III. EXPERIMENTAL

Experiments were performed in a chemical plasma reactor composed of a plasma torch with stabilization of the hydrogen plasma jet by the magnetic field,

a cylindrical copper reaction chamber with the ratio of length to diameter equal to 6.75, and a quenching chamber consisting of a system of diaphragm coolers. The reagent containing 95.5 vol. % of CH₄ was introduced into the hydrogen plasma jet at the beginning of the reaction chamber. The various parts of the reactor had their own cooling water circulation system in order to measure energy losses in each of them. The energy balance of the reactor was calculated from direct calorimetric measurements.

The contents of hydrogen, methane, acetylene and ethylene in off-gases were determined by gas chromatography (catharometric detector, external standards). These components constituted more than 99 vol. %.

The mass and the thermal balance of the reactor were calculated according to Szymanski [9].

A series of experiments was performed using constant arc discharge energy equal to $101.2 \pm 1.4 \text{ MJ}$. The ratio between the plasma gas and methane remained within the range of 0.93—5.24. Specific energy of hydrogen as high as $9.25 \pm 0.7 \text{ MJ/m}^3$ was attained.

The specific energy of the reagent varied between 9.72—39.6 MJ/m³. The mean-mass reaction temperature varied between 3050—3650 K, which corresponded to the quenching temperatures 1450—2500 K, depending upon the process conditions.

IV. COMPARISON BETWEEN THE EXPERIMENTAL AND THE CALCULATED RESULTS

The process parameters, obtained experimentally and calculated according to the above procedure (see part II), were compared. The experimental values of the arc discharge energy, the flows of gases introduced into the reactor, the energetic efficiency of the plasma torch and of the reactor were used as the starting parameters for the calculations. In these calculations it was subsequently assumed that C₂H₂, formed in the reactor chamber is decomposed only in the quenching system, due to the imperfection of the system. When this assumption is introduced, the experimental total conversion degree equals the equilibrium conversion degree ($u = u_0$). The degree of the methane-to-acetylene conversion can be calculated if u is computed and the amount of energy lost in the freezing system is measured experimentally.

The comparison of the calculated and the experimental results is presented in Table I. The values of the equilibrium and the total conversion degree are nearly equal. This confirms the assumption that acetylene is decomposed only at the quenching stage. On the other hand, considering the degree of conversion to acetylene the differences are larger, because of the relatively higher error of

Table 1

Comparison of the experimental and the calculated data of the final parameters of the methane-to-acetylene conversion process: ($E_g = 9.29 + 0.70 \text{ MJ/m}^3$)

Specific energy E_g , MJ/m ³	Total methane conversion*			Methane-to-acetylene conversion*			Quenching temperature*			Unit energy*			n
	u , %	u , %	u , %	u_g , %	u_g , %	u_g , %	T_f , K	T_f , K	T_f , K	Z , MJ/m ³	Z , MJ/m ³	Z , MJ/m ³	
10.0	61	61	1.02	55	48	1.14	1460	1456	1.00	36.4	33.1	1.09	4
12.0	73	74	0.99	65	60	1.09	1510	1510	1.00	37.1	32.4	1.14	4
16.7	91	96	0.94	84	69	1.22	1750	1754	1.00	39.2	34.2	1.14	4
22.5	97	99	0.98	91	78	1.17	1830	2014	0.91	49.3	45.0	1.10	1
27.9	99	100	0.99	93	65	1.55	2400	2309	1.05	62.6	55.8	1.12	3
38.9	99	100	0.99	89	—	—	2570	—	—	87.5	—	—	3

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

measurement of the energy lost in the quenching system and due to other reactions (the one stated above) proceeding at this stage.

The difference between the calculated and the experimental quenching temperatures do not exceed 50 K. This difference is smaller than the estimated accuracy of the T_f measurement.

The calculated and the experimental results obtained for the unit energy consumption are less consistent. This is mainly due to the not quite accurate calculation of u_g . The discrepancy between the calculated and the experimental results, found for higher specific energies, is due to the decomposition of acetylene to soot even in the reaction chamber. For the methane of the specific energies, the agreement between the calculated and the experimental values is satisfactory.

V. CONCLUSION

1. The specific energy of the reactant and the plasma gas are the main process parameters which characterize the chemical process in the reaction chamber. The specific energy of the plasma gas determines the unit plasma energy utilized in the chemical process. For a given reactant to plasma gas molar ratio, the specific energy of the reactant determines the mean reaction temperature, the quenching temperature and the conversion degree.

2. Regarding the process effectiveness, the lowest energy consumption can be expected for the specific energy of the plasma gas from 11.0 to 14.5 MJ/m³ and for the specific energy of methane from 14.5 to 25.0 MJ/m³.

3. The minimum value of the unit energy consumption is observed for the specific energy of the reactant lower than the maximum of the methane conversion and the maximum concentration of C₂H₂ (see Figs. 1—3).

4. For the most interesting values of the specific energy of methane and the specific energy of the plasma gas the model calculations are in agreement with the experimental values of the process parameters.

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ЭНЕРГЕТИЧЕСКИЕ ПАРАМЕТРЫ РЕАКЦИОННОЙ КАМЕРЫ В ПЛАЗМЕННОМ ПИРОЛИЗЕ МЕТАНА

Исследован процесс пиролиза метана до ацетилена в струе низкотемпературной водородной плазмы. Для энергетической характеристики химических процессов в реакционной камере выбраны два параметра — удельные энергии метана и водорода. Эти параметры были использованы при модельном описании исследуемого процесса. Были проведены эксперименты для проверки достоверности теоретических предположений. Эффективность процесса, предсказанная на основе используемой модели с 10-процентной точностью согласуется с экспериментальными данными.