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THERMODYNAMIC MODELS OF ACETYLENE SYNTHESIS IN AN ARGON PLASMA JET

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ABSTRACT

A quasi-equilibrium model of synthesis of acetylene from methane in an argon plasma jet was eleborated which made it possible to calculate simply the methane-to-acetylene conversion degree as well as the energy consumption. The agreement between experimental and calculated results is satisfactory.

1. INTRODUCTION

Pyrolysis of methane, a main component of natural gas, in a plasma jet is of a great importance becouse it is an effective source of acetylene, valuable chemical raw material /1,2/. Leutner and Stokes /3/ where the first publish results of investigations on the acetylene synthesis from methane in a plasma jet. Next, many papers were published /4-9/ which topics were considerations on the prediction of energy consumption and methane-to-acetylene conversion degree with formulation of the corresponding thermodynamic /4-9/ and kinetic/4,5/ models, parallely to experimental studies.
The aim of this papers is modelling of the process by using chemical thermodynamics principles. It is continuation of eariel works performed in the argon /10/ plasma concerning the effect of initial temperature of the reaction an the course of acetylene synthesis from methane.
In this paper a method the prediction of the synthesis yeld was tentatively elaborated in the from of simple algebraic relationships. Incomparison with the earlier work the polynomial of the 6th order, describing the relationship between argon and methane enthalpies and temperature, was reduced to the linear one. Also, the implicit equation, describing the equilibrium methane-to-acetylene conversion degree /11/ as a function of freezing temperature was replaced by a cubic equation in relation to freezing temperature.
The starting point of the considerations is the energy balance equation of the process at the reaction chamber input

$$E_{pj} = E\eta = V_a \Delta H_a/T_r/ + V_m \Delta H_m/T_r/ \qquad /1/$$

where: E_{pj} - energy of plasma jet [MJ]
E - energy of arc [MJ]

V_a, V_m - volume of argon and methane $[m^3/h]$,

$\Delta H_a/T_r/$, $\Delta H_m/T_r/$ - enthalpy of argon and methane at initial temperature of the reaction T_r/MJ/m^3/

The literature values /12/ of the enthalpy of argon and methane were approximated, respectively, by formulas: $a + bT_r$ and $c + dT_r$.

It results from this formula that the amount of methane which is to be introduced into reactor to obtain a required reaction temperature is:

$$V_m = \frac{E\eta - V_a \Delta H_a/T_r/}{\Delta H_m/T_r/} \qquad /2/$$

for give E, V_a and η values.

If the ratio of argon methane is denoted by X and the eq. /1/ divided by V_m a generalised energy balance equation results, which defines initial conditions of the process as a function of temperature T_r and of the initial composition of reactants expressed as X

$$V_m = \frac{E_{pj}}{V_m} = X \Delta H_a/T_r/ + \Delta H_m/T_r/ \qquad /3/$$

For given initial conditions of the process and for a calculated or assumed reaction chamber efficiency η_{rch} /13/ the generalized energy balance equation at the freezing chamber input acquires the form:

$$E_m = E_m/1 - \eta_{rch}/ + 0{,}5U_{ac}\,\Delta H^o/C_2H_2/ + X\,\Delta H_a/T_f/ + \Delta H_m/T_f/ \qquad /4/$$

where: U_{ac} - methane-to-acetylene conversion degree,

T_f - the freezing /quenching/ temperature [K]

$\Delta H^o/C_2H_2/$ - mean enthalpy value of the acetylene from methane [MJ/m^3] for T_f : 1-3 · 10^3K

$\Delta H_a/T_f/$, $\Delta H_m/T_f/$ - enthalpy of argon and methane at freezing temperature [MJ/m^3].

The literature values /12/ the enthalpy of argon and methane were approximated, respectively, by formulas: $a + fT_f$ and $g + hT_f$.

It has been assumed as in other papers /4,6,9,11,14/ that the only reaction occurring in the system is the desired one and that it attains equilibrium at freezing temperature.

It has been inferred from this assumption that U_{ac} calculated from the energy balance equation /4/ of the process

$$U_{ac} = \frac{E_m \cdot \eta_{rch} - X\,\Delta H_a/T_f/ - \Delta H_m/T_f/}{0{,}5\,\Delta H^o/C_2H_2/} \qquad /5/$$

should be equal to that resulting from the equilibrium constant K_p /expressed by pressure/:

$$U_{ac} = i + jT_f + kT_f^3 + 2X/l + mT_f + nT_f^2/ \qquad /6/$$

For temperatures above 1900 K U_{ac} was assumed to be equal to 0.999.

The final conditions of the process can be determined by solving the equation system /5/ and /6/ with respect to T_f and U_{ac}. Taking into account expression of E_m as a function of initial temperature /equation 1/ and after appropriate transformations, the following formula is obtained from right sides of equation /5/ and /6/

$$AT_f^3 + BT_f^2 + CT_f + D = 0 \qquad /7/$$

where:
$A = 0.5\,\Delta H^o/C_2H_2/$
$B = nX\,\Delta H^o/C_2H_2/$
$C = 0.5j\,\Delta H^o/C_2H_2/ + mX\,\Delta H^o/C_2H_2/ + Xf + h$
$D = \Delta H^o/C_2H_2//0.5i + Xl/ - \eta_{rch}/b + d/T_r + \eta_{rch}/aX + c/ + Xe + g$

The values of coefficient of equations /1-6/ are listed at the end of the paper.

As can be seen, equation /7/ determines the freezing temperature as a function of initial temperature reaction, reaction chamber efficiency, and reactants ratio X.

The freezing temperature of the process is calculated from equation /7/. Afterwards the equilibrium methan-to-acetylene conwersion degree U_{ac} is calculated from equation /5/ or /6/. The unit energy consumption Z defined as the ratio of arc energy to the amount of acetylene n is determined by formula.

$$Z = \frac{E}{n} = \frac{2E_m}{U_{ac}\cdot\eta} = \frac{2X/a + bT_r/ + 2X/c + dT_r/}{U_{ac}\cdot\eta} \qquad /8/$$

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

2. EXPERIMENTAL

The experimental investigation were performed using of chemical plasma reactor /7/. The reactor consisted of three principal parts:

1 - plasmatron PL-100 with swirling stabilisation of low-voltage d.c. arc of argon jet,
2 - water-cooled reaction chamber - 8 mm diameter, 54 mm long.
3 - freezing /quenching/ chamber, which incorporated a double-pipe heat exchanger.

The diameter nozzle-anode dependencing on the arc power was changed from 3.6 to 5 mm.

The effect of the initial temperature on the acetylene synthesis from methane in an argon plasma jet at constant ratio /equal to 2/ of argon to methane flows was investigate in the given apparatus system. The constant flows of argon -2 m^3/h and methane -1 m^3/h were maintained. A change in arc power from 4 to 16 kW caused an increacse of the initial reaction temperature from 1900 to 6000 K.

The initial and freezing temperature of the reaction were calculated from the material and energy balance. At start of freezing the sum of enthalpies of unchanged methane, reaction products, and argon is equal to the enthalpy received by cooling water of the freezing chamber. It was assumed that during freezing the composition of products does not change. The enthalpy received by cooling water of particular parts of the chemical reactor was determined calorimetrically.

3. RESULTS

The results of experiments and calculations are presented in Fig. 1. The experimental results are aproximated by the doted line. The full thickened line presents the results of calculations performed by earlier methodics /10/, i.e. withouth simplification in formulas describing the dependence of the enthaply of argon and methane on temperature as well of the methane conversion degree on the ratio argon/methane and the thermodynamic equilibrium constant.

It results from analysis of experimental data that:

1. the increase of temperature caused an exponential increase of methane-to-acetylene conversion degree U_{ac} from 0.2 to 0.36. Above 4000 K the conversion degree exceeded 0.8. The total methane conversion degree is higher than U_{ac}, it is similar to calculated values.
2. in the temperature range of 2600 - 4200 K a minimum energy consumption 93 - 101 MJ/m^3 C_2H_2 was observed.

It results from Fig. 1 that the model of calculations proposed render well the course of experimental relationships. It seems that in the case of homogeneous, quasi-equilibrium of decomposition of methane to acetylene the method proposed can be useful for fast and simple mathematically predicting of synthesis yield as well as experiment planning by using a chemical plasma reactor.

Our experimental values of the methane-to-acetylene conversion degree are lower and, as a consequence, of the energy consumption are higher then the calculated ones which is due to:

1. The assumption of model according to which the desired reaction is taking place only. Actually, C_2H_4 synthesis and acetylene polymerization proceed to some extend simultaneously.
2. The cooling rate of the ofter reaction mixture /5/ is too low which causes a decomposition of acetylene to the elements.

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NOMENCLATURE

The following numerical values of coefficients in equation /1-6/ were used:

$a = 4.345 \cdot 10^{-4}$

$b = 2.073 \cdot 10^{-5}$

$c = - 1.122 \cdot 10^{-1}$

$k = - 1.845$

$j = 5.544 \cdot 10^{-3}$

$k = - 2.418 \cdot 10^{-9}$

$d = 2.05 \cdot 10^{-5}$
$e = 8 \cdot 10^{-4}$
$f = 2.05 \cdot 10^{-5}$
$g = -5.78 \cdot 10^{-2}$
$h = 1.005 \cdot 10^{-4}$

$l = -0.311$
$m = 1.561 \cdot 10^{-3}$
$n = -1.708 \cdot 10^{-6}$
$\Delta H^{o}/C_2H_2/ = 18.33\,[MJ/m^3]$

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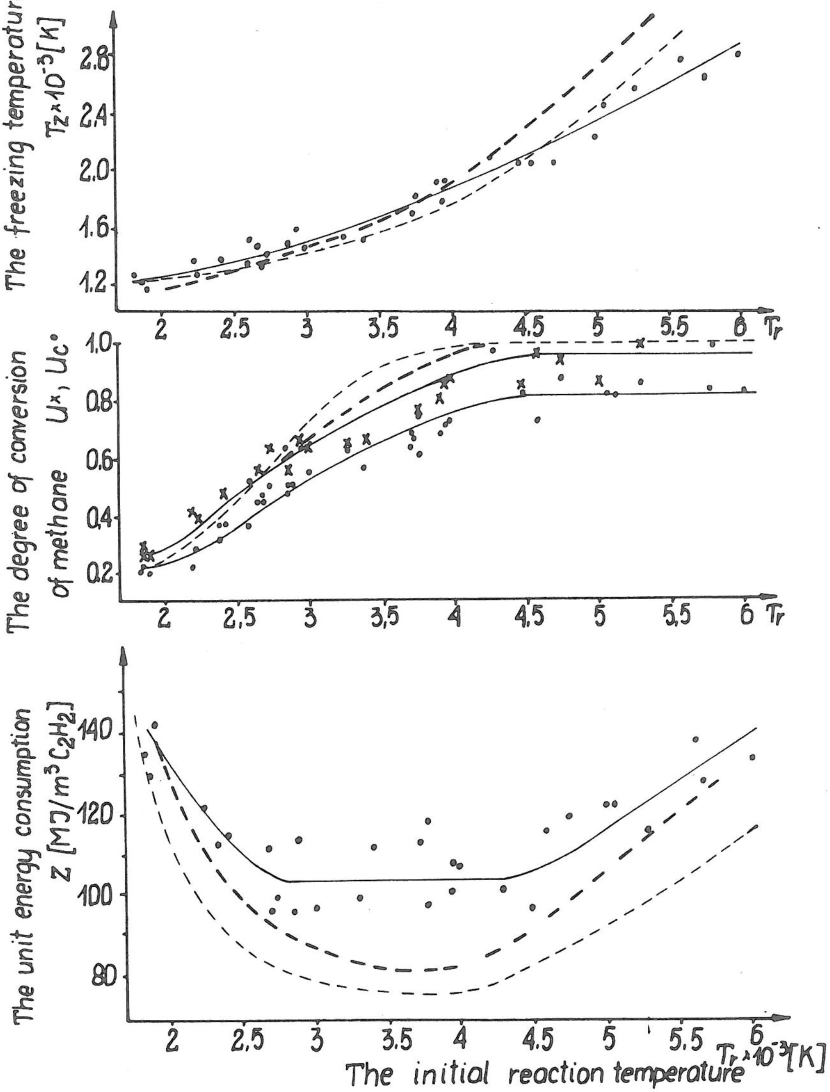

Fig.1. Effect of initial reaction temperature on the efficiences of process (explanation in the text)