# CALCULATING THE MAIN PARAMETERS OF A MEMBRANE REFORMER WITH A PRODUCTION RATE OF 40 m³/h DESIGNED FOR PRODUCING HIGHLY PURE HYDROGEN FROM NATURAL GAS

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The main design and technological parameters of a membrane reformer with a production rate of 40 $m^3H_2$/h, including its static flow rate characteristic, are quantitatively estimated on the basis of a mathematical model of membrane extraction of highly pure hydrogen from hydrocarbon steam conversion products. It is shown that the calculation results are in good agreement with the data found in the literature on testing a membrane reformer designed for producing highly pure hydrogen from natural gas.

*Keywords: mathematical modelling, technological and design parameters, membrane converter, highly pure hydrogen, natural gas.*

## 1. Introduction

The creation of efficient and economical systems for producing highly pure hydrogen (HPH) is an urgent line of research in modern hydrogen energetics and technology. Recently there has been an increasing interest in the creation of systems for producing highly pure gaseous hydrogen, which are based on the membrane extraction of hydrogen simultaneously with the catalytic conversion of methane [1–4]. This interest is mainly due to the fact that the high purity of hydrogen product is combined with high volumes of hydrogen output, smaller device dimensions and a decrease in operating temperatures from conventional 800–850 ºC for hydrocarbon steam conversion to 600–700 ºC [5–7] and even 550–500 ºC [3, 10].

A sufficiently large number of publications deal with the development of this promising technique of HPH production, some of them [1–10] being mentioned in the Reference. The results reported in [10] are of the greatest interest, namely, the results of testing (~ 3000 hours) of a steady-state experimental-industrial unit with a maximum production rate of 40 $m^3H_2$/h, based on a membrane reformer (MR), designed for producing highly pure (99.999 %) hydrogen from natural gas (NG).

On the one hand, by a large-scale experiment, this work validates the very principle of producing highly pure hydrogen from products of natural gas conversion with the use of a thin (~ 20 µm) membrane made of a palladium–rare-earth alloy with the presence of a methane conversion catalyst in the over-the-membrane space. On the other hand, the MR test results [10] can be useful for a quantitative verification of mathematical models.

In this work, the main design and technological MR parameters, including the MR static flow rate characteristic, are estimated on the basis of a mathematical model of HPH membrane extraction from hydrocarbon steam conversion products [11]. The results of quantitative evaluations are compared with the experimental data found in [10].

Vandyshev A. B. et al. / Calculating the main parameters of a membrane reformer with a production rate of 40 m³/h designed for producing highly pure hydrogen from natural gas.

http://dream-journal.org

page 109÷121

## 2. Basic principles of membrane-catalytic extraction of highly pure hydrogen from hydrocarbons

It is known that the fixed-bed membrane reformer described in [10] comprises 112 parallel operating membrane reactors with dimensions of 615×86×25 mm placed into a heating furnace. Inside a single membrane reactor there are two flat-type membrane elements with dimensions of 460×40×8 mm, a granular nickel catalyst for prior steam conversion of hydrocarbons and a monolithic fluted nickel catalyst acting as an additional reforming catalyst for methane conversion in combination with membrane extraction of hydrogen.

The structural scheme and the operation principle of each single membrane reactor reported in [10] practically does not differ from the *high-temperature converter – membrane equipment* (HTC–ME) system [5–7, 11] schematically shown in fig. 1.
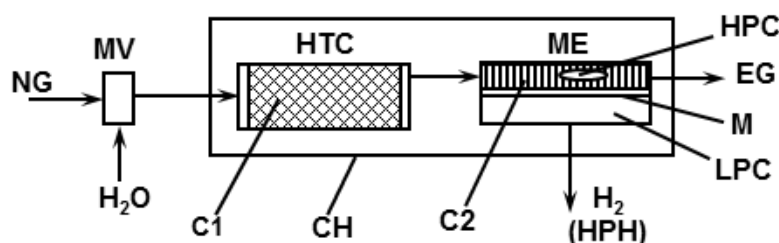


Fig. 1. A structural scheme of HTC–ME system:
NG – natural gas; MV – mixing vessel, HTC – high-temperature converter; ME – membrane equipment; HPC – high-pressure chamber of ME; LPC – low-pressure chamber of ME; EG – exhaust gas; C1 – standard hydrocarbon conversion catalyst; C2 – additional $CH_4$ conversion catalyst; M – Pd-alloy membrane; CH – common housing

The initial mixture of a hydrocarbon (methane in the simplest case) and water steam under excessive pressure is supplied into a mixing vessel MV (fig. 1) and then it proceeds sequentially into a high-temperature converter (HTC) and a high-pressure chamber (HPC) of membrane equipment (ME), both heated to the same temperature. In the HTC, the initial NG-steam mixture on a granular nickel catalyst is converted into a multicomponent gas mixture ($H_2$, $H_2O$, $CO_2$, $CO$, $CH_4$), which subsequently enters into the membrane equipment ME (fig. 1), with the addition of the $CH_4$ conversion catalyst C2 (fig. 1), where, under the effect of differential pressure, hydrogen is selectively extracted from the multicomponent gas mixture. Affected by pressure drop, hydrogen diffuses from the HPC through the membrane into the low-pressure chamber (LPC) of the membrane equipment and goes to the consumer in the form of highly pure hydrogen (99.999 %). The gas mixture depleted of hydrogen is removed from the HPC of the membrane equipment as exhaust gas (EG), fig. 1.

When molecular hydrogen is extracted from products of hydrocarbon steam conversion in the membrane equipment, the thermodynamic equilibrium in the gas phase is disturbed, and the total amount of extracted hydrogen increases due to the displacement of the chemical equilibriums

$$CH_4 + H_2O = 3H_2 + CO \qquad (1)$$

and

$$CO + H_2O = H_2 + CO_2 \qquad (2)$$

to the right.

### 3. A mathematical model of membrane extraction of highly pure hydrogen from hydrocarbon steam conversion products

The mathematical model [11] used in this study is intended for evaluating the effect of the main technological parameters (pressure in both chambers of the membrane equipment, operating temperature, the composition of the initial NG–steam mixture), and some membrane parameters (membrane area and thickness, hydrogen permeability) on the production rate of the MR and the completeness of hydrogen extraction from hydrocarbon steam conversion products.

An additional catalyst for the steam conversion of methane must be placed near the membrane surface to ensure a more rapid establishment of thermodynamic equilibrium in the gas phase in comparison with the speed of hydrogen diffusion through the membrane in the membrane equipment.

In the considered mathematical model of the HTC–ME system (fig. 1) the change in the pressures and temperatures in both chambers of the membrane equipment was not taken into account. It was supposed that the change in the conversion product concentrations along the membrane surface was caused not only by the hydrogen outflow through the membrane, but also by reversible chemical reactions (1), (2) and that the gas mixtures obey the ideal gas laws. It was also assumed that the composition of the initial gas mixture and the technological conditions of the HTC–ME system were selected so that the thermodynamic probability of carbon deposition in the gas phase can be excluded.

The calculated scheme of the HTC–ME system (fig. 1) is represented in the form of a series of cells, as shown in fig. 2.
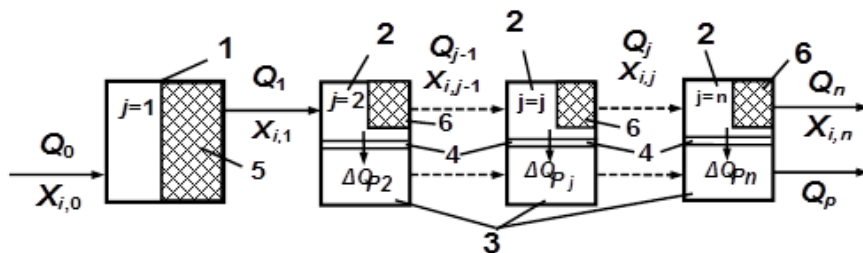


Fig. 2. A calculated scheme of the HTC–ME system
*1* – high-temperature converter; *2* – high-pressure chamber of membrane equipment;
*3* – low-pressure chamber of membrane equipment; *4* – Pd-alloy membrane;
*5* – hydrocarbon conversion catalyst; *6* – additional $CH_4$ conversion catalyst

On the calculated scheme (fig. 2) for the *j*-cell, the gas mixture, as a $Q_{j-1}$ flow with the concentrations of the components $X_{i,j-1}$, goes from the HPC of the previous *j*-1 cell to the entrance into the HPC of the *j*-cell of the membrane equipment, where the separated gas mixture goes along the membrane and becomes depleted of hydrogen. Then the separated gas mixture leaves the *j*-cell as a $Q_j$ flow with $X_{i,j}$ component concentrations. Highly pure hydrogen diffuses through the membrane in the LPC of the *j*-cell as a flow equal to $\Delta Q_{p,j} = Q_p/(n-1)$.

Some more designations are introduced: $\gamma$ – the coefficient of specific hydrogen permeability, $m^3 H_2 \cdot m \cdot h^{-1} \cdot m^{-2} \cdot MPa^{-0.5}$; $\delta$ – membrane thickness, m; $P_H$ – absolute pressure in the HPC of the ME, MPa; $P_L$ – absolute pressure in the LPC of the ME, MPa; $\Delta F_j$ – membrane area in the *j*-cell, $m^2$. The indices $i = 1, 2, 3, 4, 5$ respectively correspond to $H_2$, $H_2O$, $CO_2$, $CO$, $CH_4$.

The input and output parameters for the *j*-cell are related by the system of 7 equations which involves the material balance equations (3)–(5) for atoms of hydrogen, oxygen, and carbon respectively; Dalton's law equation (6); mass action law equations (7), (8) for reversible chemical reactions $H_2+CO_2 \leftrightarrows CO+H_2O$ and $4H_2+CO_2 \leftrightarrows CH_4+2H_2O$ respectively; Fick–Sieverts law equation (9) for the membrane area section $\Delta F$.

$$Q_j\left(X_{1,j} + X_{2,j} + 2X_{5,j}\right) = Q_{j-1}\left(X_{1,j-1} + X_{2,j-1} + 2X_{5,j-1}\right) - \Delta Q_{P,j}; \qquad (3)$$

$$Q_j\left(X_{2,j} + 2X_{3,j} + X_{4,j}\right) = Q_{j-1}\left(X_{2,j-1} + 2X_{3,j-1} + X_{4,j-1}\right); \qquad (4)$$

$$Q_j\left(X_{3,j} + X_{4,j} + X_{5,j}\right) = Q_{j-1}\left(X_{3,j-1} + X_{4,j-1} + X_{5,j-1}\right); \qquad (5)$$

$$X_{1,j} + X_{2,j} + X_{3,j} + X_{4,j} + X_{5,j} = 1; \qquad (6)$$

$$K_1 = \frac{X_{2,j}X_{4,j}}{X_{1,j}X_{3,j}}; \qquad (7)$$

$$K_2 = \frac{X_{2,j}^2 X_{5,j}}{X_{1,j}^4 X_{3,j}}; \qquad (8)$$

$$\Delta Q_{p,j} = \frac{\gamma}{\delta}\sqrt{P_H}\Delta F\left(\sqrt{\frac{X_{1,j}+X_{1,j-1}}{2}} - \sqrt{\frac{P_L}{P_H}}\right). \qquad (9)$$

In the system of equations (3)–(9) the given parameters are those indexed as *j*-1, and the unknown quantities are the parameters with the index *j*. The system of equations (3)–(9) is then reduced by transformations to a single equation (10), which is solved numerically.

$$\lambda(1 + \lambda)(a_1 + \lambda)^2 = a_1^2 a_2 a_3 a_4^2, \qquad (10)$$

where

$$a_1 = 1/K_1; \qquad (11)$$

$$a_2 = \frac{K_2}{K_1^2} \cdot \frac{2}{r_{1,j}+r_{2,j}-1}; \qquad (12)$$

$$a_3 = \frac{1-r_{1,j}+r_{2,j}}{2}; \qquad (13)$$

$$a_4 = 1 - r_{2,j}; \qquad (14)$$

$$r_{1,j} = \frac{Q_{j-1}}{Q_j}\left(X_{1,j-1} + X_{2,j-1} + 2X_{5,j-1}\right) - \frac{\Delta Q_{p,j}}{Q_j}; \qquad (15)$$

$$r_{2,j} = \frac{Q_{j-1}}{Q_j}\left(X_{3,j-1} + X_{4,j-1} + X_{5,j-1}\right); \qquad (16)$$

$$r_{3,j} = \frac{Q_{j-1}}{Q_j}\left(X_{2,j-1} + 2X_{3,j-1} + X_{4,j-1}\right); \qquad (17)$$

$$\lambda = -W_2 + \sqrt{W_2^2 + W_3}; \qquad (18)$$

$$W_1 = a_4 + 2a_3 - r_{3,j}; \qquad (19)$$

$$W_2 = [a_4 + 2a_1 a_3 + a_3 - r_{3,j}(1 + a_1)]/2W_1; \qquad (20)$$

$$W_3 = a_1(a_3 + r_{3,j})/W_1; \qquad (21)$$

$$X_{1,j} = \frac{a_1 a_4}{a_1 + \lambda}; \qquad (22)$$

$$X_{2,j} = a_4 \frac{\lambda}{a_1 + \lambda}; \qquad (23)$$

$$X_{3,j} = a_3 \frac{\lambda}{1 + \lambda}; \qquad (24)$$

$$X_{4,j} = \frac{a_3}{1 + \lambda}; \qquad (25)$$

$$X_{5,j} = \frac{r_{1,j} + r_{2,j} - 1}{2}. \qquad (26)$$

The unknown quantity $Q_j$ is on the interval $Q_{j,min} < Q_j < Q_{j,max}$, where

$$Q_{j,min} = \frac{Q_{j-1}(1 + X_{2,j-1} + X_{3,j-1} + X_{5,j-1}) - \Delta Q_{p,j-1}}{2}, \qquad (27)$$

$$Q_{j,max} = Q_{j-1}(1 + 2X_{5,j-1}) - \Delta Q_{p,j-1}. \qquad (28)$$

By specifying $\Delta Q_{p,j} = Q_p/(n-1)$, in view of the fact that, for $j=1$, $Q_{j-1}=Q_0$, $X_{i,j-1}=X_{i,0}$ sequentially for the cells from $j=1$ to $j=n$, equation (10) is solved numerically by the selection of the values of $Q_j$ in the range from $Q_{j,min}$ to $Q_{j,max}$, so that the discrepancy of equation (10) $\varepsilon = \lambda(1 + \lambda)(a_1 + \lambda)^2 - a_1^2 a_2 a_3 a_4^2$ does not exceed the required accuracy $\varepsilon_0$. After the unknown quantity $Q_j$ is determined, the mole fractions $X_{i,j}$ are calculated by equations (22)–(26).

Next, the membrane area $\Delta F_j$ in the $j$-cell is found by the formula

$$\Delta F_j = \frac{\Delta Q_{p,j}}{\frac{\gamma}{\delta}\sqrt{P_H}\left(\sqrt{\frac{X_{1,j} + X_{1,j-1}}{2}} - \sqrt{\frac{P_L}{P_H}}\right)}. \qquad (29)$$

Vandyshev A. B. et al. / Calculating the main parameters of a membrane reformer with a production rate of 40 m³/h designed for producing highly pure hydrogen from natural gas.

http://dream-journal.org

page 109÷121

The total membrane area F in the membrane equipment is found by the equation $F = \sum_{j=2}^{n} \Delta F_j$ (30). It should be noted that $\Delta Q_{p_j} = 0$ and $\Delta F_1 = 0$ for the first cell $j=1$ (HTC), where there is no membrane.

When the total number of selected cells is sufficiently large (e.g. n=100), the system of equations (3)–(9) in complex with the solution algorithm can be represented as a mathematical model of ideal displacement conditions for membrane extraction of hydrogen from hydrocarbon steam conversion products.

## 4. Numerical simulation results and discussion

The coordinates of the points of the experimental $Q_P - Q_{NG}$ dependence the membrane reformer were taken from the graphics found in [10] and put into table 1.

Table 1 – The coordinates of experimental points for the flow rate characteristic of the membrane reformer [10]

| Designation, dimension | Flow rate values, m³/h | | | | | |
|---|---|---|---|---|---|---|
| $Q_{NG}$ | 3.14 | 5.1 | 8.12 | 10.61 | 10.98 | 11.6 |
| $Q_P$ | 6.2 | 18.2 | 26.5 | 35.3 | 37.4 | 40.5 |
| Note: the flow rates QNG and QP are given for normal conditions. | | | | | | |

Almost all the necessary input data for the simulation (except for the missing coefficient of hydrogen permeability γ) and for the quantitative evaluation of the flow-rate characteristic and other parameters of the membrane reformer were taken from [10]. The operating temperature of the membrane reformer was specified as 495 °C, which is equal to the lower limit from the temperature range 540–495 °C [10]. The absolute gas pressure ($P_H$) in the HTC and the HPC of the membrane equipment was taken equal to 0.9 MPa, and the absolute pressure of hydrogen ($P_L$) in the LPC of the membrane equipment was taken equal to 0.048 MPa, which is close enough to the upper limit in the range of the input pressures of the metal hydride hydrogen booster system (0.02 to 0.04 MPa) [10].

The $H_2O$–NG mixture with the $H_2O$/C ratio equal to 3.2, which corresponds to the upper limit in the range 3.0 – 3.2 [10], was used as a feedstock to produce HPH in the membrane reformer. According to [10], natural gas from a city gas network was a hydrocarbon mixture containing 88.5 % $CH_4$, 4.6 % $C_2H_6$, 5.4 % $C_3H_8$, and 1.5 % $C_4H_{10}$. In this case, the natural gas can be considered as a mixture of hydrocarbons, its mole fraction being representable as a sum of the mole fractions of the components $X_{NG} = X_{CH_4} + X_{C_2H_6} + X_{C_3H_8} + X_{C_4H_{10}}$.

Since there were no details about the properties of the membrane material including the value of the hydrogen permeability coefficient γ [10], we specify the value of this coefficient γ=0.0041m³$H_2$·m/(m²·h·MPa$^{0.5}$) for the Pd-8Y alloy taken from [12] at 495 ºC. The membrane thickness was taken equal to 0.02 mm [10].

In view of the fact that the maximal flow rate of the initial *natural gas – water steam* mixture was equal to 11.6 m³/h [10], in order to calculate the flow rate characteristic of the membrane reformer, five fixed values of $Q_{NG}$ equal to 4, 6, 8, 10 and 11.6 m³/h corresponding to points 1–5 in table 2 were chosen from the natural gas flow rates ranging between 0 and 11.6 m³/h.

In consideration that the mole fractions of NG and $H_2O$ in the initial mixture of natural gas and water steam are respectively $X_{NG}$=0.238 and $X_{H_2O}$=0.762 for points 1–5 in table 2, the flow rates $Q_0$ of the initial gas mixture were calculated (table 2).

Vandyshev A. B. et al. / Calculating the main parameters of a membrane reformer with a production rate of 40 m³/h designed for producing highly pure hydrogen from natural gas.

http://dream-journal.org                                        page 109÷121

Table 2 – Calculated membrane reformer parameters at 495ºC

| Point number | Parameters, dimension | | | | |
|---|---|---|---|---|---|
| | $Q_{NG}$, m³/h | $Q_0$, m³/h | $Q_1$, m³/h | $F_{cal}$, m² | $Q_P$, m³/h |
| 1 | 4 | 16.8 | 17.9 | 1.6 | 13.6 |
| 2 | 6 | 25.2 | 26.85 | 2.1 | 20.4 |
| 3 | 8 | 33.6 | 35.8 | 3.4 | 27.4 |
| 4 | 10 | 42 | 44.7 | 3.7 | 34.2 |
| 5 | 11.6 | 48.7 | 51.9 | 4.0 | 39.6 |
| Note: the flow rates $Q_{NG}$, $Q_0$, $Q_1$ and $Q_P$ are given for normal conditions. | | | | | |

Then, in view of the constancy of the atomic composition (C, H, O) as in the initial NG – $3.2H_2O$ gas mixture and in the steam conversion products ($H_2$, $H_2O$, $CO_2$, CO, $CH_4$), the equilibrium compositions of the gas phase (table 3) at the HTC outlet were calculated for the temperature of 495 °C and absolute pressure $P_H$=0.9 MPa. The volumetric flow $Q_1$ of steam conversion products at the entrance into the membrane equipment for all the five points was also estimated and represented in table 2. For comparison, the equilibrium and atomic (C, H, O) compositions were calculated for the initial mixture $CH_4$ – $3.2H_2O$ at the same conditions and also represented in table 3. By using the above-described mathematical model of the membrane extraction of hydrogen from hydrocarbon steam conversion products [11], relationships have been calculated between the production rate of the membrane reformer $Q_P$ and the membrane area $F$ for each flow rate of natural gas steam conversion products: $Q_1$=17.9; $Q_1$=26.85; $Q_1$=35.8; $Q_1$=44.7 and $Q_1$=51.9 m³/h (table 2).

Table 3 – The equilibrium and atomic compositions of the synthesis gas at an operating temperature of 495 °C

| Mole fractions of the hydrocarbon steam conversion products in the synthesis gas at the HTC outlet | | | | | Atomic fractions of the chemical elements at the HTC inlet and outlet | | |
|---|---|---|---|---|---|---|---|
| $X_{H_2}$ | $X_{H_2O}$ | $X_{CO_2}$ | $X_{CO}$ | $X_{CH_4}$ | H | O | C |
| Initial feedstock: NG – $3.2H_2O$ | | | | | | | |
| 0.1575 | 0.6189 | 0.047 | 0.0023 | 0.1743 | 0.7056 | 0.2243 | 0.0701 |
| Initial feedstock: $CH_4$ – $3.2H_2O$ | | | | | | | |
| 0.1647 | 0.6171 | 0.0397 | 0.0019 | 0.1766 | 0.7123 | 0.2192 | 0.0685 |

The results of quantitative estimations were presented graphically by curves *1–5* in fig. 3 and as the calculated values of $Q_P$ and $F_{cal.}$ in table 2. The vertical dotted line *6* in fig. 3 indicates the level of the membrane area $F_1$=0.5×$F_{tot.}$. The value of the total membrane area $F_{tot.}$ has been estimated on the basis of the general number of single membrane reactors, geometric dimensions and the number of membrane elements in each membrane reactor [10] $F_{tot.}$=0.46×0.04×2×112=8.24 m².
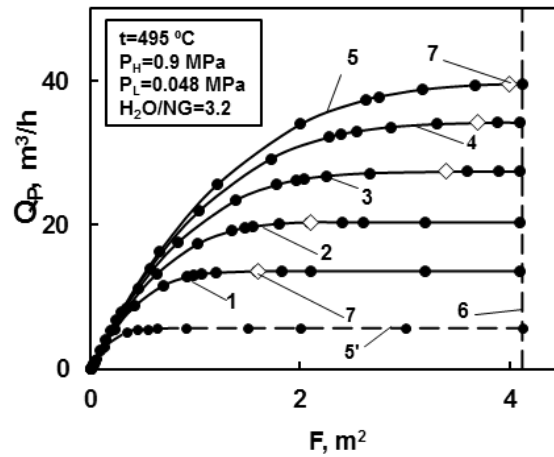
Fig. 3. $Q_P - F$ dependencies for the membrane reformer [10]:
$1 - Q_{NG}$=4 m³/h; $2 - Q_{NG}$=6 m³/h; $3 - Q_{NG}$=8 m³/h; $4 - Q_{NG}$ =10 m³/h; $5 - Q_{NG}$=11.6 m³/h, $5'$ – without the additional $CH_4$ conversion catalyst in the HPC of the membrane equipment at $Q_{NG}$=11.6 m³/h; $6$ – the level of the membrane area $F_1$=0.5×$F_{tot.}$=4.12 m², $7$ – points corresponding to complete hydrogen membrane extraction

For each of the chosen natural gas flows $Q_{NG}$ (points 1–5 in table 2), the hydrogen production rate $Q_P$ of the membrane reformer [10] has been calculated. The values of $Q_P$ increase with the increasing membrane area $F$ (curves $1$–$5$ in fig. 3) and $Q_P$ reaches the maximum values, respectively, $Q_P$=13.6 m³/h for $Q_{NG}$=4 m³/h; $Q_P$=20.4 m³/h for $Q_{NG}$=6 m³/h; $Q_P$=27.4 m³/h for $Q_{NG}$=8 m³/h; $Q_P$=34.2 m³/h for $Q_{NG}$=10 m³/h and $Q_P$=39.6 m³/h for $Q_{NG}$=11.6 m³/h. By comparing the calculated membrane area $F_{cal.} \approx 4$ m² for $Q_{NG}$=11.6 m³/h (table 2) with the total membrane area $F_{tot.}$=8.24 m², it can be concluded that the latter is more than sufficient to ensure the experimentally achieved maximum HPH flow $Q_P$=40.1 m³/h [10] under the indicated conditions. The difference between the calculated maximum HPH flow rate $Q_P$=39.6 m³/h for $Q_{NG}$=11.6 m³/h and the experimentally measured $Q_P$=40.1 m³/h [10] is negligible (1.2 %).

When the feedstock flow $Q_0$ discretely decreases from 48.7 to 16.8 m³/h (table 2) at fixed ratio $H_2O/C$=3.2, the hydrogen production rate $Q_P$ of the membrane reformer decreases due to a lower content of the total amount of free (molecular $H_2$) and chemically connected hydrogen ($CH_4$) in the separated multicomponent gas mixture flow, and this is represented by $Q_P - F$ dependencies (curves $1$–$5$, fig. 3). The calculated values $Q_P$ of $Q_P - F$ dependencies (curves $1$–$4$, fig. 3) reach saturation when the values of the estimated membrane area $F_{cal.}$ (table 2) is smaller than the membrane area $F_1$=4.12 m² (dotted line $6$ in fig. 3). Curve $5'$ (fig. 3) is calculated with the application of the model [13] of membrane hydrogen extraction from multicomponent chemically non-interacting hydrogen-containing gaseous mixtures (e.g., $H_2$-$N_2$, $H_2$-$H_2O$) under the same conditions as curve $5$ (fig. 3), but only in the assumption that there is no additional catalyst of methane conversion in the  membrane reformer [10].

The HPH production rate of the MR in this case does not exceed $Q_P$=5.71 m³/h because only molecular hydrogen with small initial concentration equal to 15.75 % (table 3) participates in the membrane extraction process. When the additional $CH_4$ conversion catalyst is present in the over-the-membrane space, not only molecular hydrogen with initial concentration equal to 15.75 %, but also methane with initial concentration 17.43 % (table 3) takes part in the membrane extraction of hydrogen mainly through the shift of the chemical equilibrium (1), and this leads to a significantly increasing value of HPH flow, up to $Q_P$=39.6 m³/h, at the membrane area $F_{cal.}$=4 m² (table 2 and curve $5$ in fig. 3).
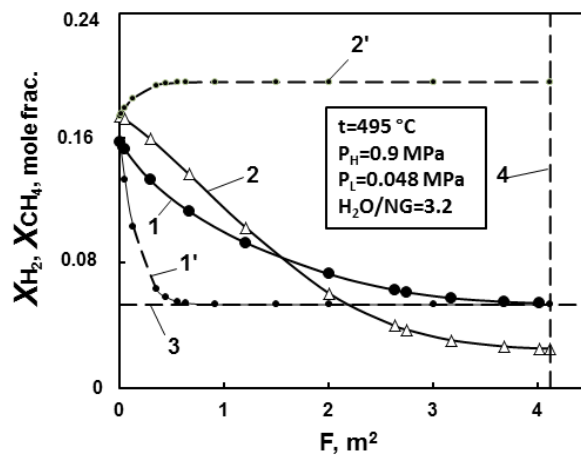
Fig. 4. Hydrogen (*1, 1′*) and methane (*2, 2′*) concentrations as dependent on membrane area (*F*) for MR [10] for $Q_{NG}$ =11.6 m³/h:
*3* – the level of the concentration limit $X_{lim}$= $P_H/P_L$=0.0533 (mole fractions) for MR;
*4* – the level of the membrane area $F_1$=*0.5×$F_{tot.}$*=4.12 m²; *1′, 2′* – without CH₄ conversion catalyst in HPC of membrane equipment

Then, by using the above-discussed mathematical model of membrane extraction of hydrogen from the products of hydrocarbon steam conversion [11], relationships between the gaseous phase compositions and the membrane area *F* for the membrane reformer [10] have been calculated. As an example, the membrane area dependences of the hydrogen $X_{H_2}$ and methane $X_{CH_4}$ concentrations for the maximum flow of natural gas $Q_{NG}$=11.6 m³/h (table 2) are presented in fig. 4. Figure 4 shows that, with the increase in the membrane area *F*, as hydrogen is extracted, hydrogen $X_{H_2}$ concentration (curve *1*) decreases and approaches the concentration limit $X_{lim} = \frac{P_L}{P_H} = 0.053$ mole fractions.

When $X_{H_2} \approx X_{lim}$, the driving force of hydrogen diffusion through the membrane becomes close to zero, and a further increase in the membrane area does not result in the further growth of the hydrogen production rate ($Q_P$). It is the approach of the $X_{H_2}- F$ curves (fig. 4) to the concentration limits $X_{lim}$ that explains the saturation achieved by curves *1–5* in fig. 3. The methane located above the membrane surface in the presence of the additional catalyst of CH₄ conversion is in the chemical equilibrium with the other components of the gas phase, therefore, with decreasing hydrogen concentration $X_{H_2}$, when the membrane area F increases, the methane concentration $X_{CH_4}$ also decreases, and this is represented by curve *2* in fig. 4. In other words, methane is involved in the process of hydrogen membrane extraction not only as molecular hydrogen, but also indirectly through the shift of the chemical equilibrium (1) when the hydrogen is removed through the membrane.

Curves *1′* and *2′* (fig. 4) have been calculated on the basis of the model of membrane extraction of hydrogen from chemically non-interacting hydrogen-containing gaseous mixtures [13] in the absence of an additional CH₄ conversion catalyst in the HPC of the membrane equipment, and this illustrates the behavior of curve *5′* (fig. 3). In this case the HPH flow value is only $Q_P$=5.71 m³/h (fig. 3), which is achieved when the membrane area *F* is equal to 0.65 m².
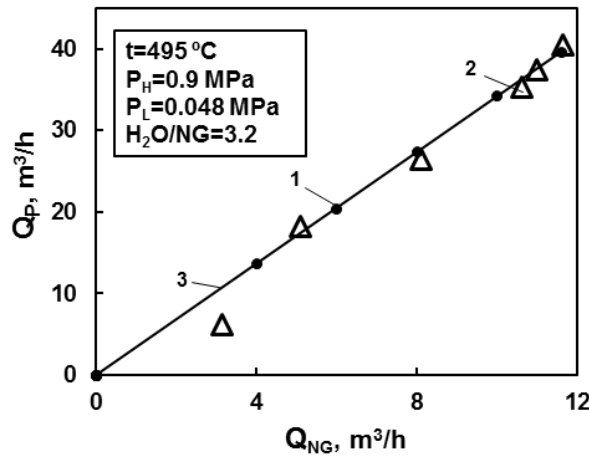
Fig. 5. Steady-state flow rate characteristic of the membrane reformer [10]:
*1* – calculated points (table 2); *2* – experimental data (table 1); *3* – steady-state flow rate charac-
teristic of the membrane reformer [10]

The maximum values of $Q_P$ calculated for each of five different $Q_{NG}$ (table 2) are entered in fig. 5 as points *1* in the coordinates $Q_P - Q_{NG}$. The calculated points *1* fall well on the straight line *3* passing through the origin. It is this straight line *3*, passing through points *1*, that represents the flow characteristic of the discussed membrane reformer [10]. Next, in fig. 5, points *2* in the form of triangles represent experimental data [10] from table 1. These points *2* fall well on the calculated flow characteristic *3*.

For the specially selected composition of the initial chemically non-interacting gaseous mixture $0.785H_2 - 0.215N_2$, it has been found by mathematical modelling [13] that one and the same initial mixture flow $Q_1$=51.9 m$^3$/h (table 2) can yield HPH production rate $Q_P$=40 m$^3$/h under the same conditions as in the membrane reformer [10]. The results of comparative calculations are presented in figs 6 and 7.
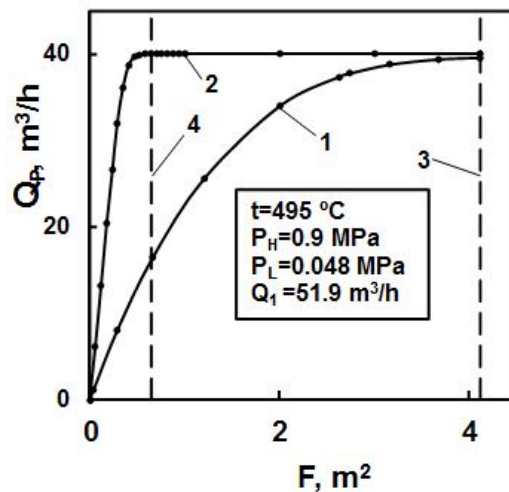


Fig. 6. Hydrogen production rate ($Q_P$) as dependent on the membrane area ($F$):
*1* – feedstock: NG – 3.2H$_2$O for $Q_1$ = 51.9 m$^3$/h; *2* – feedstock: 0.785 H$_2$ – 0.215 N$_2$ for $Q_1$ = 51.9 m$^3$/h; *3* – the level of the membrane area $F_1$=0.5×$F_{tot.}$=4.12 m$^2$; *4* – the level of the membrane area $F_2$=0.65 m$^2$

In this case, due to a higher initial concentration of hydrogen in the gas mixture $0.785H_2 - 0.215N_2$ and a more intensive hydrogen outflow through the membrane, the hydrogen extraction process ends with the membrane area $F$=0.65 m$^2$.

For the gas mixture $0.785H_2 - 0.215N_2$ the average density of hydrogen diffusion flow through the membrane is $j_{av.}$=40/0.65=61.5 $m^3H_2/(m^2 \cdot h)$. On the contrary, for the natural gas steam conversion products ($X_{H_2}$ = 0.1575, $X_{H_2O}$= 0.6189, $X_{CO_2}$= 0.047, $X_{CO}$= 0.0022, $X_{CH_4}$= 0.1743 mole fractions table 3), the average hydrogen diffusion flow density is $j_{av.}$=40.1/4.12=9.7 $m^3H_2/(m^2 \cdot h)$ (table 4), which is much lower and the hydrogen extraction process ends in this case with the membrane area $F$=4 $m^2$.

The quantitative estimate of the degree of $CH_4$ conversion in the preliminary converter of the MR at 495 °C has shown that its value is 22 %, and it is consistent with the interval of the conversion degree (21–29 %), presented in [10]. The calculated degree of $CH_4$ conversion in the membrane equipment at the same temperature of 495 °C constitutes 92 %, and it is also consistent with the data (80–95 %) reported in [10].



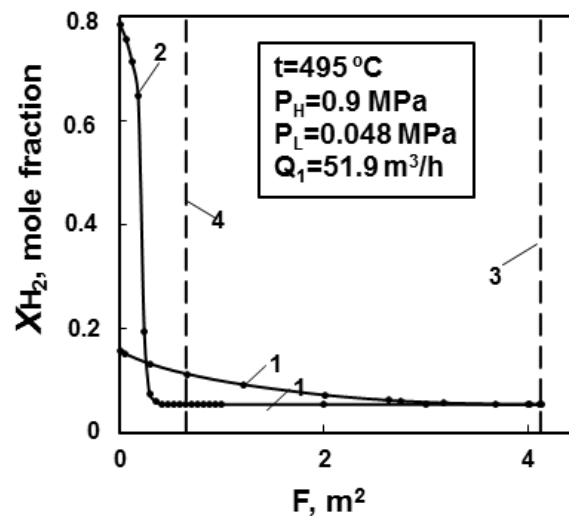Fig. 7. Hydrogen concentration ($X_{H_2}$) as dependent on the membrane area ($F$):
*1* – feedstock: NG – $3.2H_2O$ for $Q_1$ = 51.9 $m^3$/h; *2* – feedstock: $0.785H_2$ - $0.215N_2$ for $Q_1$ = 51.9 $m^3$/h; *3* – the level of the membrane area $F_1=0.5 \times F_{tot.}$=4.12 $m^2$; *4* – the level of the membrane area $F_2$=0.65 $m^2$

As already noted above, the results of the quantitative estimation of the membrane area $F_{cal.}$=4 $m^2$ (table 2) for the maximum volumetric flow of natural gas $Q_{NG}$=11.6 $m^3$/h has practically the same value as the membrane area $F_1=0.5 \times F_{tot.}$=4.12 $m^2$ in the membrane reformer [10].

These circumstances indicate that the mathematical model of hydrogen membrane extraction from hydrocarbon steam conversion products [11] not only adequately, but also fairly accurately describes the experimental data for the membrane reformer [10], intended for HPH production from natural gas.

In selecting technological conditions for a membrane reformer with an additional $CH_4$ catalyst in the over-the-membrane space, it is important to prevent carbon deposition in the gas phase.

The probability of carbon deposition has been estimated with the use of the criterion $\omega=P_C/P_H$ proposed in [11], where $P_C$ is carbon deposition pressure, $P_H$ is absolute pressure in the over-the-membrane space. The value of the carbon deposition pressure $P_C$ has been calculated by the formula $P_C = X_{CO_2} \cdot K_3 \cdot P_0^0/X_{CO}^2$, where $X_{CO_2}$ and $X_{CO}$ are the equilibrium molar fraction of carbon monoxide and dioxide in the gas phase above the part of the membrane area $\Delta F_j$, $P_0^0$ is absolute standard pressure ($P_0^0$=0.1 MPa in our case), $K_3$ is the constant of the chemical equilibrium $C + CO_2 \leftrightarrows 2CO$, calculated on the basis of thermodynamic data. When $\omega$ >1, there is no carbon deposition in the gas phase; on the contrary, when $\omega \leq 1$, carbon deposition is possible. The results of the quantitative estimation of carbon deposition probability are graphically represented in fig. 8

Vandyshev A. B. et al. / Calculating the main parameters of a membrane reformer with a production rate of 40 $m^3$/h designed for producing highly pure hydrogen from natural gas.

http://dream-journal.org

page 109÷121

as a membrane-area dependence of the criterion $\omega$ for the membrane reformer [10] at 495 °C (curve *1*). It is obvious that $\omega > 1$ in the whole range of membrane areas from 0 up to $F_1 = 4.12$ m$^2$ and that there is no carbon deposition in the membrane reformer (fig. 8).



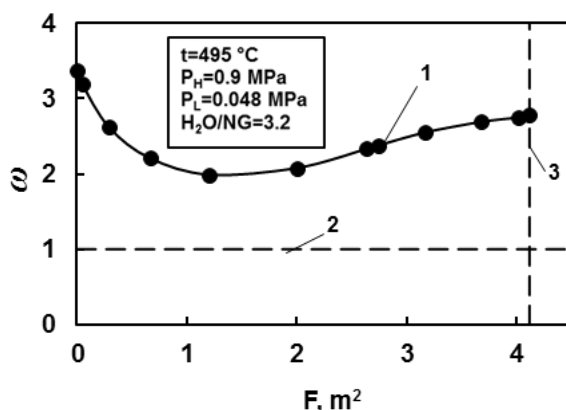Fig. 8. The thermodynamic carbon-deposition probability criterion $\omega$ as dependent on the membrane area $F$ for MR [10]:
*1* – the calculated membrane-area dependence of the criterion $\omega$;
*2* – the carbon-deposition boundary ($\omega = 1$);
*3* – the level of the membrane area $F_1 = 0.5 \times F_{tot.} = 4.12$ m$^2$ for MR

Note that this method for estimating the probability of carbon deposition from the gas phase offers the same results as the method of C-H-O ternary diagrams [6–8].

**5. Conclusion**

The mathematical model simultaneously taking into account the hydrogen outflow through the membrane and the chemical interaction in gaseous phase [11] for the *high-temperature converter – membrane equipment* system practically accurately describes the experimental data of the membrane reformer [10]. This model can be useful for developing, analyzing and optimizing the effective and efficient membrane equipment (membrane reformers) designed for producing highly pure hydrogen from natural gas and other hydrocarbons.

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Vandyshev A. B. et al. / Calculating the main parameters of a membrane reformer with a production rate of 40 m$^3$/h designed for producing highly pure hydrogen from natural gas.

http://dream-journal.org                                                    page 109÷121