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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Leninetz Holding Company, NIPGS as follows: The process of decomposition of liquid hydrocarbons (kerosene) is complicated by coke formation reactions. To reduce the mentioned phenomenon to a minimum, the contractor offers to use the two-stage scheme of steam reforming of liquid hydrocarbons. The proposed work is a logical follow-on of research of the reactor of coaxial type done previously on an EOARD grant. The new reactor is planned to be of the rectangular form for the purpose of understanding the influence of geometry on parameters of hydrodynamics and heat-mass-exchange. Also, the length of the reactor will be increased, quantity and arrangement of thermoelectric couples and samplers will be changed for determination of structure of the convertible mixture. An improvement to the technology of deposition of planar catalysts with the purpose to achieve thermal stability and thermal-cyclical strength of coatings. The tests of the new reactor with the improved catalyst will be carried out at the flow parameters, corrected by results of the previous experiments. It concerns initial temperature of the mixture entered the reactor, its speed and ratio

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Introduction

Now in many industrially developed countries the intensive work is conducted in the field of hypersonic technologies development to create aerospace transport systems and hypersonic airplanes of different purposes. The hypersonic technologies by virtue of novelty, science capacity and multifunctionality fulfill a role of motive power of technological progress in a broad spectrum of areas bound not only by aviation. Their assimilation will allow countries to remain among the advanced states of a world that are capable to create a technique of XXI century.

In Russia the research and experimental work "Oryol" is devoted to the problem of development and creation of reusable space transport systems and hypersonic airplanes [1]. Among the foreign programs it is necessary to mark the program of US Air force on hypersonic technologies (HyTech), supposed to be realized in 1995-2003. The purpose of this program is development of demonstration sample of a hypersonic air-breathing engine (HABE) on hydrocarbon fuels for Mach numbers of flight $M=4 - 8$ [2]. The nearest object of application is winged rocket of long range (> 1500 km) of the "air - ground" class. Though this program is focussed on making of one-use systems with flight time no more than 12 min, it is called to make a scientific, technical and technological basis for development of hypersonic vehicles on endothermic hydrocarbon fuels of a broad spectrum of application: reusable rockets, airplanes, trans-atmospheric means. The HyTech program for Mach numbers $M \leq 12$ is intimately coordinated with activity of NASA in the field of hypersonic technologies of liquid hydrogen air-breathing engine for high Mach numbers of flight.

The problems of application of hydrocarbon fuels for hypersonic flight vehicles (HFV) are periodically considered in literature. The first works in this direction are referred to 60-s years [3-4]. Then the attention of the aviation specialists was for a long time switched to the designs connected with use of liquid hydrogen as a fuel. Liquid hydrogen has a number of unique properties such as large heat capacity, high mass-heat value and kinetic characteristics of processes of ignition and combustion etc. At the same time, liquid hydrogen, as an aviation fuel, has also a number of essential flaws. Small density and low boiling point (cryogenic features) are main ones. It results in necessity to place large fuel tanks with shield-vacuum isolation aboard an airplane that increases weight, sizes, drag, and worse lift-to-drag ratio. Besides, the changeover to liquid hydrogenous fuel will increase time of flight preparation of airplane and change completely the aerodrome infrastructure. Reasons of operational air safety and the economic indexes also speak for the benefit of hydrocarbons. Therefore, in parallel with the development of hydrogen-fuel projects of hypersonic flight vehicles, the ways for "life prolongation" of hydrocarbon fuels for hypersonic aircraft are under investigation. Then the attention of the aviation specialists was for a long time switched to the designs connected with use of liquid hydrogen as a fuel. However now interest to hydrocarbon endothermic fuels again has increased. Today many experts are convinced, that for HFV of restricted size or small mass of hydrocarbonaceous fuels are, apparently, unique possibility for providing of high speeds of flight [5].

The designs of hypersonic airplanes with use of heat-absorbing reactions for cooling of separate parts of vehicles were surveyed in [6,7]. However the most energetically integral the concept "Ajax" is seemed [8,9], developed by the “Leninets” Holding Company.

1. Thermochemical principle of cooling

The thermochemical method of cooling of heat-stressed surfaces is a means of intensification of heat exchange, accumulation and heat regeneration. Chemical heat regeneration and deriving of new modified fuel are one of corner stones of the “Ajax” concept.

This concept is based on active energy interaction between a vehicle and air flowing around it. One of channels of energy interchange is the system of active thermal protection. It represents a combination of recuperative heat exchangers, which are placed in the most heat-stressed parts of airframe and engine. Various physical and chemical processes, from elementary heating of coolant to endothermic catalytic reactions, proceed there. The hydrocarbon fuel (aviation kerosene) is coolant and reactant, and utilized heat from aerodynamic heating and power plant is energy source for realization of physicochemical transformations. Thus, from the point of view of energetics, Ajax flight vehicles utilize the primary energy, which is reserved aboard as chemical energy of fuel, fuller than other designs. It helps to increase the efficiency of a thermodynamic cycle of engine.

The considered heat-shield system executes not only usual function, providing temperature conditions of the airframe, but also serves simultaneously as the system of preparation of new modified fuel containing molecular hydrogen. It is a prominent aviation example of using the thermochemical conversion of hydrocarbon fuel on basis of the method of chemical heat regeneration.

Unfortunately, the process of decomposition of liquid hydrocarbons (kerosene) is complicated by coke formation reactions. To reduce the mentioned phenomenon to a minimum, we offer to use the two-stage scheme of steam reforming of liquid hydrocarbons. At the first step, the low-temperature (300-400 °C) conversion of liquid hydrocarbon runs:

$$aC_nH_m + bH_2O \rightarrow dCH_4 + eCO_2 \ (1)$$

This reaction goes in the auxiliary block of gasification and has insignificant thermal effect.

The main process of heat absorption and generation of molecular hydrogen occurs further in accordance with high-temperature (700-900 °C) reaction:

$$CH_4 + H_2O \rightarrow 3H_2O + CO \ (2)$$

This reaction proceeds in heat protection reactors of airframe and engine. That is why main attention in our researches is paid to the reaction of steam reforming of methane (2) as essentially important one.

It is necessary to note that the catalytic steam reforming of hydrocarbons exceeds by thermal effect and amount of received hydrogen in some times the non-catalytic endothermic processes such as pyrolysis, cracking and depolymerization of hydrocarbon. As for cooling resource the composition hydrocarbon+water being subjected to a lot of physicochemical transformation, comes nearer to version of cooling with liquid hydrogen. Complete cooling resource $\Delta H = \Delta H_{phys.} + \Delta H_{chim.} \approx 10$ MJ/kg of a mixture, and the amount of produced hydrogen can reach 70 % (vol .).

The synthesis-gas obtained at conversion, has higher combustion heat. So, for example, the mixture $CO+3H_2$, formed from one kilogramme of methane, has calorific capability of Q=62900 kJ comparison with 50100 kJ at methane, i.e. for 25 % is higher. And, at last, use of gas having a endothermic reaction presumes also a considerable intensification of heat exchange. It is reached both at the expense of a raise of an effective thermal capacity of gas, and at the expense of transfer of a considerable proportion of heat, brought to gas, by the diffusion mechanism.

2. Special features of catalysis onboard a flight vehicle

In a number of our works [10,11] the requirements to onboard catalysts and thermochemical reactors as elements of a heat protection system and transformation of fuel were formulated. A number of existing technologies was defined also, which modification allows one to create on their basis catalysts and reactors which are capable to operate on plants of aerospace technique. In particular, with the purpose of further development, the class of catalysts synthesized directly on a heat-transfer surface (a skin of airframe, ridge of wings and air intake, walls of combustion chamber and other parts of a construction) is chosen. The plotted catalytic coat (planar catalyst) should have, first of all, high adhesion to a substrate in conditions of vibration, shock stresses and action of big value and variables in time thermal loadings. Use of planar catalysts in thermochemical reactors of a thermal protection allows one to make their constructions light, strong, of different shape and having small hydraulic resistance. A high thermal conductivity of a substrate (the walls of a reactor) and of the porous coat hinder for occurrence of local overheating of a construction and dangerous temperature transverse gradients at utilization of great heat fluxes.

2.1 Production process of catalytic specimens

Before producing a metal thermochemical reactor with a catalytic coat the samples of planar catalysts were explored in laboratory. A technological process of their manufacture and some test results are stated below. With the purpose of convenience the samples were made in the shape of metal tape, which was put into a quartz laboratory reactor.

Usually walls of heat-shielding designs are rather smooth and do not provide good adhesion with supported catalyst. Therefore it is necessary to cover these smooth surfaces with fine-layered porous coating, on which then the active component (catalyst) is applied. Porous coating – catalyst carrier - serves for formation of high-developed surface, provides stronger fastening of the supported catalyst, promotes thermal stabilization of a surface, catalyst poisoning resistance and selectivity increase. Schematic picture of the porous carrier and active component is given on fig. 1. Elementary reaction of steam methane reforming for the heat absorption Q is considered.

At the analysis of existing ways of obtaining carriers the attention was called to the technology of the plasma spraying of porous cover on the base $\gamma - Al_2O_3$. This oxide has the developed surface with needed porosity and acidity, that allows to synthesize nickel catalysts of methane reforming resistant to high-temperature sintering (up to 900° C).

The developed technology includes the following main stages:

- Plasma spraying of porous cover on a metal foil;
- Heat treatment of the carrier;
- Synthesis of catalyst.

Plasma spraying. Plasma spraying of porous cover on a metal foil, obviously, is one of the main operations in the chosen technology which must provide reproducibility of thickness of cover, chemical and phase structure, necessary free surface up to (40-60 m^2/g) and strength of adhesion of cover with the basis ~ (100 kg /cm^2).

At embodying plasma spraying powders of aluminium and hydroxides of aluminium are transferred by plasma jet on metal substrate (foil), aluminium hydroxide - gibbsite losing water passes in this case in bemit (AlOOH), which, in turn, passes in $\gamma - Al_2O_3$. Such kind of decomposition of hydroxides of aluminium ensures a developed interior surface of a porous coat. The subsequent heat treatment allows one to get uniform by chemical and phase composition porous coats from oxide of aluminum on a metal basis. The introduction in sprayed composition of a aluminum powder is necessary to reach a required adhesion of a porous coat to a basis and formation of "honeycombs" for hydroxide of aluminum.

As the metal basis for deposition on it $\gamma - Al_2O_3$ porous cover materials are chosen that endure the high temperatures ~1000° C. For manufacturing of nickel catalyst specimens for steam reforming methane the alloy X15 U5 50 microns thick was chosen.

Sprayed composition of powders is fed by a dosing apparatus to plasma jet having temperature up to 8000°C in the core. The powders are heated up and fused in a flow. At the shock against a surface the deformation of particles and chemical interaction with a material of a base layer occur.

For obtaining porous cover with required properties it is necessary by practice to define a distance and corner sprayed, temperature of a surface of porous cover and uniformity of its thickness. Besides on these parameters the kind of a material (metal, ceramics etc.) on which cover is put influences. The achievement of high quality of porous cover and reproducibility of its basic parameters at each following sample grows out of search of an optimum for each characteristic plasma sprayed. So, for example, distance from a nozzle exit section up to a surface of the basis does not falls outside the limits 50-200 mm. Temperature of a basis surface during the process of plasma spray of qualitative porous covers changes within the limits of 300±50°C. Density of porous cover and structural characteristic of pores is adjusted by rate of plasma forming gas. At plasma spraying process the volume rate is about 3,0-4,0 m^3/ hour.

The research of chemical and phase composition of porous sprayed coating was conducted on the installation "Dron-3". Effects of a X-ray diffraction analysis of porous cover on the metal basis are the following:

- hydroxide of aluminum 88-93% (mass.);
- aluminium 8-6% (mass.);
- $\gamma - Al_2O_3$ up to 3% (mass.);
- $\alpha - Al_2O_3$ lower than 2 % (mass.).

The thickness of cover is 45-50 microns. It is visible, that alongside with hydroxide phases (gibbsite and bemit) the porous cover contains oxide phases of aluminium. Probably, the porous cover also includes other intermediate phases of aluminum oxides, but their quantity is so small, that it is not registered by a X-ray diffraction analysis. Aluminum hydroxides are basic material for obtaining $\gamma - Al_2O_3$ in the process of heat treatment.

Oxide of aluminum $\gamma - Al_2O_3$ has sufficient for spraying of active component porosity (up to 50%) and great specific surface (up to 40 m^2/g). The surface $\gamma - Al_2O_3$ has acid character, that allows one to disperse and to stabilize the sprayed active component. The oxide of aluminum $\alpha - Al_2O_3$ is the most thermodynamic stable phase and widely spread in a nature in the form of known mineral - corundum. Its porosity is about 2 %, and the specific surface makes $0{,}1 \div 2$ m^2/g.

Heat treatment. The purpose of heat treatment is the acceleration of decomposition processes of aluminium hydroxides (gibbsite and bemit) up to $\gamma - Al_2O_3$, oxidation of the rests sprayed of aluminium also up to $\gamma - Al_2O_3$, increase of adhesion of porous cover to the metal basis, formation of a texture and structure of porous cover (thickness, porosity and specific surface area). Thus all processes which allow to synthesize the carrier for deposition of active component are initiated and completed.

The decomposition of components of porous cover 50 microns thick goes in three areas of temperature. In range 300-500 $^{\circ}$C basic processes of decomposition gibbsite in bemit go. In range 550-600 $^{\circ}$C gibbsite is decomposed directly in $\gamma - Al_2O_3$ and steam. In range 680-850 $^{\circ}$C the aluminium is oxidized up to $\gamma - Al_2O_3$ and, at last, in an interval 900-1000 $^{\circ}$C the phase transition $\gamma \rightarrow \alpha$ begins. Obviously, that the transition $\gamma \rightarrow \alpha$ results in loss of porosity and decreasing specific surface area. The results of examinations conducted at study of process of synthesis of the carrier of particular phase composition with high specific surface and a porosity are shown in tab. 1.

Table 1.

Parameters of the carrier depending on temperature of calcination during 1 hour.

Temperature of calcination, °C	Phase composition, % mass.	Specific surface, m^2/g	Thickness, μm
450°	Gibbsite > 80% Bemit > 3% $\gamma - Al_2O_3 < 5\%$ $\alpha - Al_2O_3 < 3\%$ $Al^0 < 5\%$	≈ 10	55
600°	Gibbsite < 1% Bemit < 3% $\gamma - Al_2O_3 > 80\%$ $\alpha - Al_2O_3$ 4% $Al^0 < 1\%$	≈ 80	50
850°	Gibbsite < 1% Bemit < 1% $\gamma - Al_2O_3 < 80\%$ $\alpha - Al_2O_3$ 8% Al^0 -	≈ 40	48

From results, given in Table 1, it is seen, as temperature influences on the phase composition, specific surface and thickness of the porous coat on the metal base. Calcination of samples at 450°C does not change the initial phase composition of a porous coat, and it in basically consists of hydroxides of aluminum, which have a low interior surface till 10 m^2/g. The temperature rise up to 600°C is coordinated with a sharp modification of structure and phase composition of a porous coat. The hydroxides of aluminium are decomposed on the surface of a metal base for $\gamma - Al_2O_3$ and water (steam). Probably, this process includes decomposition of gibbsite to bemit, which in its turn participates in the process of formation of $\gamma - Al_2O_3$ and steams of water. This conclusion is based on the fact of increasing of content of $\gamma - Al_2O_3$ at the sharp drop of a gibbsite content. Content of $\alpha - Al_2O_3$ will increase in accordance with vanishing because of an oxidizing of aluminium. At last, calcination of samples at the temperature of 850°C, which is typical for our conditions of steam conversion process for methane, conducts to increasing of the $\alpha - Al_2O_3$ content .At the same time there is a drop of specific surface of a porous coat from 80 m^2/g till 40 m^2/g.

Synthesis of active component and research of the catalyst characteristics. Nickel catalysts were synthesized by impregnation of the carrier by salts of a nickel with subsequent air calcination at temperature 500 ° C during 2 hours. By weighing of the initial carrier and synthesized sample of catalyst the contents of nickel oxide was determined. Then a sample of catalyst was placed in the research reactor. The test of catalyst on activity has been conducted according to a technique designed by us for tests of planar catalysts.

Test conditions on the installation of a flowing type are the following:

Temperature of process - 800 ° C, atmospheric pressure, ratio steam/methane is equal 2:1, volumetric velocity on methane $\omega = 2000\,hr^{-1}$. Catalyst activity was estimated on a degree of conversion of methane - X.

The test data have shown, that the degree of conversion of methane on the planar catalyst at the above mentioned requirements depends on a content of a active component (fig. 2). The samples with the smaller content of an active component have a smaller activity. At synthesis of catalyst by a method of impregnation of the porous carrier, any disturbance of porous cover visually is not revealed.

During service life tests within ten hours the degree of transformation of methane has decreased (fig. 3, blue) a little. One of the possible reasons of this undesirable phenomenon is decreasing of a specific surface area of catalyst because of thermal instability of phases of oxides of aluminium, received at plasma spray. To increase a thermal stability it was used a chemical modification of the carrier by means of introduction of La^{3+} (2% mass.) ions in it.. The effect of stabilization is seen on fig. 3 (red). The X-ray analysis shows, that the stabilizing activity of a lanthanum is based on formation of a firm solution of lanthanum ions in a lattice of oxide of aluminium that interferes with diffusion of ions of aluminium, and accordingly, with its reorganization in high-temperature modifications having a smaller specific surface area.

The work on the further examination of systems $MnOm - Al_2O_3(M = La, Mg, Zr...)$ is prolonged. It is necessary to study influence of a nature, structure, ratio of initial components, mode and temperature of processing on a phase structure, dispersity, porous structure, mechanical strength and their catalytic activity in considered process of steam conversion of methane.

3. Experimental installation and measurement procedure

Methane was selected as one of reactants in the considered reaction at the thermal testing of thermochemical reactor (TCR). This choice is not random; it is dictated by technological features of offered system of heat protection. As noted above, heat-shielding reactors is fed by gas mixture based on methane. The gas mixture is the product of gasification of an initial liquid hydrocarbon aviation fuel (kerosene, for example) in the auxiliary device. Methane and water are the initial reagents for hydrogen producing. Steam reforming of methane has maximal heat-absorbing effect and minimal tendency to the coking.

The installation for steam reforming of methane is intended for:

- experimental investigation of the thermochemical reactor operation under the action of stationary and non-stationary heat flows with the aim of determination of the limit value of the heat absorption, operating characteristics of TCR and the process data of the steam reforming;
- search for the optimum constructions and technology of the TCR manufacturing with use of planar and frame catalysts, and means of intensification of the heat- and mass exchange.

The principal parameters of the installation are:

- the methane flow rate – up to 5 g/s;
- the steam flow rate – up to 15 g/s;
- the pressure in TCR – 0,2÷2 MPa;
- the temperature at the TCR inlet – 773÷973 K;
- the maximum temperature of the TCR wall – 1273 K.

For realization of experiments the existing installation on conversion of methane was essentially modernized. The modernization is connected with installation of the new slot reactor of large length and change of the method of heating the walls of reactor for supplying of energy necessary for realization of heat-absorbing reaction. Instead of heating by the plasma jet with variable heat flux along the reactor length now a direct ohmic heating ensuring a constancy of a heat flow on length of the reactor is utillized. In this connection the technique of data processing was corrected also. The scheme of the installation is shown in a fig. 4.

The water is heated and evaporated in the evaporator (1). The heating of steam and methane from the vessel is implemented in electric heaters (2 and 3, accordingly). Then the reactants are mixed and at temperature of 500°C move in the thermochemical reactor (4), where there is a chemical endothermic reaction. The heat supply to steam-methane mixture implements by direct heating of walls of the reactor. As the current source the transformer (5) serves. During experiment the following quantities are measured:

- flow rate of methane and steam;
- temperature of a steam-gaseous mixture on the reactor inlet and outlet;
- distribution of wall temperature along reactor;
- pressure of a steam-gaseous mixture on the reactor inlet;
- voltage drop in an electroheated channel;
- strength of current;
- composition of dry conversion gas on evidence derived from mass-spectrometric analysis of gas samples.

The basic unit of installation, where the process of steam conversion of methane proceeds, is the slot-hole rectangular reactor (fig. 5), on which interior walls the lamina of nickelous catalyticly active coat is put. Optimizing of the experimental technique and processing of results of the first experiments are conducted on a trial reactor, and the final experiments are conducted on a reactor with cross-section of 34×4 and length of 750 mm. As a material of a reactor was chosen nichrome alloy with operating temperature 1000°C. The direct passage of an electric current through a heated wall allows one to implement boundary conditions $q \approx Const$ and to gain necessary thermal loadings with good regulating of the supplied power. Temperature of walls of a reactor is fixed by a chromel-alumel thermoelectric couples. The reactor is thermally insulated from an environment by the kaolin cotton wool jacketed surface of which is applied by a compensating heater. It allows to minimize a thermal losses on the majority of length of a reactor.

The distillated water is forced out of the water container by nitrogen at the pressure up to 15 atm and is delivered to the evaporator. Steam is generated in the device composed of two main units: the water evaporator and the steam superheater. The evaporator is the steel container of internal volume 40 litres with thick walls and the resistance heating element. The maximum power of the heater of the evaporator is 4 kW.

To prepare TCR to the working state the reduction of the catalyst is carried out in the hydrogen flow with the rate of 50 g/h and the temperature of 600 deg C. The blow-through the system before the work and the conservation of the catalyst after the experiment is carried out with the neutral gases Ar or N_2.

The experimental set-up is supplied with process instrumentation to provide the measurement and control such parameters of the steam, methane, gas-steam mixture, nitrogen and hydrogen as temperature, pressure, flow rate, gas composition, and others. The correspondent transducers are connected to the computer installation to provide automatic measurement and processing of the experimental data according to the developed software.

Measurement and calculation procedures

Temperature. The temperatures of reactor walls and used hot gases were measured by chromel-alumel thermocouples with recording of the indications on an automatic potentiometer. The statistical characteristics of thermocouples were defined before experiments by method of comparing of the indications on the researched thermocouple with the exemplar thermocouple at various temperatures of its working tip and fixed temperature of free tips. The maximum checking error at maximum temperature 1200 deg C is ±5 deg C. The total measurement error of temperatures of the wall and steam-methane mixture in view of an error of the device is estimated as ±7 deg C.

Steam flow-rate. In all conditions, the steam flow-rate in active channel of the facility is only determined by the electric power fed to the evaporator, and by thermal losses into environment. To reduce the losses the exterior of the evaporator is coated with a thick layer of thermal insulation made from "keramzit" (expanded clay).

The thermal losses can be estimated with the help of expression:

$$Q_n = \left(c_{stainless} m_{stainless} + c_{Cu} m_{Cu} + c_{H_2O} m_{H_2O}\right)\left(dt/d\tau\right)_{\tau=0}, \quad (1)$$

where $m_{stainless}$ and m_{Cu} are masses of the evaporator details made from stainless steel and copper; m_{H_2O} the mass of water in the evaporator; $c_{stainless}$, c_{Cu}, c_{H_2O} the heat capacities of stainless steel, copper and water at $t = 100$ deg C; $(dt/d\tau)_{\tau=0}$ the time gradient of the temperature, that corresponds to the moment when the heater of the evaporator is just turned off.

The assessment of thermal losses in the evaporator was made with the help of Eq.1. All details of the evaporator were weighed. To determine $(dt/d\tau)_{\tau=0}$ the special experiments were done. During the experiments, the change of water temperature was fixed depending on cooling time, since a moment of the heater cutoff; in doing so, the vessel neck was closed.

With the help of the received relationship $t = f(t)$ the gradient of temperature at the first moment of cooling $(dt/d\tau)_{\tau=0} = -0{,}0071$ deg/s was found. The value of thermal losses $Q_n = 0{,}311$ kW was calculated by Eq.1.

The relation between the electric power of the evaporator and the steam flow-rate is displayed in Fig. 6.

Methane flow-rate. To achieve stable fixed methane flow-rate we used the convergent nozzle with the local sound speed reached in the nozzle throat. The mass gas flow-rate in the nozzle throat is determined by the following equation [12]:

$$G = f(k)PF\sqrt{RT/M}\,, \qquad (2)$$

where F is the area of the nozzle aperture, $f(k)$ the known function of gas adiabat k, P the total gas pressure in the chamber before the nozzle, T and M are temperature and molar gas mass correspondingly, and R is the universal gas constant.

The described procedure of measuring of the flow-rate was also tested by immediate calibration of the nozzle with the help of the gas counter and has shown the reliability. The error of measurement of gas flow rate does not exceed ±2 %.

Flow-rate and linear velocity of steam/methane mixture

It is obvious, that the mass mixture flow-rate is equal to the sum of mass flow-rates of methane and steam: $G_{mix} = G_{CH_4} + G_{H_2O}$.

According to known expression for mass flow-rate:

$$G_{mix} = \rho_{mix} V_{mix} S\,,$$

it is possible to determine the linear velocity of mixture V_{mix} in the reactor inlet. Here $\rho_{mix} = 1 \Big/ \sum_i^n \frac{m_i}{\rho_i}$, m_i and ρ_i are the mass fraction and the density of components respectively at given temperature in the reactor inlet, S the area of the reactor section.

The gas analysis. The analysis of gas samples taken during the experiments was performed in laboratory on mass-spectrometric installation, which includes a magnetic mass spectrometer and the system of sampling into an ionic source of this device. The scheme of mass-spectrometric device is shown in Fig. 7.

Main elements of the sampling system are the mercury manometer (5), capacity of adjusted volume (7) and gas admission cylinder (9).

During the analysis on mass-spectrometric installation, gas sample goes from sampler (1) into capacity (7). Then, gas from this capacity bypasses into the gas admission cylinder (9). From the cylinder, the gas through an aperture in the thin diaphragm falls in an ionic source of the mass spectrometer. It consists of the following units:

– source of ions (10);

– chamber-analyzer (11);

– devices for ion reception and registration, and for the measuring of intensity of ion current for each component (12-14).

Besides the units listed above, the spectrometer also includes vacuum system with pumps and electronic circuits of power supply and control for operating mode of the device (15).

The natural gas conversion products leaving the reactor of the test facility contain H_2, CO_2, CO and CH_4 as main constituents. To determine the contents of these components in gas samples at quantitative analysis the factors of sensitivity for each component in relationship to the one, accepted as "the internal standard", were previously determined. Hydrogen was selected as the standard. The factors of sensitivity for CO_2, CO and CH_4 were determined in relationship to hydrogen. These coefficients are listed in Table 1.

Table 1

Component	H_2	CO_2	CO	CH_4
Relative factor of sensitivity	1,00	4,38	4,17	3,30

At the quantitative analysis, it was necessary to take into account that during the ionization of CO_2 by the method of electron impact, besides molecular ions with *m/e* 44 (CO_2^+) there are also formed fragments with *m/e* 28 (CO^+) and *m/e* 16 (O^+). During the recording of mass-spectrum the intensities of the specified fragments are superposed on intensities of molecular ions of corresponding masses with *m/e* 28 (CO) and *m/e* 16 (CH_4); these ions are also in gas samples.

To take into account this superposition the mass-spectrum of CO_2 was measured separately and the relative structure of fragments CO^+ and O^+ was determined in relationship to primary molecular mass-spectrum with *m/e* 44. These data were subsequently used at the quantitative analysis of structure of conversion products. This analysis was executed in the following order:

1. The mass-spectrum registration was done in the range of masses between *m/e* 44 and *m/e* 15 for each gas sample. In doing so, the intensities of peaks corresponded to molecular ions H_2, CO_2, CO and CH_4 were measured.
2. The correction for background presence in the device was entered. The hum was measured before the start of research of sample containing conversion products.
3. At processing of the received mass-spectra the corrections for superposition of intensities of fragments formed at ionization CO_2 and intensities of peaks appropriated to molecular ions with m/e 28 (CO^+) and with m/e 16 (CH_4^+) were entered.
4. To account the factors of sensitivity for main components in relationship to hydrogen the correction was added.
5. The sum of intensities of molecular peaks for components H_2, CO_2, CO and CH_4 was determined.

6. Relying on the received results the concentrations C_{CO_2}, C_{CO}, C_{CH_4} and C_{H_2} were determined.

7. Based on the received values C_{CO_2}, C_{CO} and C_{CH_4} the degree of conversion of methane was calculated under the formula:

$$X = \frac{C_{CO_2} + C_{CO}}{C_{CO_2} + C_{CO} + C_{CH_4}} \cdot 100\% .$$

Calculation of a heat flux. The density of a heat flux was calculated as a difference $q = q_e - q_{loss}$, where q_e - electrical power, q_{loss} - density of thermal losses. The q_e value was determined by measuring a current and voltage drop, and q_{loss} was estimated on temperature difference of a wall of a reactor and heated housing. The thermal losses at the expense of radiation heat exchange were neglectful small, the leakage of heat because of a thermal conduction were essential only on the extremities of a reactor.

4. Results of experiments

In this section the results of experiments on steam conversion of methane are shown under following conditions:

- $H_20/CH_4=2$,
- Temperature of a steam-methane mixture on an inlet in a reactor is about 500°C,
- The rate of flux of a mixture varied in a range 0,0005÷0,0025 m^3/s.

The tests of a slot-hole reactor were conducted under the uniform plan. The start of installation was carried out on inert gas (nitrogen) and after reaching temperatures required under the rules of the process, in a reactor reagents (steam, methane) were given. The experimental data were registered at reaching a quasistationary operation regime of an experimental bench under condition of an invariance of the basic parameters of process. At switching on of installation this time was not less than half-hour, at passage from one regime to other - 10 minutes.

On a fig. 8 the typical profiles of temperatures of a wall of a reactor are shown at constant rate of an original mixture for different densities of a heat flux. In the case of neglecting end effects, at transition of electric current on a wall of a reactor the heat is released, which practically completely is transmitted to the catalyst. On the catalyst the endothermic process proceeds and through it the part of heat is transmitted to a gas current by a convection. In such system the catalyst is a source of heat for a gas stream. Temperature of the catalyst is fixed at a level ensuring equality of a heat flux, stipulated by an electric current, and total of sinks of heat due to chemical process and physical heating of a gas stream. On an inlet in the channel the maximal concentration of methane ensures with other things being equal maximal velocity of process of methane conversion. Minimum temperature of a stream also promotes decreasing of the temperature of a wall of reactor and catalyst. Hereinafter along with driving a stream in the channel because of drop of methane concentration the velocity of process decreases. But density of a heat flux in requirements of an electrical heating on all stretch of the channel practically does not vary. Therefore marked tendency to slowing down of process rate is completely compensated by increasing temperature of the catalyst. Increasing of temperature of a gas flow, which is already began to heat up, also conducts to rise of temperature of a source of heat.

The described mechanism reflects ability of a system to self-regulation, expressed in maintaining of approximately constant value of efficiency (velocity of process) on all stretch of the channel under affect of a heat flux with a constant density.

It is necessary to mark, that far from an equilibrium the influence of concentration of initial substances to velocity is much less, than temperature effect. The growth rate of temperature of a wall is rather insignificant. As approaching an equilibrium at a sufficient residence time of a mixture in a reactor and particular value of a heat flux the velocity of process is hardly reduced, that can cause temperature rise of a wall leading to its thermal breakdown. The curve at $q=70$ kW/m^2 corresponds to the described above situation of approximation to an equilibrium on a segment of 0,45÷0,65 m.

The said is confirmed also by rise of a degree of methane transformation calculated by results of analysis of the outcoming gas mixture, at incresing of a heat flux (fig. 9). This graph shows an influence of a thermal loading of the catalyst to a macrokinetics of process of steam conversion of methane. Increasing of activity of catalyst with rise of a thermal loading indicates a limiting role of exterior heat and mass transfer in considered process.

The most important mean to control the regime of a reactor operation is the rate of flux of an original mixture. Its raising conducts to increasing of concentration of methane (drop of a degree of transformation) and decreasing of temperature of a wall in all cross-sections of the channel.

In a fig. 10, 11 the dependence of a degree of transformation of methane and densities of an absorbed heat flux versus the rate of an original mixture are presented. It is visible, that with magnification of the rate of an original mixture the density of a heat flux is increased with simultaneous lowering of a degree of transformation of methane.

Measuring the supplied electrical power and knowing temperatures and composition of mixture on an inlet and output of a reactor it is possible to estimate parts of heat expenditures for chemical process and physical heating. On a fig. 12 the dependence of the supplied reaction heat versus of the rate of an original mixture is shown. It is visible, that the parts of expenditures of heat on chemical process and physical heating vary feeblly and make accordingly 62 - 67 % and 38 - 33 %.

The analysis of a fig. 10, 11 leads to an idea on necessity to have onboard an airplane a system of reactors for departure of different functions:

- Absorption of a maximal amount of heat;
- Deriving of a maximal amount of hydrogen for combustion chamber.

These reactors can be divided in space and in time. They can have different construction designs, have different catalysts and conditions of operation. All this influences a relation of different components in composition of converted gas given to combustion chamber.

Performed tests showed, by us together with a TsAGI, that the kerosene combustion happened only under thermal choking at the end of the combustor. Herewith, a flow of the type of a pseudoshock arised upstream. The relative fraction of methane and hydrogen in the fuel mixture acts substantially on the behaviour and efficiency of the working process in the combustor, as well as on the operation range of a flow temperature at the entrance. In increasing the content of methane and hydrogen from 0 to 0.05 in the fuel mixture the combustion efficiency at the end of the combustor rises from 0.8 to 1.0. Herewith, the minimum stagnation temperature, at which the combustion stall takes place, decreases from 1100 to 750÷800 K. When the relative mass fraction of methane is not less than 0.2 and mass fraction of hydrogen is not less than 0.1 in the fuel mixture, the behaviour and efficiency of the working process, as well as the operation range of a flow temperature at the entrance change and are defied by kinetic properties of these components rather than kerosene. Alongside with combustible components in combustion chamber such non-combustible components as vapour of water can be brought. The influence of vapour of water to combustion is ambiguous. In particular requirements the reactions of combustion can be intensified at the expense of occurrence of an additional amount of a hydroxyl radical OH. Therefore today is very actual problem of carrying out of complex experiment, in which the operation of combustion chamber with a thermochemical reactor will be combined. The calculations display, that the components of conversion of hydrocarbon fuel going to the combustion chamber are more inclined to combustion and have smaller ignition delay time, than traditional conventional hydrocarbon fuel. Thus conversion of hydrocarbon fuel before its combustion will allow one to decide a problem of ignition and stabilization of flame in scramjet. Besides the preliminary preparation of liquid hydrocarbon fuel ensures multi-regime of combustion chamber of an apparatus, that gives it ability of flight in a broad band of numbers M and heights H.

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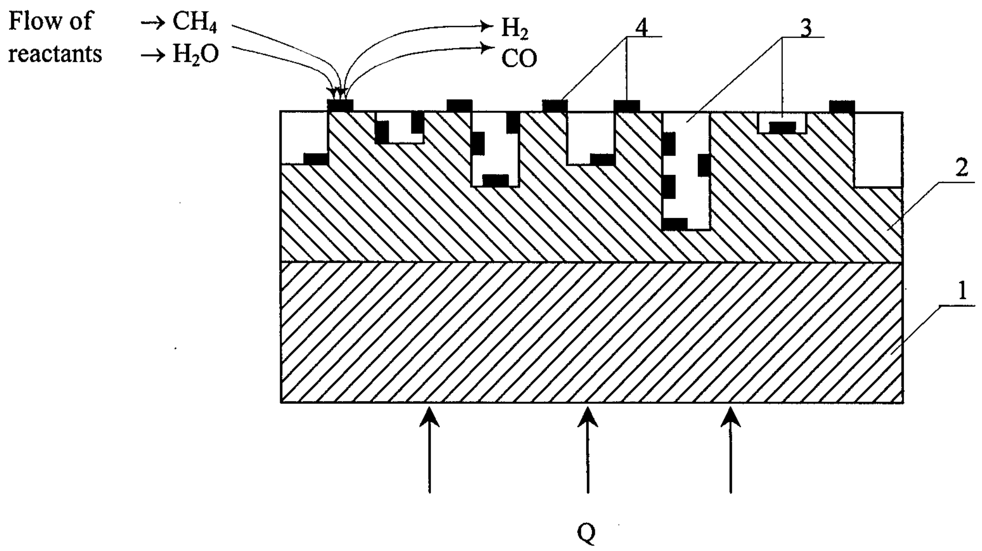


Fig. 1. Schematic picture of a fragment of a catalytic wall
(Not in a scale).
1 - wall of a channel (substrate)
2 - porous carrier
3 - pore
4 – active component (catalyst)

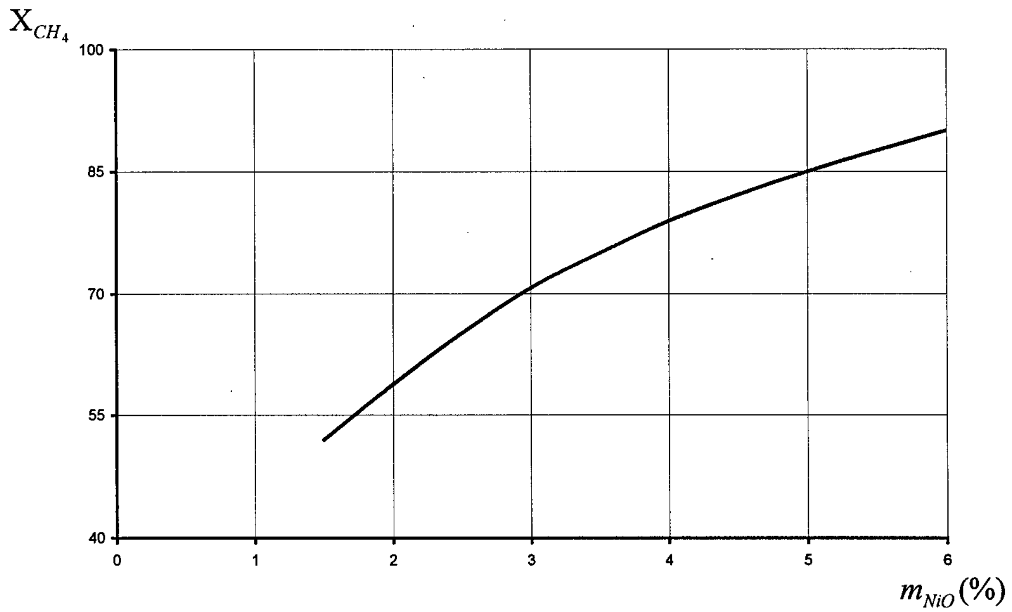


Fig. 2. Conversion degree of methane vs. the contents of active component
(t = 800 °C, volume velocity $\omega = 2000\,ч^{-1}$, $H_2O/CH_4 = 2$.)

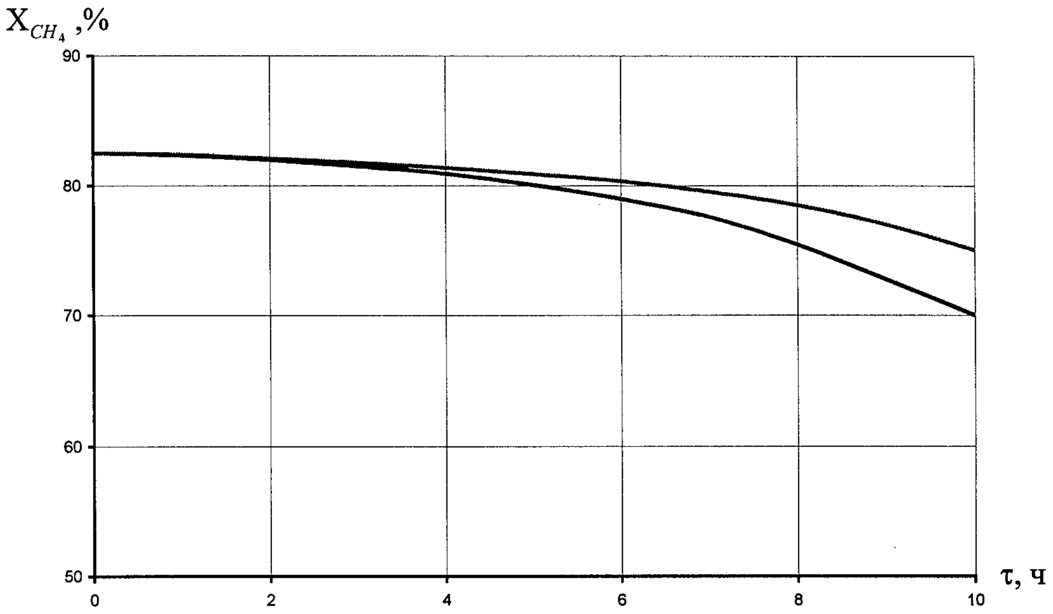
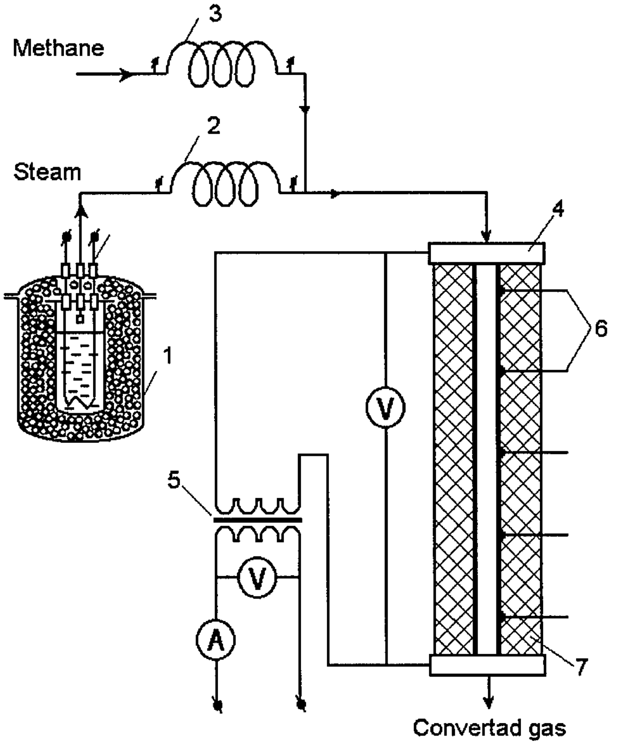


Fig. 3. Influence of the stabilizing component
($m_{NiO} = 4{,}2\%$ mass., $T = 800$ °C, $\omega_{CH_4} = 2000\ \mathrm{h}^{-1}$, $H_2O/CH_4 = 2/1$).



1. evaporator
2. steam electric heater
3. methane electric heater
4. thermochemical reactor
5. transformer
6. thermocouple
7. thermal insulation

Fig. 4. Experimental set-up

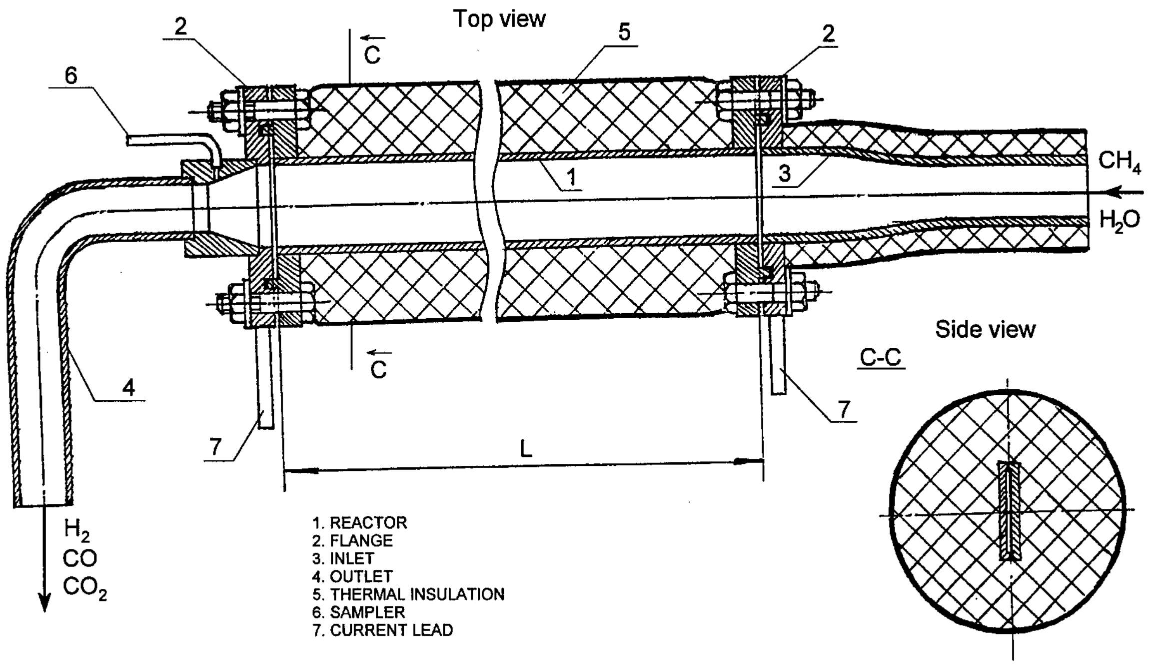


Fig.5. Experimental thermochemical reactor

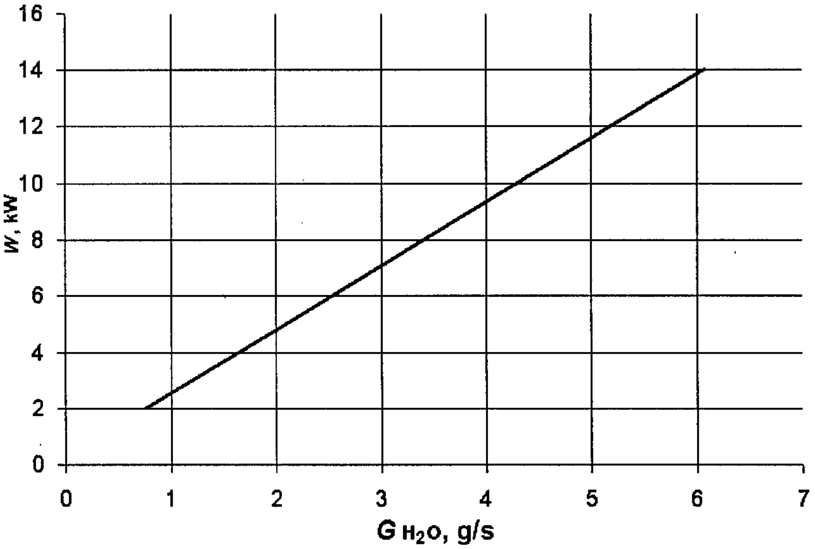


Fig.6. Relation between the electric power of the evaporator *W* and the steam flow-rate G_{H_2O}

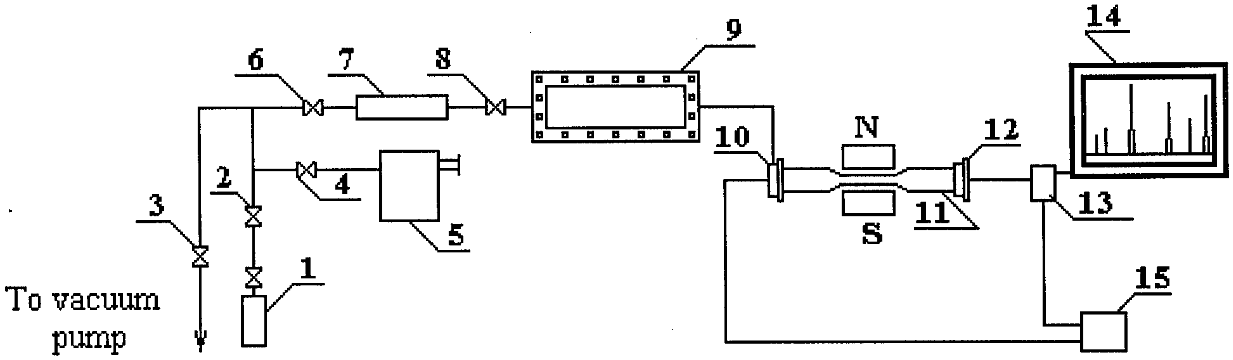


Fig.7. Scheme of the laboratory mass-spectrometric device

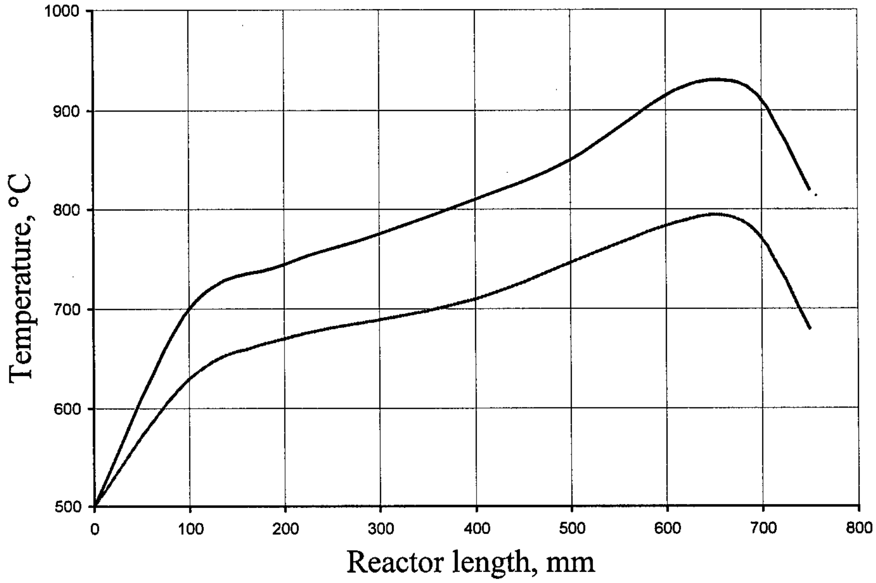


Fig. 8. Temperature distribution along reactor length for various heat loads (red - $q = 40\,\mathrm{kW/m^2}$, blue - $q = 70\,\mathrm{kW/m^2}$)

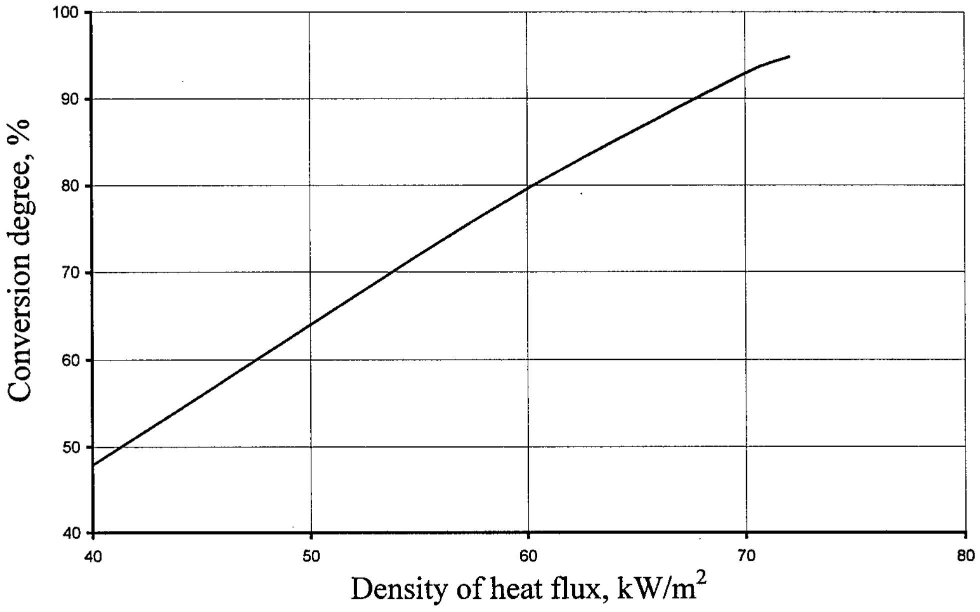


Fig. 9. Conversion degree of methane vs. density of heat flux

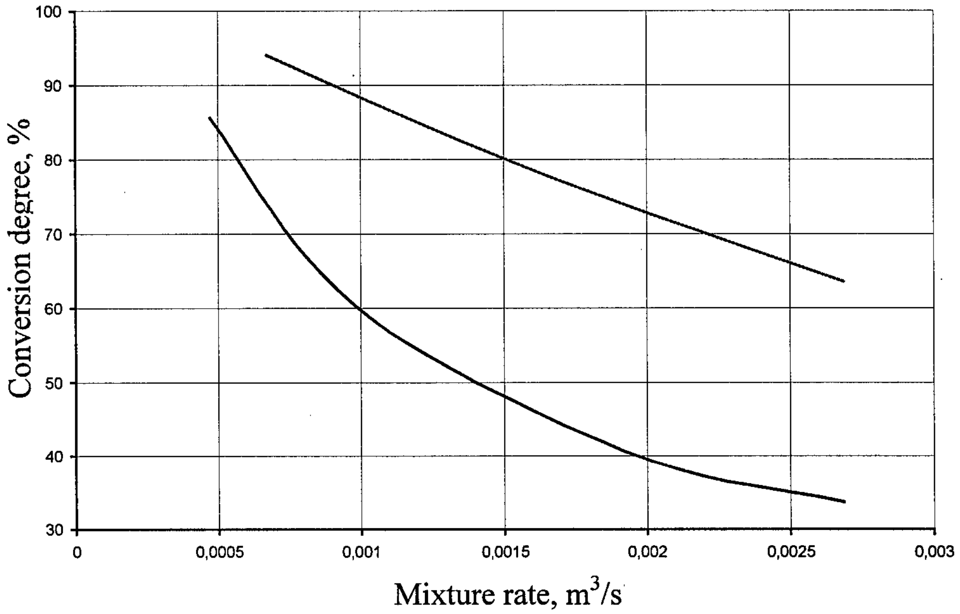


Fig. 10. Conversion degree of methane vs. mixture rate
(red – T_w=900°C, blue – T_w=800°C)

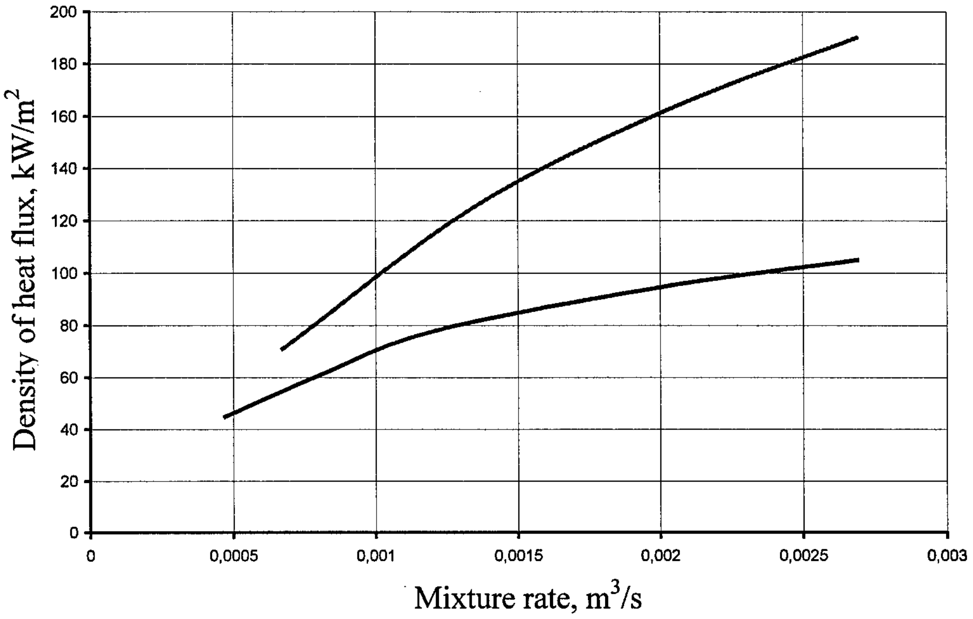


Fig. 11. Density of heat flux vs. mixture rate
(red – T_w=800°C, blue – T_w=900°C)

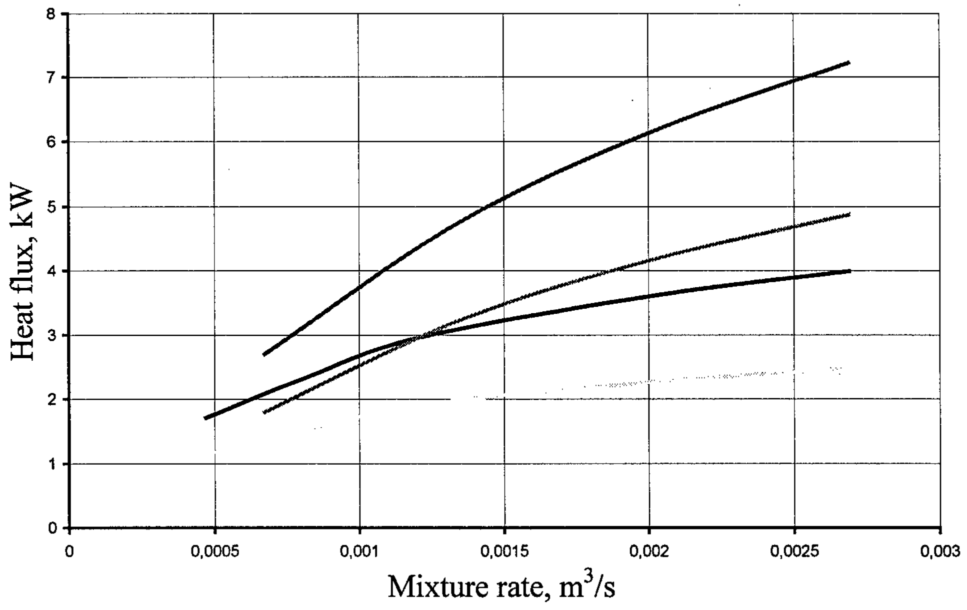


Fig. 12. Heat flux and heat of reaction vs. mixture rate
(blue – energy supply at T_w=800°C, red – energy supply at T_w=900°C,
yellow – absorbed in reaction at T_w=800°C, green – absorbed in reaction at T_w=800°C)