EXPERIMENTAL STUDIES OF METHANE STEAM CONVERSION IN THEROCHEMICAL REACTOR

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Introduction

The use of hydrocarbon fuel conversion for cooling heat-stressed areas of high speed vehicles and organization of their burning in supersonic air flow have been considered by the experts from the sixties of the last century [1-5]. The reviews of modern conceptions on hypersonic vehicle's thermal management are presented in [6,7].

Hydrocarbon steam conversion is highly endothermic process requiring large amounts of heat supply. For example, the steam conversion of methane is described by two reactions:

$$CH_4 + H_2O = CO + 3\,H_2 — 206\ \text{kJ/mol}$$

$$CO + H_2O = CO_2 + H_2 + 41\ \text{kJ/mol}$$

The first of them is highly endothermic, and the second one is slightly exothermic. But the total process of steam conversion is endothermic. The above reactions are carried out in the presence of catalysts.

When running a process of liquid hydrocarbon fuel steam conversion, a serious problem appears which is associated with the emergence of carbon in the conversion yields.

To exclude precipitation of carbon it is recommended to divide the process of conversion into two stages [8]. During the first stage the fuel must be subjected to gasification at the reduced flow of water vapor, and temperatures not exceeding 500º C while using highly active nickel catalysts resulting in methane formation at that. The second highly active endothermic stage consists of vapor catalytic conversion of the formed methane at the temperatures no less than 700 - 800 º C.

1. Manufacture of a setup with a model thermo-chemical reactor on the base of plasmotron ЭДП-109/200М

To make a thermo-chemical reactor (TCR), the heat-resisting structural material ХН78Т was selected. This alloy is used for manufacture of flame tubes of high-temperature combustion chambers of turbo-jet engines operating at temperature range of 1000 – 1100 º C [9].

The two-channel reactor structure of 592 mm length is presented in Fig.1. A high-temperature jet of nitrogen, heating heat-transfer walls of the two slot channels (4) was fed into the central rectangular channel of the reactor (5) from plasmotron (1) via adapter (2). Preheated mixture of hydrocarbons and water vapor was fed to the channels (4) which actually were the reactive zone with 571 mm length, 60 mm width, and 4 mm height.

Thermal environment in the reactor was controlled by chromel-alumel thermocouples located in the upper channel. There were seven (7) thermocouples there registering the temperature of the reactor wall t_w at different distances from the inlet (65mm, 153mm, 332mm, 421mm, 501mm, and 559mm), and three (3) thermocouples determining temperature of the gas t_g at the distances 65mm, 332mm, and 559mm from the inlet to the slot channel.

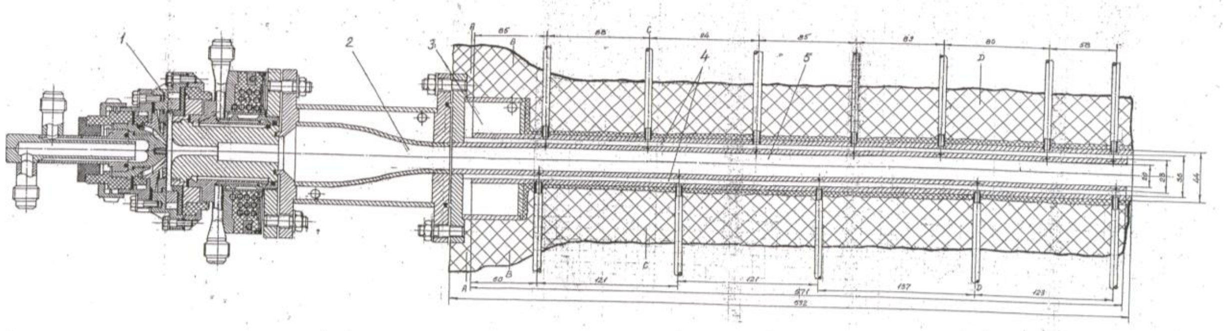

Fig.1Experimental reactor made of XH78T alloy

For the input of thermocouples determining gas temperature in the slot channels, the fittings were used which were designed for gas sampling. Junctions of these thermocouples have been adjusted near the inner surface of the reactor walls at a distance of 1mm from the surface.
Methane and over-heated vapor, preliminary heated in their electric heaters, were fed to the mixing chamber of the reactor via tangentially channels improving the process of mixing of the components prior to their inlet to the slotted channels. To reduce heat loss into the environment, the outside surface of the reactor was covered with insulation.

2. Experimental studies of steam catalytic conversion of methane in the slotted reactor

One of the purposes of the experimental reactor testing was verification of its work capacity at the maximum allowable temperatures for its heat-transfer walls, as well as evaluation of the possibility to use the reactor with no catalysts at all. Therefore, these walls were heated up to 1100 – 1175 º C.
The parameters providing the greatest impact on the process of steam catalytic conversion of methane, apart from the temperature of heat-transfer walls, should include also mass flow rates of methane and water vapor, as well as the ratio of the two.
The tests of the experimental reactor were carried out in three (3) stages. When conducting experiments of the 1st stage, the largest mass flow rate of gas-vapor mixture amounting to approximately 0.69 g/sec was chosen. It made ≈ 0.69 g/s. The ratio of the mass flow rate of vapor to the methane mass flow rate, at that, was 2.2.
The original thermal conditions were determined by the wall temperature t_{2w} registered by the second (2nd) thermocouple at a distance of 153 mm from the reactor inlet. During the 1st stage of testing temperature $\boldsymbol{t}_{2w}$ values have been maintained at a level close to 1100 º C. The results obtained during these tests are presented in Table 1.

Table 1 – The main parameters of the conversion process in the slot channel of the reactor in implementation of the 1st stage of testing

Parameters	Parameter Values				
1	2	3		5	
Sequence of gas sampling from the reactor for analysis	1	2		4	
Distance of sampling site from entrance to reactor	5 01	4 21	47	1 53	5
Consumption of natural gas, g/s	0 ,212	0 ,217	,217	0 ,217	,220
Flow of water vapor, g/s	0 ,480	0 ,482	,482	0 ,482	,470
The ratio of water vapor flow to natural gas consumption	2 ,26	2 ,22	,22	2 ,22	,14
Nitrogen consumption through plasmotron, g/s	9 ,0	9 ,0	,0	9 ,0	,0
Plasmotron power, kW	3 0,97	3 0,97	0,97	3 0,97	0,97
Vapor-gas temperature at the outlet of the heater, º C	4 43	4 46	46	4 46	465
The temperature of the reactor wall t_{1w} at a distance of 65 mm from the entrance, º C	1 000	9 80	80	9 80	80
The temperature of the reactor wall t_{2w} at a distance of 153 mm from the entrance, º C	1 100	1 090	095	1 095	095

The temperature of the reactor wall t_{3w} at a distance of 247 mm from the entrance, º C	112	125	1130	130	151
The temperature of the reactor wall t_{4w} at a distance of 332 mm from the entrance, º C	115	1145	163	170	175
The temperature of the reactor wall t_{5w} at a distance of 421 mm from the entrance, º C	065	125	143	152	160
The temperature of the reactor wall t_{6w} at a distance of 501 mm from the entrance, º C	017	079	104	115	119
The temperature of the reactor wall t_{7w} at a distance of 559 mm from the entrance, º C	25	82	018	030	033
The temperature of the gas in the reactor t_{1g} at a distance of 65 mm from the entrance, º C	85	80	80	80	80
The temperature of the gas in the reactor t_{4g} at a distance of 332 mm from the entrance, º C	60	48	65	40	35
The temperature of the gas in the reactor t_{7g} at a distance of 559 mm from the entrance, º C	85	45	80	95	90
Velocity of the gas in the reactor at a distance of 65 mm from the entrance, m/s	,28	,28	,27	,27	,18
The degree of methane conversion in %	.85	,6	,7	,3	.5
Composition of “dry” gas samples without water in % of volume					
CH_4	1,7	3,1	7,2	3,3	8,7
CO	,1	,8	,5	,8	,8
CO_2	,6	,7	,2	,5	,5
H_2	,6	,4	,1	,4	

The main conclusion that can be drawn from analyzing the data in Table 1 is that at specified mass flow rate of gas mixture equal to 0.69g/s and its temperature at the reactor inlet equal to 446 º C, the heating of the reactor’s heat-transfer walls to high temperatures (up to 1100 º C and above) did little to promote intensive development of the conversion process in the slot channels of the reactor. Maximum value of the degree of methane conversion that was determined based on the results of analysis for composition of gas samples taken at a distance of 501 mm from the entrance to the reactor was equal only to 5, 85 %. It should be noted however, that in preparing the reactor for testing, the internal surfaces of its slot channels were not subjected to any special treatment. Their state was consistent with the original surface of the material used.

During realization of the 1st stage of testing, 5 gas samplings have been taken from 5 fittings located along the axis of the reactor at 65, 153, 247, 421, and 501 mm from the entrance (inlet). Samples were taken starting from the last fitting. Duration time of sampling was 30 minutes. As shown in Table 1, there was a considerable increase of the walls temperature in the center and exit sections of the reactor, despite the maintaining t_{2w} at the same level over this period. The values of t_g also increased significantly during sampling, but only in the exit section of the reactor. The observed heating of the reactor and gas over 30 minutes at a permanent power of plasmotron being 30,97 kW, can be explained by the inertia of heating of the massive walls of the reactor which had a thickness equal to 4 mm.

The results obtained during realization of the 1st stage of the reactor testing show clearly, that in order to achieve higher values of conversion degree of methane without the use of catalysts in the slot channels, it is necessary to significantly reduce the mass flow rate of the incoming vapor-gas mixture, thus increasing the time of its stay in the high-temperature reaction zone.

In this context, during the 2nd phase of the slot reactor testing, mass flow rate of vapor-gas mixture was reduced by 4, 7 times. It averaged 0,149 g/s. The ratio of vapor mass flow rate to the methane flow rate at that was 2, 2. The average value of the temperature t_{2w} during gas sampling from 7 fittings made 1130 º C, and the average temperature of vapor-gas mixture at the reactor inlet was 410 º C.

During the experiments, the temperature of heat transfer wall was monitored with the help of thermocouples at 7 points, and the temperature of gas – at 6 points. The locations of these thermocouples are given in Table 2. It also presents the main results obtained in the implementation of the 2nd stage of the reactor testing.

Table 2 – Parameters of the conversion process in the slot channel of the reactor in implementation of the 2nd stage of testing

Parameters	Parameter Values						
1							8
Gas sampling numbers							7
Distance of gas sampling site from entrance to the reactor, mm	59	01	21	32	47	53	6 5
Start time of sampling since plasmotron initiation, min	0,5	3,7	7,5	1,4	5,6	1,3	3 7,0
Plasmotron power, kW	6,78	6,78	6,78	5,34	4,48	5,06	2 5,06
Nitrogen consumption through plasmotron, g/s							9
Consumption of natural gas, g/s	,047	,047	,046	,046	,046	,046	0 ,0465
Flow of water vapor, g/s	,106	,103	,099	,100	,106	,013	0 ,100
The ratio of water vapor flow to the consumption of natural gas	,23	,29	,13	,15	,28	,215	2 ,215
Vapor-gas temperature at the outlet of the heater, º C	10	05	10	12	10	12	4 08
Wall temperature at the 1st sampling site t_{1w}, º C	045	040	042	025	015	012	1 050
Wall temperature at the 2nd sampling site, t_{2w}, º C	135	135	140	140	122	118	1 112
Wall temperature at the 3rd sampling site, t_{3w}, º C	095	115	140	145	130	125	1 125
Wall temperature at the 4th sampling site, t_{4w}, º C	055	100	135	145	145	135	1 125
Wall temperature at the 5th sampling site, t_{5w}, º C	85	020	070	095	100	105	1 105
Wall temperature at the 6th sampling site, t_{6w}, º C	75	37	85	015	022	025	1 025
Wall temperature at the 7th sampling site, t_{7w}, º C	15	51	82	20	20	25	9 27
Gas temperature at the 1st sampling site, t_{1g}, º C	62	05	30	42	67	68	6 80
Gas temperature at the 2nd sampling site, t_{2g}, º C	32	38	41	42	35	42	6 52

Gas temperature at the 3rd sampling site, t_{3g}, º C	52	67	75	95	94	81	80	6
Gas temperature at the 5th sampling site, t_{4g}, º C	30	80	52	52	63	69	70	9
Gas temperature at the 6th sampling site, t_{5g}, º C	20	60	00	15	05	10	10	9
Gas temperature at the 7th sampling site, t_{6g}, º C	40	88	30	53	68	72	75	8
Gas velocity at the 1st sampling site, m/s	,265	,282	,298	,324	,414	,389	,379	1
Conversion degree of natural gas, %	5,4	4,0	0,6	8,2	9,2	1,5	,1	3
Composition of “dry” gas sampling without water in % of volume								
CO_2	,5	,2	,8	,3	,4	,5	,3	2
CO	9,0	6,8	4,8	3,2	4,2	,8	,7	0
CH_4	1,1	9,5	4,6	7,5	6,8	6,7	4,6	9
H_2	,4	,4	,8	,0	,6	,1	,4	2

During these tests, gas sampling was carried out from 7 fittings which were on the outer wall of the slotted channel. Analysis of the composition of these samples showed that a significant reduction in mass-flow rate of vapor-gas mixture resulted in significant increase in the degree of methane conversion. At the end of the reactor at a distance of 559 mm from the entrance, the degree of conversion reached 35,4 %. In this case there was a significant convergence of temperatures t_w and t_g in the exit section of the reactor. However, in the front section the difference in these temperatures exceeded 400 º C.

The results of the two stages of the slotted reactor tests proved correctness of selection of this structural material. It allowed rather prolonged (for more than 2 hours) operation of the reactor under high temperatures (exceeding 1100 º C) with no visible traces of melting and destruction on its surface. But expectations of the reactor workability without special treatment of inner surfaces of its slotted channels and without use of catalysts in them were not justified. Therefore, at the 3rd stage of testing a metal grid complete with a nickel catalyst on its surface was inserted in the channels of the reactor. Test conditions were the same as at the 1st stage.

Table 3 presents the main parameters of the steam catalytic conversion of methane which were recorded during final 3rd stage of testing.

Based on the results presented in the Tables 1, 2 and 3, dependencies depicted in Fig.2, were plotted which characterize changes in the degree of methane conversion S along the length L of the reactor corresponding to each stage of testing. Fig.3 presents temperature changes T_w in the heat transfer wall along the channel from which samplings were taken for analysis.

Analysis of sample composition of conversion yields was carried out during experiments using a mass spectrometer MC7-100. Fig.4 shows the dependencies characterizing the change in volume concentrations of components of the conversion products (CH_4, H_2, CO, CO_2) along the length of the rector, which were observed during the 3rd stage of testing.

Table 3 - The main parameters of the conversion process in the slot channel of the reactor in implementation of the 3rd stage of testing

Distance of sampling site and	6		3	

measurement of wall temperature T_w from the entrance to the reactor, mm	0	81	02	39
Consumption of natural gas, g/s	,215	,225	,260	,265
Flow of water vapor, g/s	,431	,452	,522	,531
Nitrogen consumption through plasmotron, g/s	,02	,02	,02	,02
Power of plasmotron, kW	0,1	0,1	0,1	0,1
Temperature of natural gas at the reactor inlet, ° C	55	60	60	58
Temperature of water vapor at the reactor inlet, ° C	00	10	10	12
Temperature of the heat-transfer wall of the reactor, ° C	044	035		70
The degree of methane conversion, %	6,74	7,7	3,96	1,08
Composition of the “dry” gas samplings without water in % of volume				
H_2	,02	2,15	6,64	0,18
CH_4	4,90	3,77	5,18	,08
CO	3,51	1,35	5,75	8,78
CO_2	,55	,36	,85	,04
O_2	,02	,37	,58	,92

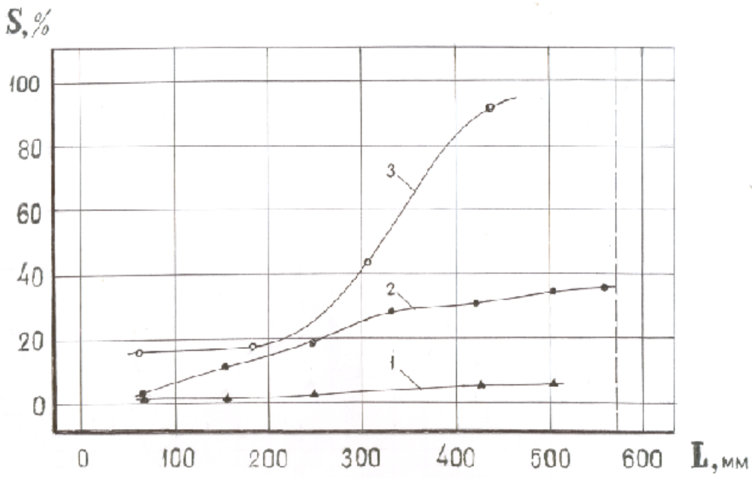

Fig.2 – Alteration of conversion degree of methane *S* along the length of the reactor *L*; 1, 2, 3 – numbers of testing stages

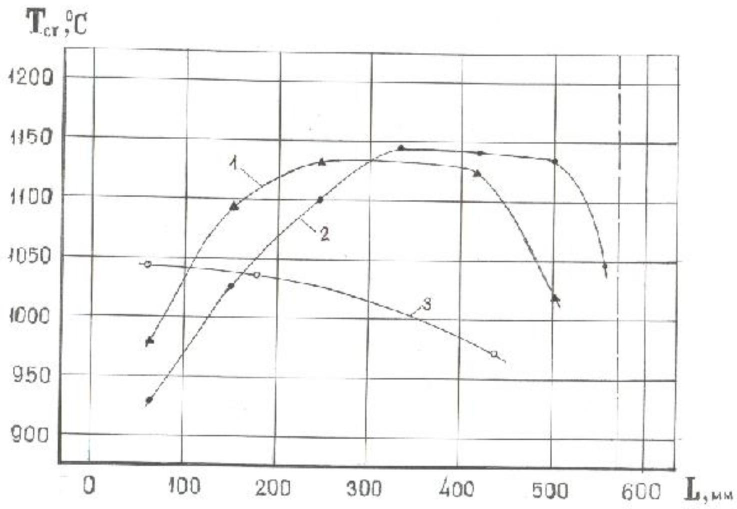

Fig.3 – Temperature alteration for heat transfer walls T_w along the length of the reactor L; 1, 2, 3 – numbers of testing stages

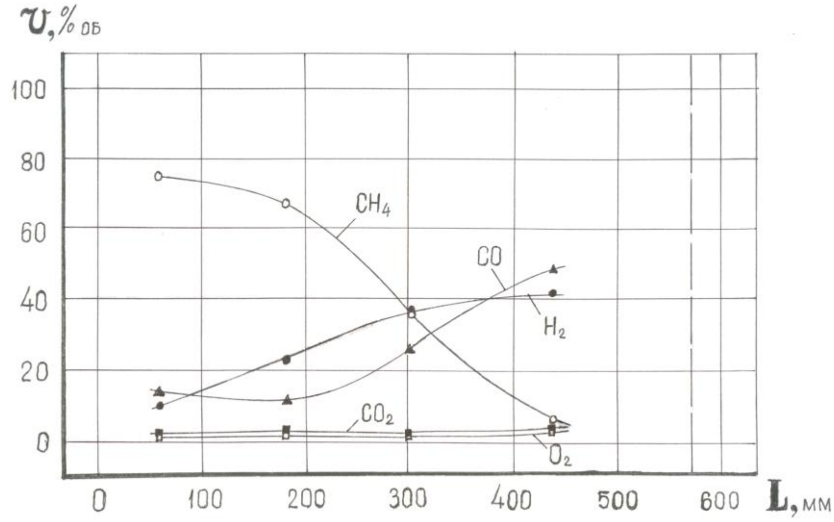

Fig.4 – Alteration of the volume concentration of conversion products V along the length of the reactor L during the 3rd stage of testing

Conclusion

Analyzing experimental results obtained during realization of three stages of the reactor testing the following basic conclusions can be drawn:

1. The selected compositional material for the reactor allows to heat its heat transfer walls and exploit them for a long time at the temperatures (1000 – 1100 º C) which are characteristic of the working conditions for combustion liners (flame tubes) of combustion chambers of the modern air-breathing propulsion systems.
2. Confirmed is the need for a catalyst for obtaining hydrocarbon conversion rate close to 100 %, with the implementation of the conversion process in the reactor under the above-mentioned thermal conditions.
3. When using the mesh catalyst in the double-split model reactor under adopted conditions of its testing, the degree of methane conversion was achieved close to 100 %, while hydrogen content in the products of conversion was exceeding 40 %.

REFERENCES:

1 **Yaffee M**. Fuel may cool manned flights at Mach 4.- Aviation week, 1960, March 14, pp.89-96

2 **Lander H., Nixon A.** Endothermic fuels for hypersonic vehicles. AIAA 68-997, pp.1-12
3 Oil hasn't lost turbine-fuels race yet.- The oil and gas journal.-1969, T.67, pp.56-57
4 **Isaak J.J., Cookson R.A.** Supersonic combustion aid for liquid and gaseous fuels.- AIAA Journal, 1973, v.11, № 7, pp.1036-1037
5 **Cookson R.A., Isaak J.J.** Aided supersonic combustion of transversely injected fuels.- AIAA Journal, 1976, v.14, № 1, pp.3-4
6 **Griethuysen V.J., Glickstein M.R., Petley D.H.**, et al. High-speed flight thermal management. –In.: Progress in Astronautics and Aeronautics, 1996, v.165., pp.517-579
7 **Maurice L.**, **Edwards T.** Liquid hydrocarbon fuels for hypersonic propulsion.- In.: Progress in Astronautics and Aeronautics, 2000, v.189, pp.757-822
8 **Veselov V.V.** The kinetics and catalytic conversion of hydrocarbons, Kiev, "Naukova Dumka," 1984
9 **Anuriev V.I.** Reference book for designer-mechanical engineer, v.1, Moscow "Machine-building industry", 728 pp., 1980
10 **Keis V.M** Convective heat-and-mass transfer. Moscow, "Energia" Publishing House, 1972