Prospects for the use of methane conversion for increasing energy and environmental efficiency of energy installations

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Abstract. The reduction of proven hydrocarbon reserves stimulates research on the implementation of the comprehensive program “Hydrogen Energy and Fuel Cells”. The high calorific value of hydrogen and the ecological purity of its combustion products determine the prospects of using hydrogen fuel in large-scale and small-scale energetic.

1. Introduction

In world practice, the most developed area of hydrogen production is by electrolysis of water [1]. But due to the high energy intensity of this process, its use is effective only with the use of electricity generated during the night period at nuclear power plants and hydroelectric power stations. It is more promising to obtain hydrogen fuel by converting methane contained in natural gas. The most cost-effective way to produce synthesis gas (a mixture of hydrogen and carbon monoxide) is the steam oxidative conversion of methane. This endothermic process is carried out in tube furnaces (steam reformers) at temperatures of 750°C – 850°C by burning fuel in burners. Syngas production reaction:

\[ \text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2; \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2. \]

Here we should take into account the results of studies carried out by CIAM staff on comparing the performance of a low-emission combustion chamber when operating as methane and syngas fuels [2], where it was concluded that «... the thesis is about obtaining an environmentally friendly exhaust using synthesis -gas as a fuel in homogeneous combustion chambers when burning ultra-poor mixtures is not justified». It is necessary to speak not about replacing natural gas with fuel synthesis, but about the use of additives for sustainable combustion of the "ultra-poor" mixture.

2. Systems for low-emission combustion of methane-hydrogen mixtures

The key technology to reduce the toxicity of emissions of nitrogen (NOx) and carbon (CO) oxides by the combustion products of gaseous carbon fuels is the technology tested in [3] for burning natural gas in a gas turbine combustion chamber with additives of pure hydrogen and hydrogen-containing synthesis gas produced in particular in a stand-alone catalytic reactor. The following results were obtained:

1. The addition of pure hydrogen or synthesis gas to natural gas can significantly expand the range of sustainable combustion of a substantially depleted mixture.

2. The addition of synthesis gas (a mixture of H2 and CO) to natural gas (the main fuel for onshore gas turbines) has the same effect as the addition of pure hydrogen, the cost of which is 3-5 times higher.
3. When testing in the compartment (figure 1) a methane-hydrogen mixture (balloon supply of 60% CH₄ and 40% H₂) with simulated low gas turbine operation at αₕ = 2.5, a decrease in CO emission from 1200 mg / m³ to 250 mg / m³, and on αₕ = 2 from 250 mg / m³ to 20 mg / m³. Similar results were also recorded in tests performed previously with a synthesis gas generator developed by the Federal State Unitary Enterprise «RFNC – VNIIEF» in Sarov.

![Figure 1. Tests of the low-emission combustion chamber compartment.](image)

Based on the obtained results, for a number of converted gas-fired GTU – NK-16ST, NK-37 and NK-38ST, fueled by natural gas, systems for low-emission combustion of methane-hydrogen mixtures in low-emission double-circuit burners (figure 2) using synthesis gas generators that ensure their operation in a wide range of stable combustion with a low level of emission of NOₓ and CO [4]. The low-emission burner has a standby and main combustion zone. The supply of synthesis gas additives only to the on-duty combustion zone is provided.

![Figure 2. Low emission burner (a) section view (b) photo;](image)

1 – casing with nozzle, 2 – swirl with hollow blades, 3 – associated step-turbulator, 4 – a rod with channels 5 and 6 for supplying fuel to the main and standby zones; 7 – fuel supply openings from the annular manifold 8 to the main combustion zone; 9 – poorly streamlined central body, 10 – openings for supplying air to the standby combustion zone, 11 – openings for supplying fuel to the standby zone from the annular collector 12 through the central channel 13.
In FSUE «RFNC – VNIIEF», Sarov, a design of a synthesis gas generator with partial oxidation of methane with the addition of a mixture of H₂ and CO in fuel has been developed for use in the duty zone of a double-circuit burner of a low-emission GTU combustion chamber (figure 3).

Figure 3. Low emission burner (a) scheme (b) three-dimensional model.

Promising combustion chambers have been created at JSC «Metalist-Samara», which ensure the environmentally friendly operation of gas turbines of ground-based applications with acceptable levels of NOₓ and CO emissions. It was established (figure 4) that the conversion of 10% of natural gas to synthesis gas by its catalytic oxidation can reduce NOₓ emissions from 150 mg / m³ to 20 mg / m³ and CO from 300 mg / m³ to 60 mg / m³ in a low emission combustion chamber.

Figure 4. Dependence of the content of NOₓ and CO in the exhaust gases of a gas turbine engine on excess air ratio for various fuels.

In this case, no radical alteration of the combustion chamber is required to achieve the greatest environmental and economic effect. This technology will allow the modernization of 600 gas turbines NK-16ST and AL-31ST, operating at compressor stations of gas pipelines.

3. Operation of gas turbines using methane-containing gas
In [5], a method for the operation of gas turbines using methane-containing gas as a fuel was proposed. According to this method, comprising supplying compressed air and a methane-containing gas mixture to the gas turbine combustion chamber, expanding the combustion products in a gas turbine. Their cooling is carried out in a waste heat boiler by evaporation and overheating of high pressure steam, which is used to obtain additional work of a gas turbine installation. Natural gas is sequentially mixed with superheated high-pressure steam and heated in a recovery boiler to 350 – 530°C. The resulting mixture is sent to the first catalytic reactor to produce a methane-
containing gas containing up to 3% hydrogen. Then this mixture is heated to 620 – 680°C with the heat of an additional external source and fed to the second catalytic reactor where the hydrogen concentration is increased to 20%. The resulting methane-hydrogen gas mixture is fed into the gas turbine combustion chamber.

In the patent [6], an improved method for operating on a methane-hydrogen gas-vapor mixture of a gas turbine installation of a gas pumping unit is developed.

![Figure 5. Schematic diagram of a gas pumping installation on methane-hydrogen gas mixture: 1 – compressor, 2 – shell of the combustion chamber 3, 4 – first catalytic reactor, 5 – second catalytic reactor, 6 – power gas turbine, 7 – natural gas supercharger, 8 — mixer of natural gas and superheated high-pressure steam, 9 – boiler utilizer.](image)

Most of the superheated steam (figure 5) generated in the waste heat boiler 9 is fed into the combustion chamber 3, and its smaller part is mixed with natural gas 8, heated by the heat of the exhaust gases of the gas turbine 6, and passed through the first catalytic reactor 4 located in cooling jacket 2 of the combustion chamber 3, where it is heated to 620 - 680°C, using the heat of cooling of the combustion chamber and sent to the second catalytic reactor 5 with an increase in hydrogen concentration in it above 20%. These methods employ steam reforming of natural gas in low temperature 4 and high temperature 5 catalytic reactors.

It is of interest to obtain a hydrogen-containing gas in a non-catalytic manner in which water and hydrocarbon fuel are converted into a hydrogen-containing gas. This method [7] was practically implemented in the VGTU-1 and VGTU-2 hydrogen turbogenerator units used for the fire treatment of concrete products. The method is based on the implementation of the oxidation process of a mixture of water and liquid hydrocarbon fuel in three stages in a multi-stage process cylinder. At the first stage, water is introduced into the cylinder, it is heated with heat from an external source and transferred to a vapor state. Steam is mixed with liquid fuel. At a temperature of 500°C, a mixture of water and hydrocarbons decomposes into hydrogen and carbon dioxide. This mixture in a fire torch is heated to 1000 – 1200°C, air is supplied and the mixture is burned out, raising the temperature of the torch to 1935 – 2100°C. Due to the use of water and liquid fuel, the complexity of the installation design and the low pressure of the resulting hydrogen-containing gas, this method is not applicable in power plants.

4. Method for producing a hydrogen-containing gas from natural gas

In the application [8], a method for producing a hydrogen-containing gas from natural gas is proposed, which is based on the high-temperature steam conversion of methane (figure 6). Its essence lies in the fact that superheated steam is mixed with natural gas and fed into the cooling jacket of the afterburner of the GTU combustion chamber containing catalyst granules. Formed in a cooling jacket and heated methane-hydrogen mixture and compressed air are fed into the afterburner and ignite the resulting «rich» fuel mixture.

An additional amount of air is supplied to the main combustion chamber and hydrogen-containing products of combustion are burned up with an increase in the flame temperature to 2000°C. Then the combustion products coming out of the main combustion chamber are diluted with excess compressed air and fed to the gas turbine with the desired temperature.
Figure 6. Schematic diagram of the burner device with high-temperature two-stage steam conversion of natural gas: 1 – combustion chamber body, 2 – afterburner stage of the combustion chamber, 3 – main combustion chamber, 4 – rotary blades for regulating air flow, 5 – hollow swirl blades with holes, 6 – cooling tube, 7 – spark plugs, 8 – burners, 9 – catalyst, 10 – control device.

Preliminary analysis shows that the use of this method in gas turbine power plants will allow the use of a methane-hydrogen mixture as fuel, with a ratio of the proportions of steam and natural gas from 7:1 to 8:1.

In the patent [9], a gas-turbine installation of a gas-pumping unit, working on a mixture of synthesis gas and natural gas, is proposed (figure 7). Hydrogen production in synthesis gas occurs due to the conversion of methane contained in natural gas by compressed air oxygen in an exothermic reaction $\text{CH}_4 + 0.5\text{O}_2 = \text{CO} + 3\text{H}_2$.

Figure 7. Gas turbine installation of a gas pumping unit:
1 – jet compressor, 2 – convection heater, 3 – natural gas reducer, 4 – compressor, 5 – combustion chamber, 6 – cooling jacket, 7 – gas turbine, 8 – burners, 9 – spark plugs, 10 – catalytic reactor.

Gas from the gas pipeline and atmospheric air compressed in the compressor 4 are fed through a jet compressor 1 and a convective heater 2, where they are heated to 450 – 500°C due to the heat of the exhaust gases of the gas turbine 7 and fed into the cooling jacket 6 of combustion chamber 5. B catalytic reactor 10 is placed on the cooling jacket, where a thermochemical oxidation reaction of methane by atmospheric oxygen takes place to produce synthesis gas. In the cooling jacket 6, the synthesis gas is heated to 700 – 750°C by the heat of cooling of the combustion chamber 5 and fed to the input of the combustion chamber. Natural gas is supplied to the burners 8 through a reducer 3. The introduction of synthesis gas into the combustion chamber 5 improves the combustion process, improves the environmental friendliness and efficiency of the gas turbine unit. Using the technology
of oxygen conversion of methane allows you to increase the amount of energy released during the combustion of synthesis gas, higher by 18% than when burning methane, which allows this unit to reduce the consumption of natural gas [10].

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