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Innovative Methane-Hydrogen Fuel Production and Application Systems

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Abstract

The use of methane-hydrogen mixtures with high hydrogen content (up to 50%) as a fuel gas to the existing compressor stations with gas pumping units subject to reconstruction will significantly improve performance, reduce fuel gas consumption and significantly reduce emission rates.

Introduction

One of the important circumstances, determining the inevitable transition to extensive use of new energy technologies, is the principal change in environmental requirements in the power and transport sector, set forth by legislation of the developed countries.

The lack of high hydrogen content alternative fuel production technologies hinders the transition to the more stable and diversified energy supply and to the mitigation of industrial, transport and energy sector impact on the environment.

The technology of production of methane-hydrogen mixtures (MHM), produced with adiabatic methane conversion (AMC), has been developed and experimentally validated. Being developed in connection with getting heat from a high-temperature reactor, the AMC technology becomes an innovative basis for energy technologies of natural gas conversion to highly efficient energy sources.

The AMC technology substantially simplifies the production process, as it does not require oxygen generation and is performed under lower temperatures (below 700^{o}C); the production does not require energy and cost demanding water electrolysis and is based on technological solutions, operations and catalytic materials, which have already been well developed in bulk chemicals manufacture.

Under the proposed MHM production technology the end product is manufactured in one stage, using the AMC procedure, instead of mixing together natural gas and pure hydrogen, generated in a separate unit, which considerably reduces production costs and makes the whole process a lot simpler.

Technologies

The basic concept of using methane-hydrogen mixture is as follows:

1. Fuel gas will not be pure hydrogen, but a mixture of hydrogen and natural gas (one order cheaper solution) – methane-hydrogen mixture

2. The use of adiabatic methane conversion at a conversion temperature of 650-680 °C max

3. Installation of a compact-block plant producing the triple mixture near the gas turbine drive: “Natural gas – hydrogen – water steam” (fig. 1)

4. The introduction of the above process to the facilities of GAZPROM

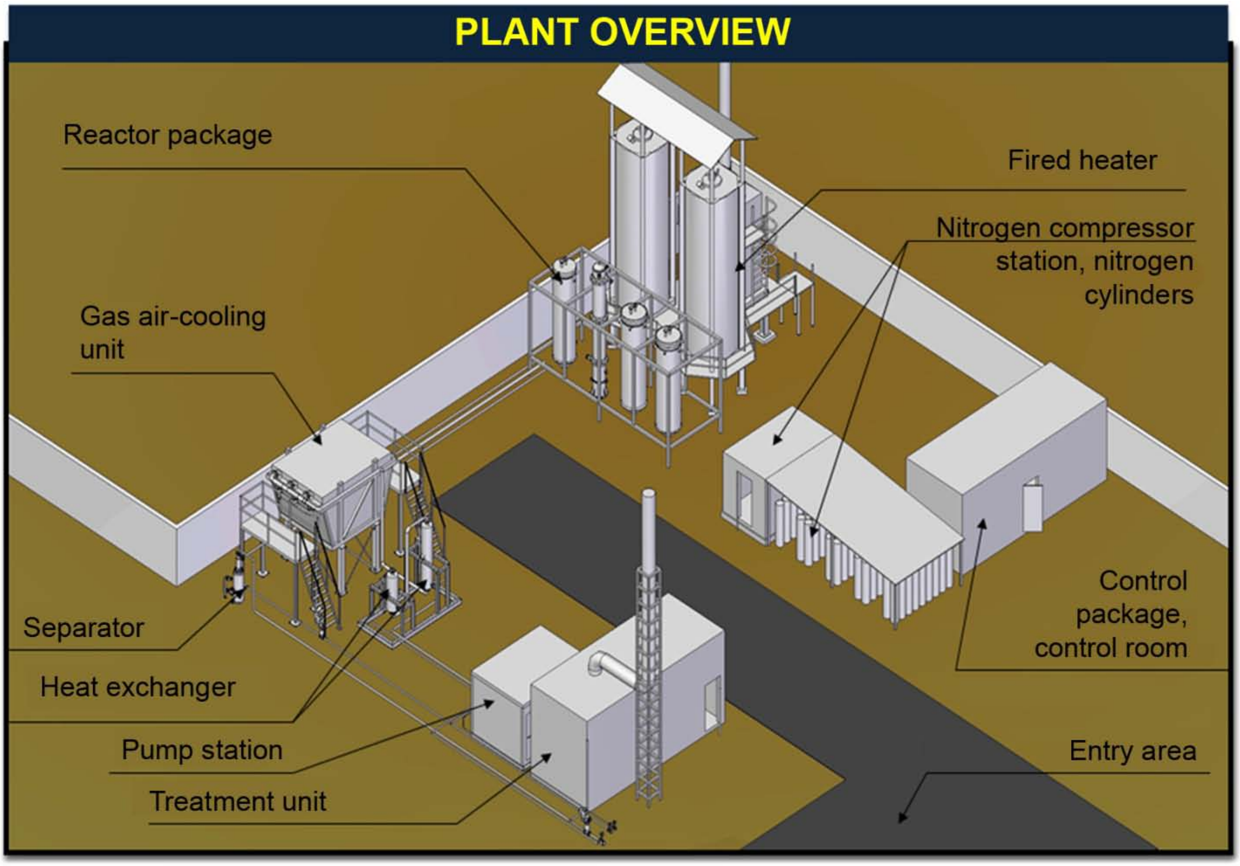


Fig. 1. Overview of MHM production plant

The AMC process presupposes max heating temperatures of steam-gas mixture of about 700°C that allows MHM output with high hydrogen content (fig. 2).

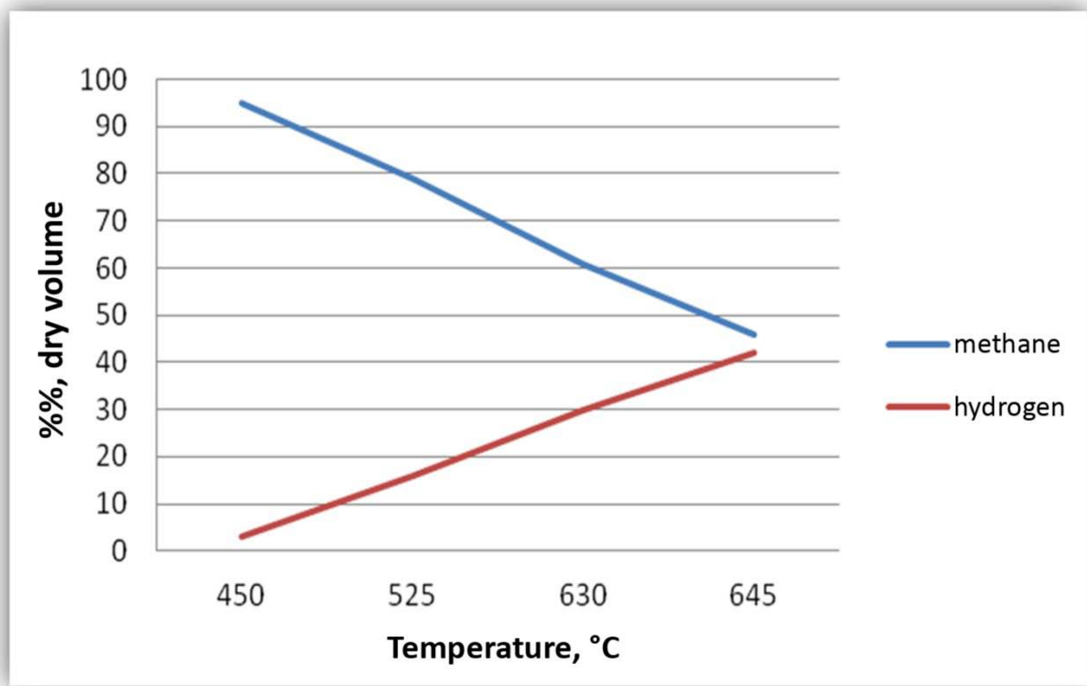


Fig. 2. MHM hydrogen concentration - temperature relation

The use of methane-hydrogen mixtures with high hydrogen content (up to 50%) as a fuel gas to the existing compressor stations with gas pumping units subject to reconstruction will significantly improve performance, reduce fuel gas consumption and significantly reduce emission rates.

In case of packages with relatively low initial effectiveness shifting to MHM will allow to increase gas efficiency by 20 – 25% and cut emissions of NO_X and CO will down to the next lower order.

In accordance with the approved Work program, a pilot sample plant producing methane-hydrogen mixture with the performance of 1,000 m^3/hour is being developed; it is designed to decrease fuel gas consumption at the compressor stations and reduce harmful emissions through the implementation of effective environmentally sound technologies.

In particular, more than 1,100 units of NK-16ST packages have been produced since the beginning of serial output in 1982; all these packages could be improved in their performance by shifting to MHM.

The design novelty is that a sample plant producing methane-hydrogen mixture is being developed for the first time and exceeds similar plants available in the world in all major indicators (performance, hydrogen content in the mixture, energy consumption rate, harmful emissions volume). The designed plant will allow testing the main catalytic processes of methane-hydrogen mixture production with meaningful performance of production units and reactors of 1,000 m^3/h of output.

Kuznetsov Company carried out a number of pilot tests of combustion chamber burner at different modes with different compositions of methane-hydrogen mixture; the tests evidenced that the use of methane-hydrogen mixture would substantially improve emission figures of gas turbine plants allowing to reach low NO_x values (down to 10 – 12 mg/m^3) and simultaneous sharp decrease in CO emissions (down to 4 – 8 mg/m^3) at high operating values of α (Table 1).

Table 1.

The results of GTP burner tests when using MHM

N of meas.	P_1	P_2	α_Σ	O_2	NOx	NO	NO_2	CO	CO_2	Gw	Gs
	kg/cm^2	kg/cm^2	-	%	ppm	ppm	ppm	ppm	%	g/s	capacity, %
10	0.3	1.2	1.74	9.5	16	16	0	12	6.5	70.97	0
11	0.3	1.3	1.78	9.8	14	14	0	10	6.3	71.51	50
12	0.3	1.3	1.78	9.8	8	8	0	11	6.3	71.53	75
14	0.3	1.2	1.72	9.3	15	14	1	27-62	6.6	71.35	0
15	0.3	1.2	1.75	9.5	12	11	1	21	6.2	71.04	50
16	0.3	1.2	1.81	9.9	8	8	0	17	6.2	71.04	100, burner was off

Presence of hydrogen in the main burner circuit significantly (approximately ~ 2 times) extends stable operating range when talking about the air speed in the burner, as well as about the use of gas with a relatively high water steam content.

The increase in mixture temperature always leads to an increase in chemical reactions rate and growth of normal Su flame rate.

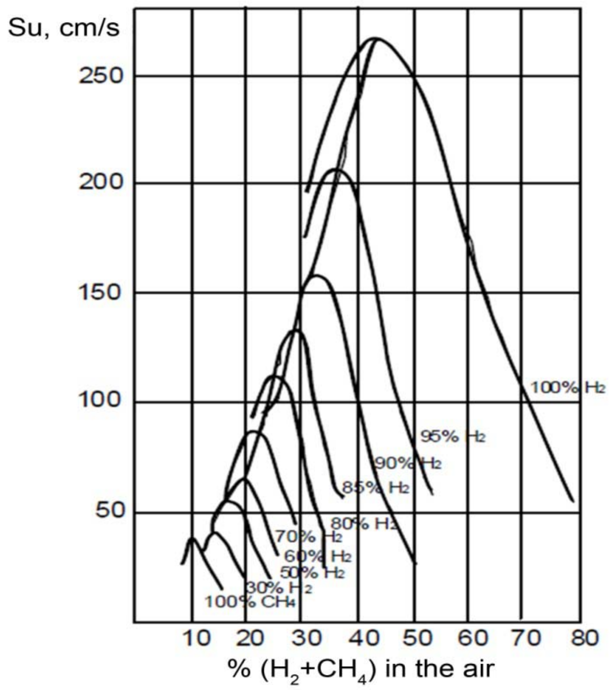


Fig. 3. MHM combustion rate in the air (under normal conditions)

Normal flame rate depends on the pressure. In lean mixtures with hydrogen content of 15% and less, combustion rate decreases as the pressure increases. In mixtures containing 20% hydrogen and above the non-monotonic pressure-relation is observed. In hydrogen rich mixtures with natural gas the rate increases at a low pressure, but decreases at higher values, as shown in fig. 3. Non-monotonicity is still present even in the most rapidly combusting mixtures, which contain about 40% of H_2. Max rate predicted by numerical simulations with detailed kinetics has been calculated for the region near 0.3 MPa.

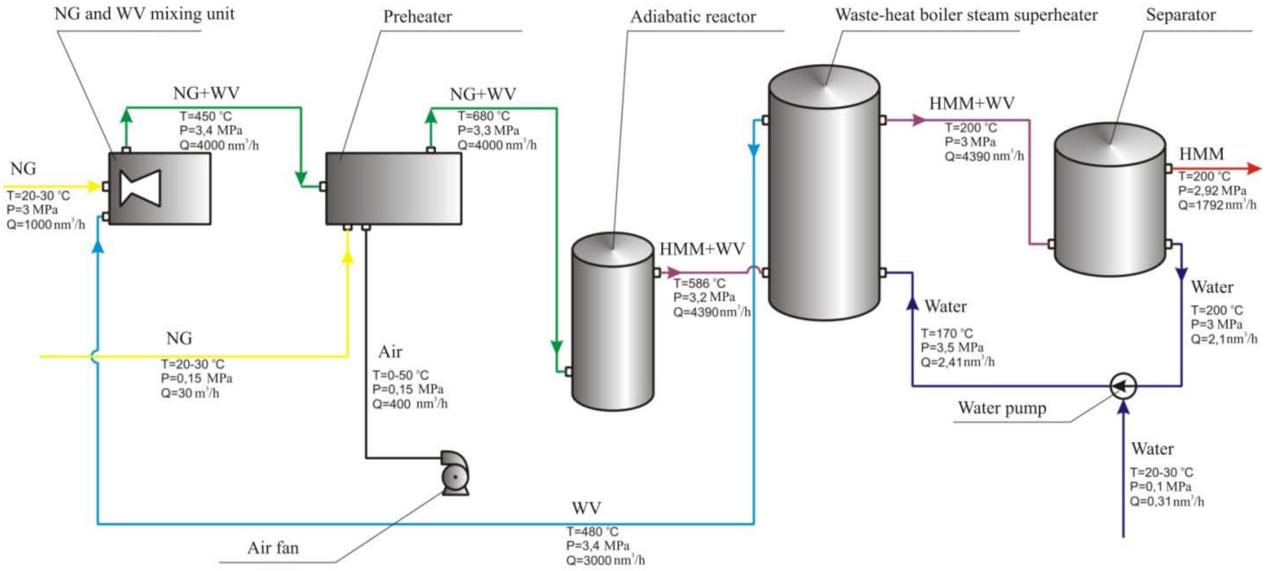
As the initial temperature increases, the limits of concentration of all hydrogen-containing mixtures alter so that the combustibleness region expands. The lower concentration limit is decreasing, and the upper one is increasing.

Critical diameter is reduced as the mixture combustion rate and pressure increase. Critical tube diameter and critical gap are clearly related to the value of minimum ignition energy. These factors must be taken into account when designing MHM combustion units.

An increase in the turbulence intensity results in faster mixing of combustion products with the original mixture and in turbulent combustion rate increase.

There has not been detected any notable influence of the initial pressure on the turbulent combustion rate in all hydrogen-containing mixtures.

Table 2 lists compositional analysis of the original product (natural gas) and resulting commercial gas outgoing from the MHM plant that employs AMC process [plant diagram is shown in fig. 4].



NG – natural gas
HMM – hydrogen-methane mixture
WV – water vapour

Fig.4. Basic diagram of the methane-hydrogen mixture production unit using adiabatic methane conversion technology

AMC process significantly facilitates production since:

- ✓ it does not require oxygen production
- ✓ production requires lower temperatures (up to 680°C)
- ✓ it does not require energy consuming and capital intensive water electrolysis
- ✓ production is based on technological solutions, modes and catalysts well-developed in large-scale chemistry

Table 2. The compositional analysis of incoming and outgoing products in methane adiabatic conversion process in obtaining methane-hydrogen mixture

Compositional analysis, volume % (wet)	incoming	outgoing
	Natural gas	Methane-hydrogen mixture (wet)
Carbon dioxide, CO_2	0.065	3.262
Carbon monoxide, CO	0.000	0.233
Hydrogen, H_2	0.000	13.621
Nitrogen, N_2	0.780	0.145
Argon, Ar	0.000	0.000

Water, H_2O	0.000	67.694
Methane, CH_4	98.836	15.045
Ethane, C_2H_6	0.242	0.000
Propane, C_3H_8	0.055	0.000
Butane, C_4H_{10}	0.016	0.000
Pentane, C_5H_{12}	0.006	0.000
Total	100.00	100.00

As can be seen from the table, outgoing product is a mixture of the three main components: water steam – 68%, hydrogen – 13.6% and methane – 15%. The combustible components also include carbon monoxide – 0.23%.

The content of hydrogen in the produced dry mixture will be about 47% with all the combustible components taken as 100%.

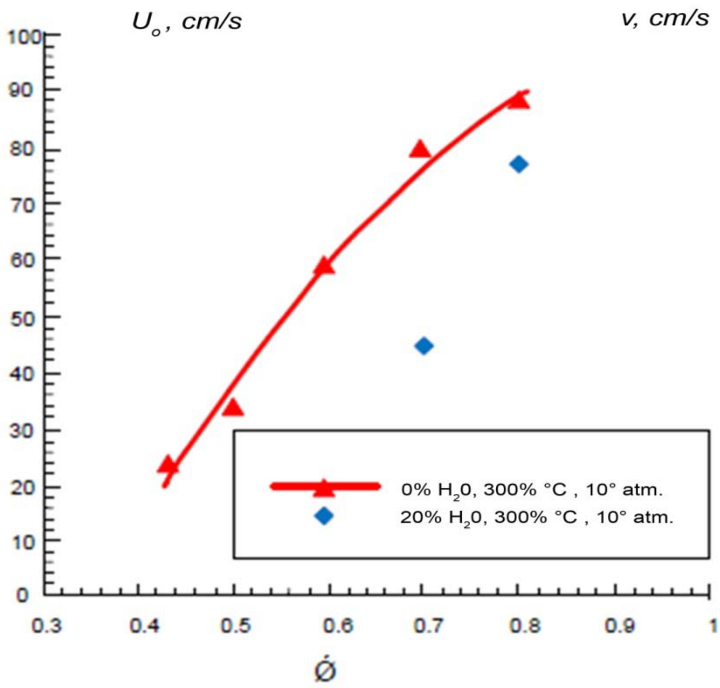
High content of hydrogen (up to 47%) in MHM allows reducing fuel carbon index and reducing carbon dioxide and other greenhouse gases emissions.

Pilot studies of MHM combustion have shown, that there is a strong dependence of MHM normal combustion rate on ø fuel-air equivalence ratio when injecting water steam at p = 10 atm. and T_0 = 300°C. It has been shown that MHM demonstrates stable combustion even at substantial content (20% - 30%) of water steam as shown in fig. 5.

When injecting 20% of water steam at ø = 0.7, MHM combustion rate is about 45 cm/s, and without injecting water steam MHM combustion rate is about 78 cm/s.

The combustion rate is also influenced by the initial temperature and pressure. In the figure, when *ø = 0.7*, the MHM (20% H_2 + 80% CH_4) combustion rate at p_0 =1 atm., T_0 =22°C is 19 cm/s, and the MHM (20% H_2 + 80% CH_4) combustion rate in the air at p=10 atm. and T_0 =300°C so far is 78 cm/s.

An important conclusion, which is of practical importance: MHM demonstrates stable combustion in presence of large oxidizer (air) excess, which makes it possible for the engine to run at leaner mixtures.



Fuel-air equivalence ratio

Fig. 5. Impact of injecting 20% of water steam on normal combustion rate of the mixture (20% H_2 + 80% CH_4) in the air at p = 10 atm. and T_0 = 300°C

Conclusions

Process integration of waste gas heat recovery with low-temperature adiabatic methane conversion would allow designing a gas turbine plant of a new type with high energy and environmental performance ("Tandem" process). The increase in gas turbine plant capacity as compared to basic GTP design can be up to 70-80%, fuel consumption can be reduced by 35-40%, accompanied by a sharp decrease in NO_x emissions (4 to 8 times) and simultaneous CO emissions decrease (up to 10 times).

The use of production process and implementation of methane-hydrogen mixtures corresponds to the benefit of Gazprom, including the implementation on compressor stations, on gas production fields, in gas chemistry, as well as its use as a high-tech exportable energy carrier, being a promising direction for diversification and enhancement of natural gas efficiency.