## PERSPECTIVES OF USING NEW ENERGY SOURSES BASED ON METHANE-HYDROGEN FUEL

O.E. Aksyutin, A.G. Ishkov – **Gazprom JSC**, V.G. Khloptsov, V.A. Kazaryan – **Podzemgazprom Ltd**, A Ya. Stolyarevsky, **Centre Kortes** 

# International Gas Union Research Conference Republic of Korea, 19-21 October 2011.

## Summary

Nowadays efficient use of energy resources appears to be the main factor of different industries competitiveness and necessary condition to socio-economic development of Russia. Now more than 50% of the energy balance fall to the share of natural gas, so gas-saving in all industries is of paramount importance. Energy-saving is also of great nature conservation significance, and it facilitates solving global environmental problems.

Prospects for application of innovative hydrogenous energy carriers produced from natural gas in gas industry are dealt with in the report. There are innovative trends of natural gas economy formulated, that allow efficient production of hydrogen-methane mixtures (HMM) with H-share of 44-48% to be organized on the basis of routine technologies, procedures and catalytic agents.

#### Progress in application of hydrogen and hydrogen-methane mixtures

Hydrogen is the most efficient and environmentally friendly fuel. World's production of hydrogen exceeds 550 billion m<sup>3</sup>. Hydrogen 2.75 times exceeds benzine in terms of a mass unit lower heating value, and it features a higher lowest limit and significantly wider range of inflammation when mixed with air (from 4 to 75% of volume); by a factor of ten higher laminar flame spreading rate (approximately 3 m/sec); much lower values of stoichiometric mixture inflammation initiation energy (0.018 mJ) and extinguishing distance (0.6 mm), and much higher combustion (2300 K for laminar flame in air) and autoignition in air temperatures (850 K). These unique features of hydrogen ensure the possibility to increase the heat engine performance indexes by 1.5-1.7 times,

and hydrogen engine's actual cycle is essentially closer to theoretical one, than that when any hydrocarbon fuel is used. Conversion to an alternative fuel becomes an important stage of pure hydrogen application as fuel for motor vehicle transport, and namely developing hydrogen electric vehicle with fuel element and electric drive. In this case emission toxicity is dramatically reduced (by 2-4 times), hydrogen fuel consumption decreases 35-40%, and operating efficiency increases 20-25%.

According to methane adiabatic conversion technology (MAC), when off-site hightemperature energy sources are applied (nuclear, solar), more than 4000 m<sup>3</sup> of hydrogen are produced of each 1000 m<sup>3</sup> of natural gas. The HMM output with H 48% makes only 1500 m<sup>3</sup> per 1000 m<sup>3</sup> of natural gas when using MAC process for producing HMM without off-site energy carriers.

The MAC technology considerably simplifies the production process because there is no need in oxygen production and it runs under lower temperatures (to 680°C); neither it requires high power and capital consuming water electrolysis and is based on large-tonnage chemistry routine technologies, procedures and catalytic agents.



Fig. 1. HMM production layout at convective heating: RP – reactor plant; HTHC – high-temperature heat carrier; GVM – gas-vapor mixture; HMM – hydrogen-methane mixture.

## HMM production technology peculiarities

As a catalytic agent activity is of an empirical value and can differ from desired parameters, as well as it can be decreased in the run, there is a possibility to preheat to be converted gas-vapor mixture (GVM) up to the higher temperature than rated one.



Fig. 2. Dependence of the required heating temperature on catalyst agent activity.

Hereupon, GVM temperature when coming out of the preheaters and coming into the adiabatic reactors is considered to be equal 680°C.

As far as hydrogen-methane mixture produced in experimental unit is intended to be used as fuel in gas pumping plants, so its fuel thermodynamic parameters are defined (table).

Thermodynamic parameters of flows when producing HMM from natural gas

Parameter	Dependence of a parameter value on direction of gas flow	
	Input <b>Natural gas</b>	Output Hydrogen-methane mixture to consumer
Consumption, kg/hour	423.2	2304.0
Pressure (excess.), atm.	30.000	29.73
Temperature, °C	10.000	540.7
Molar mass, kg/kmol	16.21	16.42
Density (RP), kg/m <sup>3</sup>	22.685	7.384
Enthalpy, kJ/h	-1.976E6	-2.371E7

Parameter	Dependence of a parameter value on direction of gas flow	
	Input <b>Natural gas</b>	Output Hydrogen-methane mixture to consumer
Vapour/gas ratio	0.000	2.095
Composition (% humidity)		
Carbon dioxide, CO2	0.065	3.262
Carbon monoxide, CO	0.000	0.233
Hydrogen, H2	0.000	13.621
Nitrogen, N2	0.780	0.145
Argon, Ar	0.000	0.000
Water, H2O	0.000	67.694
Methane, CH4	98.836	15.045
Ethane, C2H6	0.242	0.000
Propane, C3H8	0.055	0.000
Butane, C4H10	0.016	0.000
Pentane, C5H12	0.006	0.000
Total	100.000	100.000

If modern gas-turbine compressor or power plants are equipped with heat recovery units based on MAC technology producing HMM, the efficiency factor can exceed 50% even without using regeneration and steam installations, and when loaded by heating appliances the useful application of gas can reach 60-62% with a dramatic reduction of NO<sub>x</sub> emission indexes to 10–25 ppm (20–50 mg/m<sup>3</sup>).



Fig. 3. Influence of hydrogen content in HMM on natural gas flame speed.

In methane-air mixtures (with the same laminar flame speed), turbulent combustion rate is, on the contrary, higher within the poor range, than within the rich one. Addition of hydrogen into poor air-hydrocarbon mixtures (retaining poor composition in general) dramatically rises the turbulent mode flame speed (with slight change of laminar flame speeds), herewith, the comparative effect is higher with heavy hydrocarbons, whereas the highest combustion rate is achieved when hydrogen is added to methane.

Fig. 4 below shows the engines' characteristics designed by P&T project when working on pure hydrogen (NO<sub>x</sub><2 mg/nm<sup>3</sup> or <5ppm), and on natural gas with NO<sub>x</sub> emission corresponding to TA-LUFT (NO<sub>x</sub><500 mg/nm<sup>3</sup>) and  $\frac{1}{2}$  TA-LUFT (NO<sub>x</sub><250 mg/nm<sup>3</sup>).



Fig. 4. Hydrogen fuel efficiency in terms of nitrogen oxide emission.

When working on natural gas (NO<sub>x</sub><250 mg/nm<sup>3</sup>) excess air ratio  $\lambda$  was  $\lambda$  = 1.62 (exhaust gases temperature = 530°C), and when working on hydrogen –  $\lambda$  =2.58 (exhaust gases temperature = 395°C).

Besides the fact that the engines when working on hydrogen demonstrated higher indicated efficiency (owing to higher flame speed), and also due to lower temperature in combustion chamber,  $NO_x$  emission level was extraordinarily low (less than 2 mg/nm<sup>3</sup> at 5% O<sub>2</sub>). This actually allows to admit zero emission of hazardous substances (CO and  $NO_x$  emission is absent when working on hydrogen, because there is no carbon within fuel composition).

Figure 5 demonstrates an example recently achieved  $NO_x$  emission levels of GE Jenbacher engines when working on pyrolysis, coke, ferroalloy and other hydrogenous gases.



Fig. 5. Efficiency of different composition hydrogen-methane mixtures on nitrogen oxides emission.

The first column reflects  $NO_x$  emission when gas-piston plants are working on pyrolysis gas (gasification of waste). In this case mean effective pressure in a cylinder is accepted as =1.0 MPa. In general it is possible to drop  $NO_x$  emission below 70 mg/nm<sup>3</sup> by means of further depletion of the mixture, but this will lead to the engine capacity decreasing and aggravation of the general economic indexes of the station.

There is a HyGen brand gas, which is a mixture of methane and hydrogen. Taking into account GE Jenbacher experience it is possible to assert that it is expedient to use a hydrogen-methane mixture with  $H_2$  proportion from 15% and up in order to drop  $NO_x$  emission below 50 mg/nm<sup>3</sup>. The lower hydrogen content does not accelerate the mixture combustion rate, and this does not allow working with higher air excess. It is shown below how the hydrogen proportion in methane accelerates the combustion rate and thus widens the "gap" of the mixture combustibility.

Works performed by specialists of the Institute of Chemical Physics of the Russian Academy of Science demonstrated that hydrogen addition into natural gas improves combustion stability in poor mixtures range (combustion with fuel excess ratio  $\varphi = 0.43$ ).

## Works on HMM production technology.

Nowadays an experimental plant with the capacity of 1000 nm<sup>3</sup>/h of HMM is being constructed at Perm compressor station (CS), the plant to be tested together with a gasturbine engine. The functional diagram of the plant is given in Fig.6.



## Functional diagram of hydrogen-methane mixture (HMM) production plant

Fig.6. Functional diagram of the experimental technology of HMM production at Perm CS

Greater perspective effect can be achieved if nuclear conversion centers (NCC) are built based on MHR-T high-temperature modular helium reactor plants being developed in Russia to produce converted gas or hydrogen-methane mixtures. In this event the effect is greater both due to scaling factor, that lowers cost per unit upon increasing the power source capacity, and owing to possible use of the existing gas transportation infrastructure. Besides, the cost of the MHR-T unit itself decreases because the layout and composition of equipment are being simplified and the active zone outlet temperature is lower. Launching of the units of an S nuclear power technology station can be performed step-wise accompanied by incremental growth of HMM consumption. Practically no changes arise in hydrogen consumption plants technology, because transition to HMM causes increase in hydrogen output or synthesis of gas from the production lines. The European NATURALHY project is developing a strategy of European economy transition to hydrogen power engineering through gradual conversion of natural gas distribution structure to methane and hydrogen mixture. The project shows that such transition is technically prepared, and with tariffs (cost) for lowering green-house gas emissions as much as 30 Euro/t of  $CO_2$  transition to HMM in European countries at present produces an economic effect that covers all necessary costs of hydrogen production. In our country procedure for charging for green-house gas emissions is not yet effective due to a reserve for such emission lowering, which occurred during the country's economy collapse at the end of the past century, but it is expected that after 2012 obligations on reducing  $CO_2$  emission will be in force in Russia too. Then launching MHR will be a powerful means of this program implementation.

Functional diagram of a nuclear energy technology plant for high-potential heat generation to produce hydrogen through vapour conversion of methane (VCM) is presented in Fig.7.

Vapour conversion of methane is now the main industrially developed and accommodated process for the first stage of adoption of hydrogen production technology with the use of high-temperature helium reactor (HTHR). The world hydrogen production is based on this process. Combination of HTHR and VCM allows approximately 40 % reduction of natural gas consumption, and consequently expenses on hydrogen production. The cost effectiveness of VCM adoption is determined by gas price and by the consumed heat temperature. The required temperature of vapour-gas mixture heating should not be less 800°C, while further temperature increase does not influence the process efficiency.



Fig.7. Functional diagram of MHR -100 VCM.

Thermal energy is led from the reactor to actuating medium of the second circuit (vapour-gas mixture) in the high temperature heat exchangers (HTHE), which are a component part of a thermo-conversion installation (TCI).

## References

- V.A. Kazaryan, P.G. Tsybulsky, N.N. Ponomaryov-Stepnoy, A.Ya. Stolyarevsky, "Carbon Adiabatic Conversion Technology for Energy Carriers Production." In collection of reports at the Innovative Technologies in Oil, Gas, Energy and Communication Sectors, XIX<sup>th</sup> International Congress, 2009, Ufa. Technological Science Academy. 2010.
- Phillips, J.N. and R.J. Roby, "Enhanced Gas Turbine Combustor Performance Using H2-Enriched Natural Gas," ASME technical paper 99-GT-115, presented at ASME Turbo Expo '99, Indianapolis, June 1999.
- A.Ya. Stolyarevsky, "Technology of hydrogen-methane mixture production for motor vehicle transport", Science and Technology in Gas Industry Journal, No. 3, 2008, p.p.73-80.
- N.N. Ponomaryov-Stepnoy, A.Ya. Stolyarevsky, V.P. Pakhomov, "Atomic-Hydrogen Energy Industry. System Aspects and Key Problems". Moscow: Energoatomizdat, 2008.
- V.I. Kostin, N.G. Kodotchigov, A.V. Vasyaev et al., "MHR-T innovative nuclear technology for combined production of hydrogen and power". Report at the 2<sup>nd</sup> Conference "Materials for Nuclear Technology" (MAYAT-2), September 26-30, 2005.
- A.Ya.Stolyarevsky, "Nuclear Technological Complexes on the Basis of High-Temperature Reactors". Moscow: Energoatomizdat, 1988.
- F.V. Mitenkov, N.G. Kodotchigov, A.V. Vasyaev et al., "High-Temperature Gas-Cooled Reactor – Power Source for Industrial Hydrogen Production". –Atomic Energy, 2004, vol. 97, issue 6, p.p. 432–446.
- N.N. Ponomaryov-Stepnoy, A.Ya. Stolyarevsky, N.G. Kodotchigov, "Possibilities and Prospects of Using Nuclear High-Temperature Reactors to Supply Energy-Intensive Works with Energy Carriers". In the theses collection of the Regional Atomic Energy Industry inter-branch scientific engineering conference (Atom-Region-2009), November 17-18, 2009, Nizhny-Novgorod.