Development of Small-Size Syn-Gas Generation Units by Partial Oxidation of Natural Gas

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Since the last decade of the XX century, the third wave of natural gas popularity as a motor fuel has been extending in the world economy. The average annual market of gas-fueled vehicles has been made up about 20% for recent years, and there are over 5,3 mln. gas-fueled vehicles in operation for today, and among them 600 ths. automobiles are running on European roads [1].

Usage of natural gas, world stock thereof exceeding considerably the oil reserves (in heat equivalent), will allow in nearest term to solve partially the problem of petroleum fuel saving, to improve environment, and to create a vast infrastructure of transport supply with natural gas, which in future can become a foundation of the hydrogen infrastructure. Actually, natural gas can't solve the problem of environmentally clean and efficient energy. The mankind believes these problems to be solved via hydrogen energy.

Most likely, a wide application of hydrogen and hydrogen-containing gas (syn-gas) can start as an additive to main fuel (gasoline, natural gas), since unique properties of hydrogen as a motor fuel enables stable combustion of depleted fuel mixtures while adding even rather small amounts thereof to air-gasoline and air-gas mixtures that results in considerable fuel saving, especially in the small loads area [2].

For on-board syn-gas generation, most reasonable is to use the catalytic reaction of partial oxidation of natural gas. For last five years, a large scope of R&D works has been fulfilled in this area through cooperative efforts of several Russian institutions (Institute of Catalysis, RFNC-VNIIEF, Sarov, JSC AVTOVAZ, Tolyatti). In the result of such cooperation, several syn-gas generator samples were developed and tested. In 2001 in Tolyatti, short-term bench tests of the engine VAZ-2111 using gasoline with syn-gas additives obtained in the experimental catalytic reactor by natural gas partial oxidation were carried out. The tests confirmed the possibility of the engine stable operation on depleted air-gasoline fuel mixture with syn-gas additives. The gasoline consumption was reduced by 42% for idle running and by 24% in operation mode: Pe=0,2 MPa and n=2185 rev./min. Simultaneously, for idle running it was recorded a considerable decrease (by about 10-15 times) of the level of CH and Nox emissions, the CO content in emissions didn't exceed 0,2 vol.%. Similar results were obtained while short-term testing of the engine M406 ("Volga" car) in 2003 at NAMI (Moscow). The engine operated on the depleted mixture of natural gas and syn-gas. It was shown experimentally that while adding syn-gas the toxicity of emissions is reduced till the level of 300-400 ppм for carbon oxides and till 20-30 ppм for nitrogen oxides. Along with toxicity decrease, the natural gas consumption was lowered by 20%.

Thus, application of syn-gas as an additive to liquid or gas fuel used in spark internal combustion engines provides a considerable decrease of carbon oxide and nitrogen concentrations in engine exhaust gases and enables to meet the EURO-4 norms and regulations without using catalytic converters and to reach overall reduction of hydrocarbon fuel consumption by 20-25% under urban cycle conditions via maintaining the engine stable operation while using depleted fuel mixtures.

Based on the above work results, the JSC AVTOVAZ has developed a concept of step-by-step transition to hydrogen energy while using alternative fuels. The concept [3] envisages creation of automobiles with the ICE operating on natural gas, natural gas mixed with on-board produced hydrogen-containing gas, as well as (in long-term) creation of fuel cell-based vehicles with on-board processor to generate pure hydrogen from natural gas.

The developed syn-gas generator comprises: a catalytic reactor, a built-in heat exchanger for heat removal from syn-gas and heating of reactants; a catalyst starting unit; an air-gas conditioning unit (meter-mixer). A scheme of ICE supply with the fuel mixture containing syn-gas is presented in Figure 1 [2].

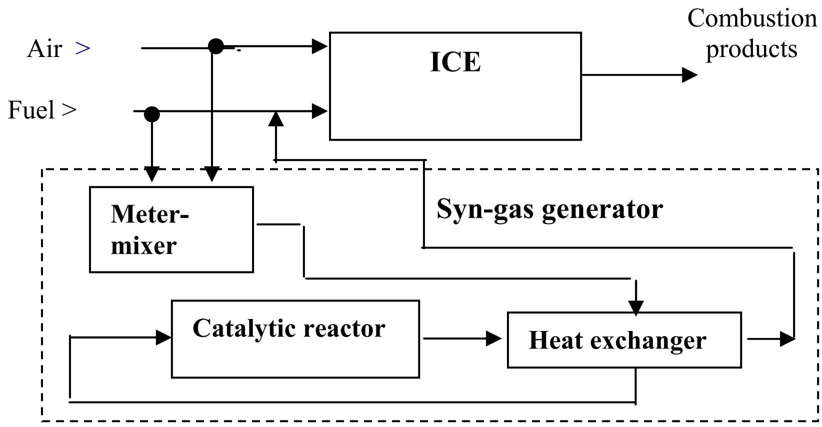

Figure 1 – Scheme of ICE supply with fuel mixture containing partial oxidation products

Some part of the fuel (natural gas) is used for partial oxidation:
$\mathbf{CH_4 + ½ (O_2 + 3{,}76\ N_2) \rightarrow CO + 2H_2 + 1{,}88\ N_2}$, and then after cooling it is mixed with main fuel and is supplied to the ICE.

The fuel partial oxidation reactor design, requirements to partial oxidation catalysts depend on the syn-gas generator application.

The process of syn-gas generation from natural gas is effected at high temperatures and high reaction rates on the catalyst. Most critical issues for the catalyst are the reactor start-up time, high dynamics of the reactor output change that affects heat and mass transfer processes, temperature distribution in catalyst and reaction products.

Unlike the syn-gas generator designed for stationary fuel cell-based power plants, which should have the lifetime of at least 40 ths. hours and rather lasting catalyst start-up period (up to several dozens of minutes), the on-board syn-gas generator at relatively small lifetime (at most 5 ths. hours) should have small sizes, a short start-up time (at most 1 min.) and more rigid operation conditions: fast change of the reactor output and a wide range of regulation thereof, a wide temperature range while operation within the automobile.

While developing the on-board syn-gas generator, much attention was paid to the catalytic reactor start-up technology.

To start a catalytic unit, the catalyst should be heated up to the temperature value of about 450÷650^{0}C (depending on catalyst type). In the process of studies it was found out that the most suitable way is the catalyst heating with fuel combustion products. The air-gas mixture is ignited with a spark at the excess air coefficient α = 0,95÷1 with further α decrease along with the catalyst heating. Using the above method, the catalytic reactor in the syn-gas generator was started during 40-70 sec.

Different catalytic layer types were investigated. While choosing a final syn-gas generator design, preference was given to radial reactors, which have smaller heat losses and hydraulic resistance.

One of the conditions to provide maximum selectivity of the natural gas partial oxidation process is preheating of the air-gas mixture at the catalyst inlet that can be effected by a recuperative heat exchanger, wherein reaction products (syn-gas) are heating the air-gas mixture. That's why, the syn-gas generator should include the recuperative heat exchanger.

We think porous metal catalysts, as well as conventional granular catalysts (e.g., Ni, La/Al_2O_3) to be most suitable catalyst types for application in the on-board syn-gas generator.

Figure 2 presents the reactor scheme, and Figure 3 - a photo of components of the syn-gas generator manufactured at the Boreskov Institute of Catalysis (Novosibirsk) that meets the above requirements.

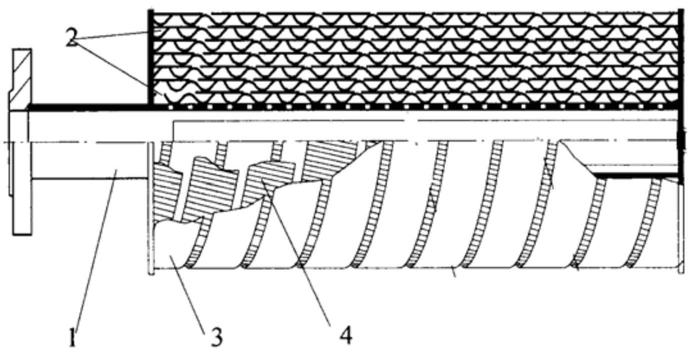

Figure 2 – Schematic diagram of a radial reactor for methane conversion into syn-gas

Figure 3 - Photo of a catalytic reactor with a gas-distributing tube and a layer of reinforced porous metal catalyst

The reactor is a cylindrical construction, inside which the gas-distributing unit 1 is located that is a perforated tube. The catalyst layer 2 is formed from plane 3 and corrugated 4 gas-permeable catalyst stripes winded round the gas-distributing tube and sintered with it.

A photo of the another radial reactor option that provides quick catalyst start-up using natural gas oxidation products is presented in Figure 4.

Figure 4 – Photo of a radial reactor

The reactor has been developed at RFNC-VNIIEF, which uses the granular catalyst Ni, La/Al_2O_3. This reactor design resolves the problem of overheating of the catalyst front layer and of rapid start-up. Figure 5 shows temperature curves T1, T2, T3 (centigrade) in the catalyst front layer, the middle layer and the catalyst outlet, respectively, in the catalyst heating mode. The air-gas mixture is ignited with a car spark. The reactor start-up time makes up approximately 35 sec.

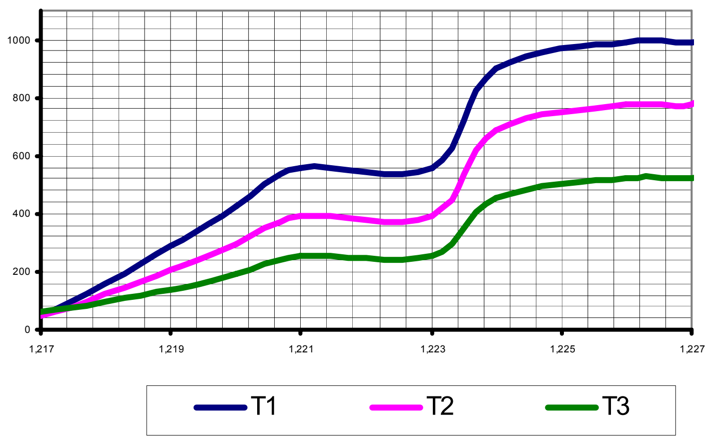

Figure 5 – Heating mode curves of the granular catalyst (Ni, La/Al_2O_3)

During initial 14 seconds within the time period of 1,217-1,221 hr. (Figure 5) the catalyst was heated with natural gas combustion products at the excess air coefficient α ~ 1, during subsequent 7 seconds the coefficient α was reduced from 1 to 0,35, and then during 14 sec. the catalyst was heated with the heat of the exothermic reaction of natural gas partial oxidation.

The radial reactor shown in Figure 4 has a maximum natural gas output of 4,5 m^3/hr. The syn-gas composition at different output values obtained while testing is presented in Table 1.

Table 1

№	Natural gas flow rate, m^3/hr	Air flow rate, m^3/hr	Syn-gas composition, % vol.				
			H_2	CO	CO_2	CH_4	N_2
1	1,5	5,25	27,80	13,84	3,45	2,01	52,9
2	1,5	3,9	32,19	15,78	2,23	3,8	46,0
3	2,7	8,1	28,93	14,83	2,71	3,30	50,23
4	4,0	11,2	30,74	15,65	2,32	2,97	48,32
5	4,5	12,6	31,34	15,79	2,25	2,82	47,8

Currently, within the ISTC Project #3234 “Development of highly efficient oxygen-conducting membranes and small-size pure syn-gas generators on basis thereof” the works on development of a syn-gas generator with a membrane reactor with oxygen-conducting membranes are being fulfilled. Such a reactor will allow to obtain syn-gas not diluted with nitrogen while partial oxidation of natural gas with air oxygen.

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