Matrix conversion of natural and associated petroleum gases to syngas – new developments and possibilities

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Abstract

The principal possibility of technological implementation of relatively simple and highly productive reformers for natural gas conversion into syngas and hydrogen based on the surface combustion (matrix partial oxidation) of natural gas has been demonstrated. It was shown the possibility to obtain syngas with $[H_2]$ up to 54%, $[CO]$ up to 31%, and ratio H_2/CO up to 1.7. The specific volume capacity of matrix reformers exceeds that of conventional steam reformers at any rate in 10 times. At that, they allow to convert into syngas without fractionation and deep cleaning hydrocarbon gases of practically any origin and composition.

1. Introduction

Methane and hydrogen are very popular as a clean energy and transportation fuels including their use for space propulsion. What is more, according to recent estimates, different kinds of traditional and nontraditional hydrocarbon gases present the most abundant hydrocarbon fossil resources which expect to provide energy for global economy during many decades [1-3]. However, the conversion of these huge gas-phase resources into hydrogen and very demanded ecologically clean synthetic liquid fuels and other petrochemicals is one of the most complex scientific and technological tasks Just this problem restricts the practical development of "hydrogen energy", as well as development of gas-chemistry. It is very difficult to transform methane, which is the main natural gas component, into hydrogen and other chemicals [4,5] due to its high thermodynamic stability and relatively low reactivity. That is why practically in all large-scale industrial gas-chemical processes natural gas is preliminary converted into syngas. However, modern technologies for syngas production are very complex, energy intensive and consume up to 60-70% of all spending for obtaining such products as methanol or synthetic liquid hydrocarbons [6]. At modern crude oil price it makes unprofitable even huge world-class gas-chemical enterprises such as recently commissioned Pearl GTL and Oryx GTL in Qatar [7,8]. These technologies can't be used as a base for profitable distributed production of hydrogen, which is the main reason that restrains the development of clean "hydrogen energy". Therefore, for the development of profitable gas-chemistry technologies that will allow conversion of huge world natural gas resources into highly demanded petrochemicals, liquid motor fuels and hydrogen to feed ecologically clean hydrogen vehicles and stationary fuel cell power plants more effective technologies for syngas production are urgently needed.

2. Matrix conversion of hydrocarbons to syngas by atmospheric air

Recently, we have suggested principally new non-catalytic method for the conversion of hydrocarbon gases into syngas. This technology is based on the flameless surface combustion of natural gas in the vicinity of the inner surface of gas-penetrable geometrically closed volumetric (3D) matrixes [9-11]. This auto-thermal method allows obtaining very high specific volume capacity, at any rate ten times higher than that of traditional technologies, thus providing the possibility for profitable operation of not only large-scale but as well small-scale reformers. It allows stable conversion of very rich hydrocarbon gas – oxidant mixtures with value of oxygen excess coefficient $\alpha = [O_2]/2[CH_4]$ as low as 0.32-0.36. The technology was previously tested at pilot plant level for methane-air mixtures with input flow up to 20 m^3/h and has shown very promising results [12]. At complete conversion of oxygen it was possible to achieve natural gas conversion above 95% with concentration of H_2 up to 24%, that of CO up to 14%, and H_2/CO ratio up to 1.7. The possibility to operate at enhanced pressures (up to 5 atm) has been also demonstrated.

The comparison of these experimental results with the calculations of thermodynamically equilibrium composition of syngas obtained at natural gas oxidation by air shows that actually the maximal possible syngas yield was achieved. Therefore, taking into account the structural simplicity and high productivity of such reformers, this approach allows to develop relatively simple and profitable reformers for small-scale conversion of natural gas or associated petroleum gas (APG) into liquid products using thus produced inexpensive nitrogen-diluted syngas (with ~50 vol.% of N_2) in subsequent series of several reactors for synthetic liquid hydrocarbons or methanol synthesis without the use of expensive oxygen plant and without recycling of outgoing syngas [13,14].

As it was shown in [12] even the slight enrichment of air by oxygen significantly improves the syngas yield. The concentration 26% of oxygen in air was enough to decrease the oxygen excess coefficient to unique low value $\alpha = 0.28$ which is very close to the stochiometric ratio $\alpha = 0.25$ of the reaction

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$$
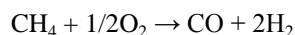
At that, the conversion of methane practically attained 99% with its residual concentration in syngas less than 0.3%. The concentration of H_2 increased to 29%, that of CO to 15.7%, and the ratio H_2/CO up to 1.85.

3. Matrix conversion of natural gas by oxygen. Experimental part

Nevertheless, there is the barest necessity in syngas undiluted by nitrogen and in undiluted hydrogen for numerous technological applications. First of all, nitrogen free syngas is necessary for the traditional synthesis of methanol or Fischer–Tropsch products. But there are also a lot of applications in different type of power production engines and devices. Partial conversion of fuel to syngas is a promising way to increase the efficiency of power engines and decrease the emission of harmful pollutants. And undiluted hydrogen obtained from syngas, apart from many other technological applications, is necessary to feed fuel cells to produce clean electricity.

In this study we have investigated the possibility of natural gas conversion with highly enriched air or oxygen. The construction of the used matrix reformer (Figure 1) was different from that used in [12]. It has two symmetrically situated matrix units that include flat round matrix with diameter 200 mm and thickness 8 mm fabricated from metallic foam or pressed twisted Chromel wire. The mixture of methane, oxygen and nitrogen enters the reformer via side flanges. Before the entrance side of the each matrix apertures with diameter 150 mm were installed to restrict the gas flow trough peripheral part of the matrix with lower temperature. At a distance of approximately 20 mm after exit side of the matrix it was installed the perforated stainless steel screen to reflect the IR radiation of the flame front back to the matrix. In both sides of the matrix and in volume before and after the matrix thermocouples were installed. The conversion products were removed through a side socket athwart to the entrance flow. The composition of conversion products was determined by gas chromatography.
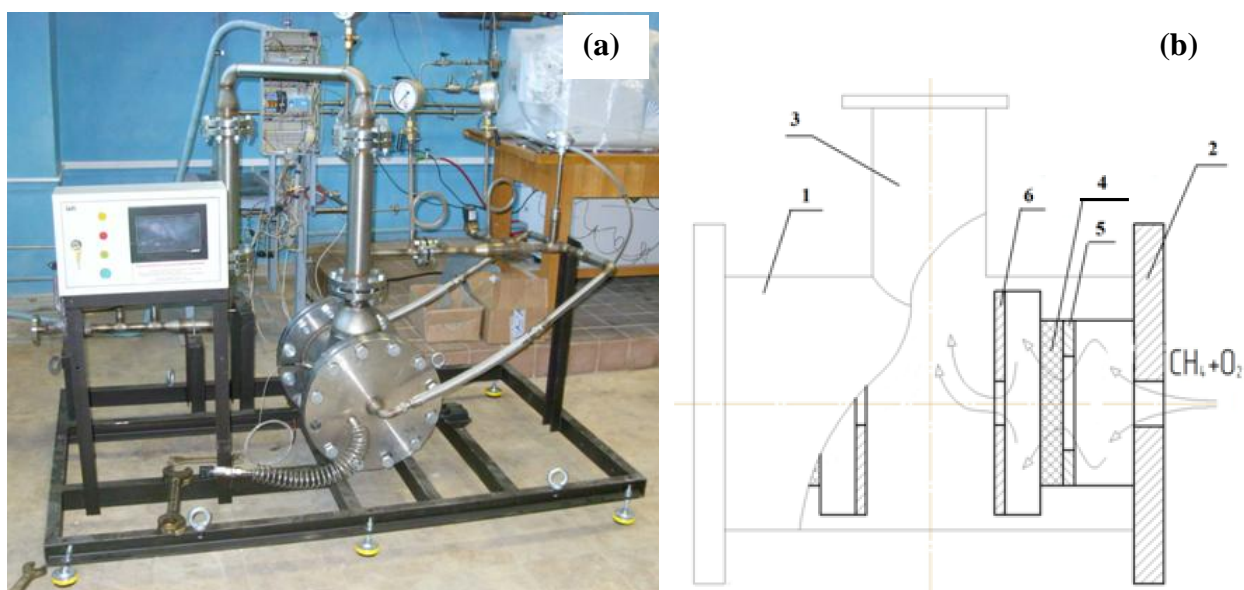

Figure 1: General arrangement (a) and the scheme of inner construction (b) of matrix reformer for natural gas conversion into syngas with enriched air and oxygen. Natural gas flow up to 10 m^3/h. 1 - core vessel; 2 – flange; 3 – discharge nozzle; 4 – matrix; 5 – inlet aperture; 6 – radiation screen.

4. Matrix conversion of natural gas by oxygen. Results and discussion

Results of the investigation of the dependence of conversion products on oxygen concentration in oxidizing gas are presented in Figure 2 and Table 1. In the optimal range of the oxygen excess coefficient $\alpha = 0.34\text{-}0.36$ the concentration of principal syngas components increases proportionally to the increase of oxygen content in oxidizing gas.
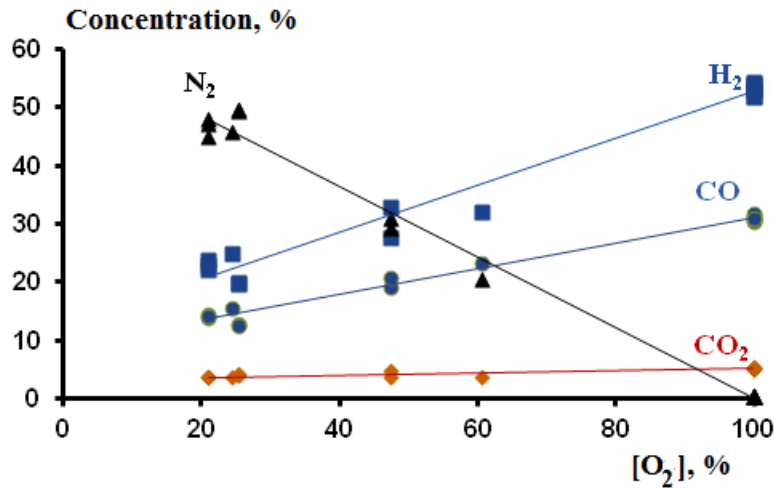

Figure 2: Dependence of the concentration of main conversion products on the oxygen content in the oxidizing gas. The oxygen excess coefficient $\alpha = 0.34\text{-}0.36$.

Table 1: Parameters of syngas obtained at matrix conversion of methane by enriched air and oxygen

O_2, %	Concentration of products, %						H_2/CO	Conversion, %	
	H_2	CO_2	O_2	N_2	CH_4	CO		CH_4	O_2
21,0	22,2	3,6	0,6	47,1	0,5	13,8	1,61	97,0	95,2
21,0	23,0	3,6	0,6	48,0	0,6	14,4	1,60	96,6	95,3
21,0	23,7	3,7	0,6	45,1	1,0	14,2	1,67	94,3	95,0
24,4	25,0	3,6	0,8	45,9	0,6	15,6	1,61	97,1	94,9
25,4	19,9	3,9	1,6	49,3	1,9	12,8	1,55	91,4	90,5
25,4	19,6	4,2	1,3	49,8	1,9	12,6	1,56	91,9	92,3
47,3	27,8	4,7	0,6	29,2	9,9	19,2	1,45	74,6	97,8
47,3	33,0	3,8	0,2	31,1	6,2	20,9	1,58	83,9	99,2
60,5	32,1	3,7	0,4	20,4	8,4	23,1	1,39	81,5	98,8
100	51,8	5,5	0,2	0,5	9,2	30,3	1,71	84,1	99,6
100	53,4	5,3	0,0	0,4	7,9	30,6	1,74	86,2	100,0
100	54,0	5,2	0,0	0,4	7,2	31,2	1,73	87,0	100,0
100	51,9	5,5	0,0	0,4	9,3	30,8	1,68	84,1	99,9
100	54,5	5,1	0,0	0,3	6,4	31,4	1,74	88,4	100,0
100	53,8	5,1	0,0	0,3	7,2	31,7	1,70	86,7	100,0
100	53,0	5,2	0,0	0,4	8,0	30,9	1,72	85,9	100,0

Although the matrix methane oxidation by oxygen proceeds at more rigid conditions with more intense heat release at matrix surface, these investigations have shown the complete conversion of oxidizer with the conversion of methane 87-88%. Additional measures to stabilize the process and increase the conversion of methane is under the

progress now. At the oxidation by enriched air the ratio H_2/CO increases 1.7 and weakly depends on the concentration of oxygen in the oxidizer (Figure 3).
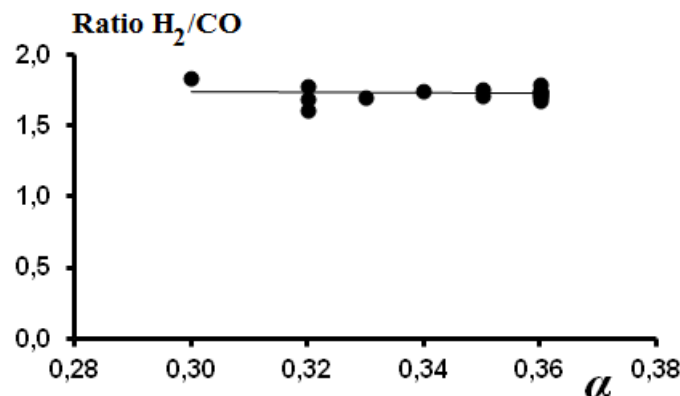

Figure 3: Dependence of the ratio H_2/CO on oxygen excess coefficient α at the methane oxidation by enriched air.

The conversion of methane increased with the increase of the oxygen excess coefficient and reached 87-88% at $α = 0.36$ (Figure 4) which, evidently, can be considered as optimal at the oxidation by oxygen.
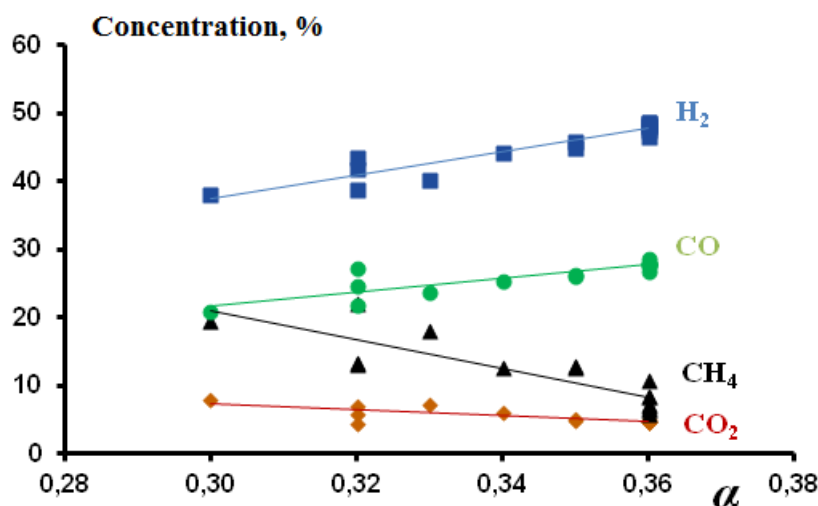

Figure 3: Dependence of the concentration of main conversion products on the oxygen excess coefficient α at the oxidation of methane by oxygen.

Although the process is only under development, it was already have been shown the possibility to achieve natural gas conversion as high as 90% with concentration of H_2 up to 54%, that of CO up to 31%, and H_2/CO ratio up to 1.7. And results of lifetime testing have shown the stability of the process in the regime providing these parameters of syngas during several hours of continuous operation.

As it was mentioned previously, the principal possibility to operate at enhanced pressures (up to 5 atm) has been also shown experimentally with this type of matrix reformer. This possibility is attractive for the use of syngas in production of methanol or synthetic liquid hydrocarbons where the use of syngas pressurized to 20-40 atm is preferable. However, very high heat release on the matrix surface which is proportional to pressure demands new technological solutions in the organization of this process, different from those which were successful for the conversion at atmospheric pressure. And in the case of conversion into syngas of associated petroleum gases with pressure usually no higher than 5 atm, it can turned out that it is economically is preferable to convert these gases just at this pressure with subsequent compression of produced syngas instead of preliminary compression of such multi-phase system as associated petroleum gas.

5. Advantageous and prospects of matrix reformers

Thus, principally new type of non-catalytic auto-thermal reformers to convert hydrocarbon gases to syngas (and hydrogen) was developed and tested at operation with air, enriched air and oxygen. Below are listed the main advantages of matrix reformers:

- Matrix reformers are based on non-catalytic partial oxidation of hydrocarbon gases and run in auto-thermal regime, therefore need no additional input of heat or energy;
- Very high specific volume capacity, at any rate 10 times exceeding that of steam reforming, makes matrix reformers very compact and significantly less expensive than traditional reformers;
- High specific volume capacity, the absence of catalyst and simplicity of fabrication and operation significantly decrease the operation costs.
- Low capital investments (CAPEX) and operation costs (OPEX) allow profitable operation not only large-scale but as well small-scale reformers;
- The absence of catalyst allows one-stage conversion of hydrocarbon gases of practically any origin and composition without need in their preliminary fractionation and deep pretreatment.

The most evident consumers of matrix reformers are companies and territories with low-resources, below 3 billion m^3, natural gas deposits, companies that produce unconventional natural gas, including shale gas, and oil companies flaring APG. Very high spending for the construction and operation of gas pipe-lines and the absence of alternative profitable technologies for small-scale natural gas conversion into more easily transportable hydrocarbon liquids [7,8] make effective small-scale conversion of natural gas into syngas highly demanded. The World Bank even has declared that it is practically impossible to stop APG flaring before 2030 [15] due to the absence of effective small-scale Gas-to-Liquid (GTL) technologies which allows profitable small-scale APG conversion into syngas. Matrix conversion opens such possibility.

The development of effective matrix reformers will allow profitable conversion of abundant small-scale traditional and non-traditional gas resources into more demanded and easily transportable liquid chemicals and fuels. Distributed small-scale production of synthetic liquid hydrocarbons immediately at the places of gas recovery basing simple and highly productive matrix reformers allows involving in industrial processing many additional low-output sources of gas phase hydrocarbons which connection to pipe-lines are unprofitable.

Compact high-productivity matrix reformers allows distributed small-scale production of synthetic liquid hydrocarbons directly in sites of natural gas recovery thus involving in industrial exploitation short-life natural gas deposits for which the connection to gas-main pipelines also economically unreasonable. Such reformers allows to stop flaring of associated petroleum gases and to use as energy and petro-chemical feedstock significant additional hydrocarbon recourses.

Matrix technology can be also used for the production of hydrogen to feed ecologically-clean fuel-cell power plants and hydrogen vehicles in gas producing regions and elsewhere. Simple and compact matrix reformers can be also demanded as a source of reducing gas for metallurgy and other applications. Taking into account that such reformers can processing into syngas practically any types of gas-phase and even some types of liquid hydrocarbons, including petrol, they can provide the real possibility for developing of different kinds of hydrogen energy.

6. Conclusions

The principally new type of non-catalytic matrix reformers for the conversion of natural gas into syngas and hydrogen was developed. The main advantages of matrix conversion are: auto-thermal and non-catalytic nature of the process which excludes the necessity of introduction of additional heat and deep purification of feed gas; very high specific capacity increasing that of traditional technologies at any rate in 10 times; the possibility to convert without separation and deep pretreatment hydrocarbon gases of practically any origin and composition.

References

[1] Paltsev, S., H. D. Jacoby, J. M. Reilly, Q. J. Ejaz, J. Morris, F. O. Sullivan, S. Rausch, N. Winchester, and O. Kragha. 2011. The future of US natural gas production, use, and trade. *Energy Policy*. 39:5309–5321.

[2] Thomas, C. K. 2011. The economic impact of shale gas extraction: a review of existing studies. *Ecol. Econ.* 70:1243–1249.

[3] Moritis, G. 2011. World shale gas resources outside US assessed. *Oil Gas J.* 109:22.

[4] Arutyunov, V. 2014. Direct Methane to Methanol: Foundations and Prospects of the Process. Elsevier B.V., Amsterdam, The Netherlands.

[5] Arutyunov, V. 2013. Low-scale direct methane to methanol – modern status and future prospects. *Catalysis Today*. 215:243-250.

[6] Arutyunov, V. 2011. Oxidative conversion of natural gas. KRASAND, Moscow. (in Russian).

[7] Wood, D. A., C. Nwaoha, and B. F. Towler. 2012. Gas-to-liquids (GTL): A review of an industry offering several routes for monetizing natural gas. *J. Nat. Gas Sci. Eng.*, 9:196–208.

[8] Savchenko, V. I., I. A. Makaryan, and V. S. Arutyunov. 2013. Analysis of foreign industrial technologies for the processing of hydrocarbon gases and the evaluation of prospects for their sale to Russia's oil-and-gas chemical complex. *Mir Nefteproduktov*. No.11:3–12 (in Russian).

[9] Shapovalova, O. V., Young Nam Chun, V. S. Arutyunov, and V. M. Shmelev. 2012. Syngas and hydrogen production from biogas in 3D matrix reformers. *Int. J. Hydr. Energy*. 37:14040-14046.

[10] Arutyunov, V. S., V. M. Shmelev, A. N. Rakhmetov, O. V. Shapovalova, L. N. Strekova, and A. A. Zakharov. 2013. Oxidative conversion of hydrocarbon gases in the surface combustion mode. *Russ. Chem. Bull., Int. Ed*. 62:1504-1509.

[11] Arutyunov, V. S., V. M. Shmelev, A. N. Rakhmetov, and O. V. Shapovalova. 2014. 3D Matrix Burners: A Method for Small-Scale Syngas Production. *Ind. Eng. Chem. Res.* 53:1754–1759.

[12] Arutyunov, V. S., V. I. Savchenko, I. V. Sedov, V. M. Shmelev, A. V. Nikitin, I. G. Fokin, S. A. Eksanov, O. V. Shapovalova, and K. A. Timofeev. 2016. Experimental Studies of Natural Gas to Synthesis Gas Converters Based on Permeable Cavity Matrixes. *Russ. J. Appl. Chem.* 89:1816−1824.

[13] Jess, A., R. Popp, and K. Hedden. 1999. Fischer–Tropsch-synthesis with nitrogen-rich syngas: Fundamentals and reactor design aspects. *Appl. Cat. A*. 186:321–342.

[14] Arutyunov, V. S., V. I. Savchenko, and I. V. Sedov. 2016. Prospects of field gas chemical technologies using nitrogen-diluted syngas. *Neftegazokhimiya*, No.4:12-21 (in Russian).

[15] End of routine gas flaring at oil production sites urged by 2030. (http://www.ogj.com/articles/2015/04/end-of-routine-gas-flaring-at-oil-production-sites-urged-by-2030.html?cmpid=EnlDailyApril202015)