New prospects of low-scale gas chemistry

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Abstract. The large-scale industrial sources of conventional natural gas are limited and can be exhausted in the nearest future. But there are still a significant number of low deposit, remote, low-pressure fields, and abundant resources of unconventional gas including coal-bed methane, shale gas, gas hydrates. However, usually these sources are less intensive, short living and spread through a large area. So gas industry very likely will have to develop new low-scale technologies to explore and process such resources into more valuable and easily transportable liquid products to satisfy consumers in any point of the world as we do it now with oil and petrochemicals.

1. The problem

Due to all reliable forecasts, Natural Gas will be the main source of energy at any rate to the end of this century. Oil resources become more and more limited and expensive. “Clean coal” proved to be too expensive for practical use. Thermonuclear synthesis still needs dozens of years of thorough and expensive investigations before possible industrial application. So call “clean alternative sources” including biofuels, sun, wind, etc. in principal can’t meet the growing need in industrial power supply [1].

On the contrary, the resources of Natural Gas are large enough, and it is the cleanest fossil fuel. The basis of the modern gas industry is the conventional gas with total amount of world resources of about 200 trillion m$^3$ and predicted supply period of about 30 years (figure 1).

Meanwhile, the annual consumption of conventional natural gas has already exceeded 3 trillion m$^3$ and rapidly increasing (figure 1). To the beginning of this century it exceeded the volume of annually discovered resources (figure 2) which provoked the tension with gas supply on the world market and the increase of its price. The similar event in the oil industry occurred about 25 years ago, approximately in 1985, with well known consequences for oil market and the whole world economy.

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Although it is difficult to expect a discovery of a significant number of new giant conventional gas fields which can feed long-distance gas pipe systems, large gas liquefying or gas chemical plants of the type that were built in recent years, there are huge amount of gas hydrates and other unconventional sources. Therefore, in the nearest future, we will have to more and more intensively exploit low deposit, remote, low-pressure fields, and unconventional gas including coal-bed methane and shale gas. The recent industrial development of shale gas in the USA which now covers about 20% of demand and guarantee at least 30 years of supply (figure 3), evidently showed the tendency to less intensive, short living and spread sources.
Although unconventional sources are yet more expensive than conventional, this difference is not dramatic (figure 4) and rapidly diminishes. The production cost of shale gas has already reached $120-140 per 1000 m$^3$ of gas which makes it quite competitive in comparison with conventional gas from shelf or arctic deposits.
One of the most difficult problems of gas industry is a high cost of gas transportation which significantly exceeds the cost of transportation of oil and in many cases significantly exceeds the cost of gas production (figure 5). Now we relay mostly on a very expensive long distant pipelines and large-scale liquefying LNG plants to make gas accessible for remote consumers.

The other problem is a high cost of gas chemical processing, especially in comparison with processing of oil. It is very desirable to convert gas into more valuable and easily transportable chemicals and liquid fuels, but modern large-scale gas chemical GTL plants demonstrate only marginal profitability and need huge gas resources to provide at any rate several decades of operation to compensate billion dollars of capital costs.

![Figure 5. The cost for different methods of gas transportation.](image)

So to meet new potential sources gas industry will have to develop new technologies to explore, distribute and process such resources into more valuable and easily transportable products to satisfy consumers in any point of the world as we do it now with oil and petrochemicals.

2. Principals and problems of low-scale gas chemistry

One of the most evident ways to develop less intensive, short living and spatially extended future unconventional gas sources is their on-sight processing into any liquid products. But as it can be seen from figure 5, the cost of such transformation is very high. Present-day complex and very expensive gas chemical technologies are unprofitable at low-scale realization (figure 6). And as it can be seen from figure 6, in many cases these technologies are inapplicable at all, especially in remote gas producing regions of Russia with severe climate and absence of transport and industrial infrastructure.

For Russia it is especially actual problem. Due to the absence of low-scale gas processing technologies it annually loses up to 50 billion m³ of flared oil associated gases and about 50 million tons of natural gas liquids (NGL) which can’t be separated from pipeline gas. Besides, there is more than 600 low deposit gas fields with total resources of about 6 trillion m³ which up to now do not involved into industrial development.

To develop and transport these resources gas industry needs simpler low-scale technologies to convert them just on site into more valuable and easily transportable liquid chemical or fuels. It must be principally new processes initially designed for low-scale applications. And it worth to note, that in
some cases even the well-known solutions that proved to be unacceptable for large-scale applications can be suitable enough for such low-scale technologies.

Some evident basic principals for such low-scale gas chemical technologies are listed below:

- Simplicity and less tonnage in comparison with existing technologies;
- Modular construction that makes it possible easily increase or decrease capacity or move the equipment into other place;
- Completely factorial production of equipment without complex constructing-and-mounting works on place;
- Universality with respect to gas composition and possible fluctuation in its debit;
- Possibility to combine different modules from different producers;
- Autonomous power supply just from producing gas, etc.

Today there are no such technologies of industrial level in Russia or anywhere else. However, the results of some Russian research engineering studies that were accomplished during the last years have created a strong base for such new technologies. There are two main directions of investigations:

- Alternative technologies for production of syngas and subsequent synthesis of chemicals or fuels using syngas (Fischer-Tropsch synthesis, methanol, DME, etc.);
- Direct conversion of hydrocarbon gases into chemicals (ethylene, methanol, etc.).

2.1. Alternative technologies for production of syngas

The economical attractiveness of indirect methods via syngas is connected with high conversion of initial gas carbon into final products and the maturity of these well developed technologies. But high capital investment and high energy consumption for syngas production make questionable their low-scale application. The well known fact that this first and most energy and capital consuming stage of all modern gas chemical plants – the conversion of natural gas into syngas - consumes up to 70% of all costs makes it evident that only the principal improvement in syngas production can give the acceptable solution [5].

Below are listed the most intensively studied alternative technologies for conversion of hydrocarbons into syngas:

- Methane oxidation with the use of oxygen permeable ceramic membranes;
- Microchannel reactors;
- Short-time catalysis;
• Production of syngas on the base of power engines;
• Production of syngas and hydrogen in radiation burners;
• Production of syngas at filtration combustion;
• Electrochemical conversion of methane to syngas.

As an example of alternative method of syngas production potentially applicable for low-scale gas processing we can mention our recent development of compact and highly productive generator of syngas and hydrogen based on gas-phase combustion of hydrocarbons in volumetric permeable matrix [6] (figure 7). Flameless combustion near inner surface of permeable volumetric matrix proceeds with much lower temperature due to intensive heat exchange with surface. And partial lock of IR radiation of combustion front in deep volumetric matrix lets to significantly widen combustion limits. This auto-thermal process let to burn very rich hydrocarbon-oxidant mixtures with oxygen excess coefficient $\alpha = \frac{[O_2]_0}{2[CH_4]_0}$ up to 0.36 for methane-air mixtures and to use practically any compositions of gas-phase hydrocarbons. At that the yield of hydrogen and CO is very close to thermodynamically equilibrium values. This device is very simple in operation and has high specific thermal power up to 30 Wt/cm$^2$. It uses no catalyst and demonstrates no soot formation in cavity. As oxidant air, enriched air or oxygen can be used.

![Figure 7. Radiation burner with a deep volumetric matrix: scheme (a) and working device with removed cavity top (b).](image)

2.2. Direct processes of natural gas conversion into chemicals

Direct processes potentially are simpler and so better adaptable for low-scale applications. They usually well compatible with power and heat production which is important for remote producing sites. But their common and very serious disadvantage is significantly lower selectivity and conversion per pass, as well as the absence of industrial experience. Among the others there can be mentioned such long-studied direct processes as:

• Oxidative coupling of methane to ethylene (OCM) [7];
• Direct oxidation of methane to methanol (DMTM) and connected processes [5, 8];
• Catalytic aromatization of methane;
• Halogenation and oxy-halogenation of methane.

As it was mentioned above, the low-scale processes needn’t to copy large-scale technologies. For example, the use of OCM for production of polymerization grade ethylene needs its thorough
separation from reaction gases and complex purification which hardly can be profitable at low-scale. But there are often can be offered more simple solutions, e.g. ethylene oligomerization to liquid fuels without its preliminary separation from reaction gases [7].

The same is true for other direct processes. The direct oxidation of methane to methanol (DMTM) although unacceptable for big multi-tonnage processes using expensive pipeline gas due to low selectivity and yield has its own vast niche where nowadays there are practically no other concurrent technologies (figure 8) [8, 9].

E.g., the integrated production of methanol by DMTM process and power on power plants not only provide the simplest and cheapest way to produce methanol without need in syngas and oxygen but as well lets to significantly reduce and even completely eliminate NOx emission by power plant practically without addition costs [8, 9].

3. Russian specificity

Today Russia severely depends on mineral raw staff export that provides about 20% of its GDP and up to 70% of its foreign currency inflow. Such situation dictates the permanent tendency of further expansion of hydrocarbon export. That is why practically all main Russian projects in gas industry are connected with developing of remote Arctic and offshore fields and building of new long distant exporting pipelines. The total cost of these projects estimates in several hundred billion dollars. Taking into account the real perspective of rapid development of unconventional gas in Europe and very possibly in China, and rapid formation of spot LNG market, it may be foreseen the further decrease of gas prices and the volume of European gas import from Russia. So this policy doesn’t seem very reliable. Meanwhile, the chemical processing of Natural Gas tenfold increases its added cost (figure 9) [10], facilitates it transportation to domestic and world markets and provide the diversification of export. It is possible to produce and process only about 10% of modern gas production to provide the same in volume and more reliable currency inflow.

Now the share of Russian petrochemistry in the world is only 2% which doesn’t correspond to Russian share in production of hydrocarbons (about 15%). The share of petrochemistry in Russian GDP is less than 2% which is incommensurable to that in other big countries (India -12%, USA - 25%, China – 30%). So it is severe need in rapidly developing of Russian gas chemistry to adjust national
economic demands and possibilities with changing gas and petrochemical markets. But this gas chemistry must rely on new technologies appropriate for specific Russian conditions.

The interest to low scale alternative gas chemical processes in Russia was initiated about twenty years ago by a severe need in processing of flared oil associated gases from remote oil fields, the need to utilize gas from low debit remote gas fields and necessity to provide remote areas with motor and domestic fuels and necessary chemicals. As a result, Russia has the advanced positions in low scale gas chemistry which gives it a chance to be among the first countries that can reach the industrial level in manufacturing of necessary equipment, and not only satisfy its own requirements but become a leader in this innovative and high-tech market with potential annually capacity of dozens billion dollars.

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Figure 9. Value of products produced from 1 million BTU of Natural Gas [10].