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Partial Oxidation of Light Alkanes as a Base of New Generation of Gas Chemical Processes

V.S. Arutyunov*, L.N. Strekova and A.V. Nikitin

Semenov Institute of Chemical Physics, Russian Academy of Sciences,
119991, Kosygina, 4, Moscow, Russia

Abstract

Recent developments in unconventional natural gas production increase the need for principally new small-scale technologies for gas processing and transportation. The promising way for small-scale gas processing is its autothermal partial oxidation to syngas or direct partial oxidation to chemicals. The paper considers some prospective gas chemical processes based on the partial oxidation of light alkanes. Among them are the conversion of natural gas to syngas in volumetric (3D) matrix burners made of a gas permeable material and direct conversion of methane to methanol without its preliminary conversion to syngas (DMTM). As a more simple technology that lets to use fat associated oil gas often flaring in remote sites, it can be suggested the selective oxidative cracking of heavier components of natural gas. This process converts heavy methane homologues from propane to pentane and heavier into ethylene, methane, ethane, hydrogen, and carbon monoxide, thus increasing methane index (octane number) of gas and making it suitable for feeding modern gas piston and gas turbine power engines. One more interesting prospect is the creation of technologies making use of the subsequent processing of valuable oxycracking products, such as olefins, CO, and hydrogen, for example, by their catalytic co-polymerization without preliminary separation from gas phase. The co-polymerization of CO and ethylene, followed by the separation of resulting liquid products, can considerably improve the economic attractiveness of the oxycracing process. Thus, despite the absence of economically proved and industrial-scale tested small-capacity direct and indirect gas chemical technologies, intensive efforts to develop such alternative technologies let to expect near bright future for them.

Introduction

The first decade of XXI century was marked by important events in the world power industry. First of all, it became evident that in spite of huge efforts and capital investments in their development, alternative renewable sources of energy are incapable to meet even current needs of the world economy. Therefore, the last, as previously, must to rely mainly on fossil resources. But rather unexpectedly, it was found out that contrary to numerous alarming prognoses these resources are huge and can meet the needs of world energetics during, at any rate, next several dozens of years. One more very important finding was that the main part of fossil hydrocarbons in the Earth's crust is presented by the gaseous resources. Due to ability of gaseous resources, the world gas production now increases much faster than that of oil [1]. But mankind needs mainly liquid hydrocarbons. Thus, one of the most important tasks of the world power industry becomes the development of technologies for effective conversion of gaseous hydrocarbons into more convenient, valuable and easily transportable liquid chemicals and fuels.

It is important to note that huge natural gas resources are presented mainly by so called "unconventional" gas, which significantly differs from conventional resources by their exploitation parameters. In the USA about 30% of natural gas output is already a result of fracturing of shale formations, and this percentage is expected to exceed 50% by 2040. In the world market the share of unconventional gas will reach 30% to 2040 [2]. The development of the technology of unconventional gas production in the USA has significantly increased natural gas resources and fivefold decreased its price relative that of oil. Low prices and availability of natural gas has initiated a new spurt in the USA gas chemistry. Nearly

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* Corresponding author. E-mail: v_arutyunov@mail.ru

100 chemical investment projects that capitalize on "unconventional" gas development had been announced, at a total construction cost of $71.7 billion. By 2020 the new plants are expected to be producing chemicals worth some $66.8 billion per year [2].

But low output, short time of active production, remoteness and spatial dispersion of unconventional gas sources make it necessary the development of principally new small-scale and more flexible technologies for its processing and transportation. For example, relatively low output of typical shale gas well, typically 1000 bpd in oil equivalent, and short time of living, usually no more than 4-5 years [3], make it unprofitable to use pipelines or to liquefied produced natural gas for transportation of these resources (Fig. 1).

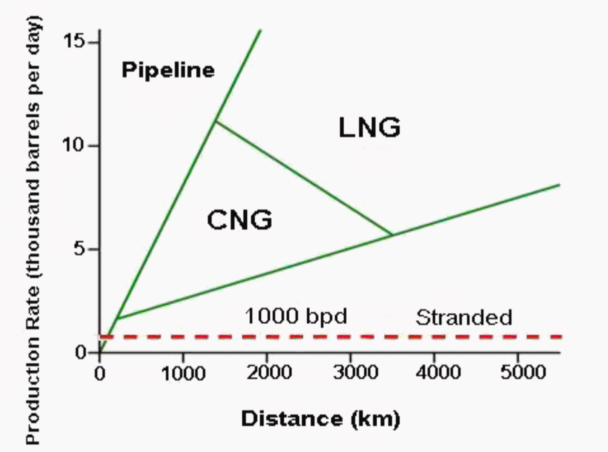

Fig. 1. Economically effective ranges of production rate and transportation distance for different methods of natural gas transportation. CNG – compressed natural gas, LNG – liquid natural gas. Dashed line – the typical output of shale gas well.

As the most promising route for monetization of remote and unconventional low output gas resources so called Gas-to-Liquid (GTL) processes can be considered. Beside of facilitating gas resources delivering to consumers, GTL processes let to produce highly demanded and valuable liquid products and fuels. But practically all nowadays GTL processes make use of preliminary conversion of natural gas into syngas. Due to the complexity and high cost of producing syngas, investments into construction of gas-chemical GTL plants are significantly higher as compared to oil refineries of similar capacity, ranging from 25 thousand to 45 thousand dollars per barrel of daily production, while for oil refineries this value is about 15 thousand dollars. The technological complexity and volume of operations of a GTL-plant with a capacity of 34 thousand bbl/d is equivalent to a refinery with capacity of 100 thousand bbl/d [4]. The high costs of syngas production by traditional technologies, reaching two thirds of the total costs of the production of methanol (Fig. 2) and GTL-products from natural gas is currently the main constraint to wider development of gas chemistry. It is hardly possible to figure on a cost-effective transfer of modern gas-chemical processes to low-scale level necessary for the economically effective development of spread unconventional natural gas resources. Due to modern assessments, the economically viable production of syngas by modern methods is no less than 300 thousand m^3/h. With decreasing production capacity, specific investment expenditures (Fig. 2), just as the specific operational and all other costs are soaring. Therefore, without the creation of fundamentally new technologies for natural gas converting into syngas or alternative technologies of direct natural gas converting into chemicals it is difficult to expect a significant development in low-volume natural gas processing.

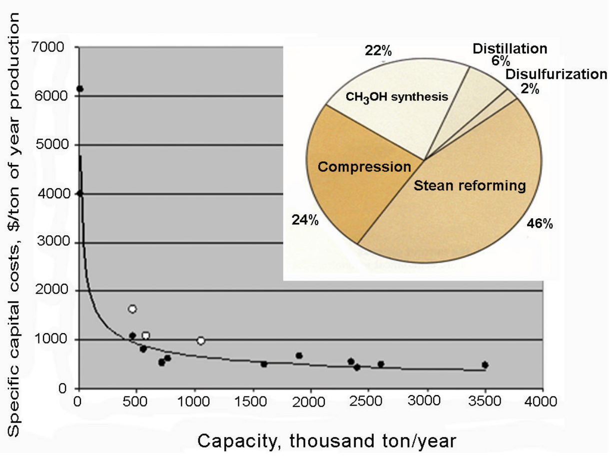

Fig. 2. Dependence of the specific capital costs of modern GTL technologies on their annual capacity and the share of different stages in the prime cost of methanol.

Partial Oxidation as a Base for Low-Scale Gas Chemistry

There exist two principal ways to develop more effective natural gas conversion processes. The first one is the elaborating of less expensive and energy consuming methods of natural gas conversion to syngas. This way, in principle, let to several times decrease total production spending (Fig. 2). The second is the developing of effective methods of direct conversion of hydrocarbon gases into chemicals and liquid fuels. We will consider the both possibilities based on the partial oxidation of light alkanes because this exothermic reaction in both cases let to develop compact and energy effective autothermal processes without additional consumption of external energy.

The high dissociation energy of the C−H and C−C bonds in the molecules of light alkanes, the major hydrocarbon components of natural gas, makes it extremely difficult to accomplish their chemical activation, which requires, even in the case of catalytic processes, rather high temperatures and, therefore, intense heat fluxes. The most effective and economical way of introducing energy into the reacting mixture of light hydrocarbons is the partial oxidation of feedstock hydrocarbons themselves. In addition, due to the radical-chain character of these processes, it is possible to produce a cross activation of various parallel reactions. That is why oxidative processes with high thermal efficiency account for a large share of the modern chemical industry. By some estimates [5], they yield more than 50% of the world's chemical products.

The partial oxidation of hydrocarbons in the gas phase occurs at moderate temperatures (intermediate temperature region), from ~300 °C to ~1200 °C, i.e. below the characteristic temperature of the gas-phase combustion of hydrocarbons, typically well above 1200 °C. The distinction between combustion and partial oxidation is of fundamental nature and is determined not only by the difference in the temperature of the process, but, above all, in the mechanism. One of the main distinguishing features of the mechanism of the partial oxidation of alkanes in the intermediate-temperature range is an important role played by peroxide compounds and radicals. In the oxidation of methane at the low-temperature end of this range, the most important species are $CH_3OO^\bullet$ radicals and CH_3OOH molecules, whereas at the high-temperature end, the leading role belongs to $HOO^\bullet$ radicals and HOOH molecules. At the same time, the role of such species as O, CH, CH_2, C_2, and excited molecules and radicals, important for combustion processes, at the partial oxidation is negligible.

The different parts of the indicated temperature range in which the oxidation of methane has been most thoroughly studied are dominated by different products (Fig. 3). As expected, with increasing temperatures, thermodynamically more stable products become most abundant, with their maximum yields increasing monotonically, reaching almost 100% in the case of syngas. Note, however, that, despite the diversity of the conditions and products, it can be reasonably assumed that the totality of the processes involved in the partial oxidation of methane in the middle-temperature range is described by a single homogeneous-heterogeneous kinetic mechanism [6].

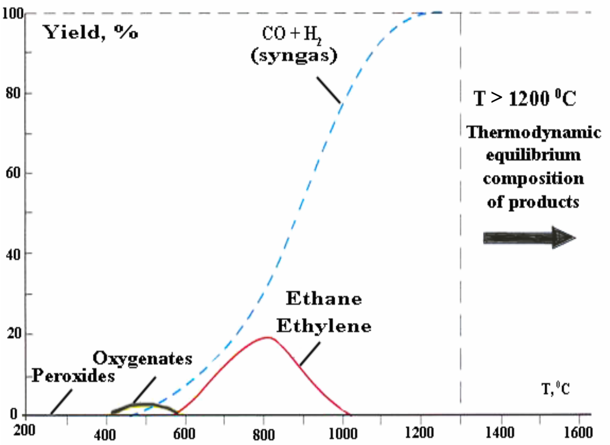

Fig. 3. Temperature ranges of formation and the yields of the main products of methane partial oxidation.

In accordance with the abundance of certain products, the intermediate-temperature range can be in turn divided into three sub-ranges: those of preferential formation of oxygenates (300-600 °C), oxidative coupling of methane (OCM) with predominant formation of C_2 hydrocarbons (600-900 °C), and preferential formation of syngas (>900 °C) (Fig. 3). This division corresponds to obvious changes in the kinetic mechanism with the temperature of the process.

At temperatures below 600 °C, the dominant reaction of the methyl radical $CH_3^\bullet$ is its reversible recombination with the oxygen molecule to form the methylperoxy radical,

$$CH_3^\bullet + O_2 \leftrightarrow CH_3OO^\bullet \qquad (1)$$

which plays a key role in the formation of oxygenates. At these temperatures, especially at heightened pressures, the equilibrium in reaction (1) is strongly shifted to the right, which gives rise to the subsequent chain of transformations that lead to the preferential formation of oxygenates. At temperatures above 600 °C, the equilibrium in this reaction shifts to the left, so that its role diminishes rapidly.

At temperatures of 600 °C to 900 °C, the reactions of endothermic oxidation of the methyl radical,

$$CH_3^\bullet + O_2 \rightarrow CH_3O^\bullet + O^{\bullet\bullet} \qquad (2)$$

$$CH_3^\bullet + O_2 \rightarrow CH_2O + OH^\bullet \qquad (3)$$

are too slow, despite a significantly higher concentration of oxygen compared to that of methyl radicals, to compete with the methyl radical recombination

$$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6 \qquad (4)$$

This reaction leads to the formation of ethane, and further, ethylene, i.e., gives rise to a temperature range of preferential formation of methane coupling products, known as the "ethylene window". Above 900 °C, the rates of reactions (2) and (3) become high enough to ensure a deep oxidation of methane, up to carbon monoxide and hydrogen, i.e. syngas [6]. The effect of temperature on the yield of the oxidation products of heavier homologues of methane is much the same, only the limits of formation of the respective groups are shifted to lower temperatures. Thus, despite a great diversity of conditions for the oxidative conversion of methane, there are three basic types of processes and the respective products of oxidative conversion of methane: the direct oxidation of methane to methanol (DMTM), oxidative coupling of methane (OCM), and partial oxidation to syngas (POM).

Production of Syngas in 3D Matrix Burners

The effective conversion of natural gas to syngas is the most technologically desirable and economically evident gas chemistry goal. From the viewpoint of thermodynamics, optimal conditions for syngas production through the partial oxidation of methane are reached at reagents ratio $O_2/CH_4 \approx 0.5$ (oxygen excess coefficient $\alpha = [O_2]_0/2[CH_4]_0 = 0.25$), temperature of 1073-1273 K, and low pressure ~1 atm. However, such a process is difficult to carry out in the absence of a catalyst. And the use of catalyst at small-scale production is undesirable due to high demands to gas purification and, thus, to significant complication of the whole technology. Therefore, the main technological challenge in the production of syngas by the partial oxidation of natural gas is to ensure a deep methane conversion at low values of the oxygen excess coefficient, within $\alpha = 0.3\text{-}0.5$. Since mixtures with such values occur well outside the flammability limits under normal conditions, this is not a trivial task.

One of the most effective ways to expand the limits of stable combustion is to reduce heat losses and partly recover heat of combustion products. Both of these conditions can be realized by the use of a burner unit designed in the form of a geometrically closed cavity (volumetric or 3D matrix) made of a gas permeable material (Fig. 4). The inner surface of such matrix is heated to high temperature due to convectional and radiative heat transfer from the flame front stabilized near the surface and from the reaction products. Due to an effective heat transfer from the reaction products to the matrix surface and, through it, to the fresh gas mixture, the latter enters the flame front preheated to nearly the matrix surface temperature. Moreover, the radiation emitted by the flame front occurs almost completely locked in the closed cavity, a feature that drastically reduces radiation loss. The joint action of these factors widened the combustion limits and enables to implement the surface burning of very rich mixtures, which is almost unattainable in other types of burners [7-9].

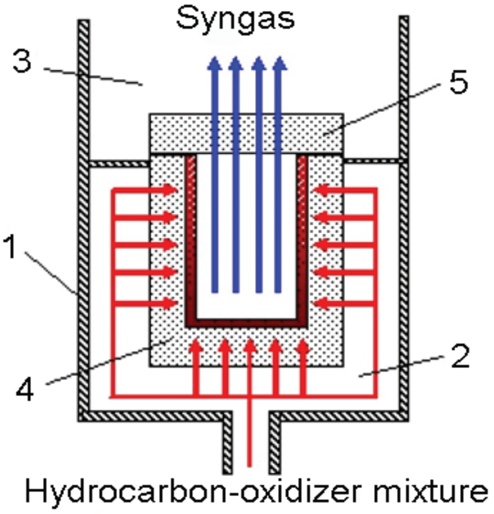

Fig. 4. 3D matrix burner: 1 – external shell, 2 – volume with a fuel–air mixture, 3 – gas outlet, 4 – side walls and bottom made from permeable for gas material, 5 – cap made from permeable for gas material.

Volumetric burners with a closed 3D matrix make it possible to extend significantly the limit of stable combustion of rich mixtures (Fig. 5).

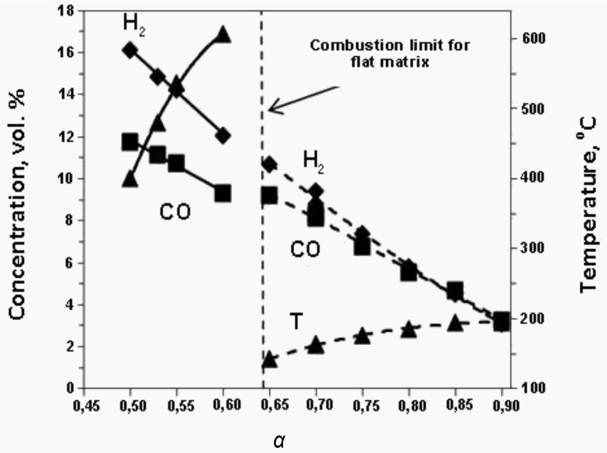

Fig. 5. Dependence of matrix surface temperature, CO and H_2 concentrations on oxygen excess coefficient $\alpha = [O_2]_0/2[CH_4]_0$ for rich methane-air mixtures. Dashed lines – flat matrix; solid lines – volumetric (3D) matrix.

The additional widening of combustion limits can be obtained by the inserting of perforated metallic screen in front of the surface, which radiates additional energy from heated combustion products to the surface thus increasing its temperature. The possibility of stable conversion in a bulk porous matrix of very rich methane-air mixtures at values $\alpha \leq 0.4$ and a temperature of ~1000 °C to hydrogen and carbon monoxide was demonstrated in [7, 8]. When air was used as the oxidant, the concentrations of hydrogen and carbon monoxide at the outlet of this converter reached ~20 and ~11%, respectively, which is very close to the thermodynamically equilibrium values for the temperature of combustion products. Thus, the possibility of an effective non-catalytic conversion of natural gas into syngas with a nearly optimal ratio of $H_2/CO \approx 2$ was demonstrated. Further widening of combustion limits and increasing of syngas yield can be obtained by using of enriched air and additional external recuperation of heat of thus produced syngas to a fresh gas feed. The latter method let to use as rough staff for syngas production even a low calorific biogas with CO_2 content up to 60% [10]. Thus, permeable 3D matrixes offer a way of designing relatively simple, compact, and efficient non-catalytic autothermal reformers for the partial oxidation to syngas of hydrocarbon gases of different origin and composition [7, 8]. Fig. 6 presents the pilot matrix reformer with natural gas capacity 8 m^3/h. A more detailed description of this technology is given elsewhere [11].

Fig. 6. Pilot matrix converter with natural gas capacity 8 m^3/h.

The above-discussed relatively simple devices based on the matrix combustion of hydrocarbons, which doesn't need the use of complex technologies and intensive flaxes of external energy will be able to not only fundamentally simplify the conversion process and increase its effectiveness, but be used for the production of small volumes of hydrogen. The practical creation of simple and efficient hydrogen and syngas sources based on the conversion of gaseous and liquid hydrocarbons in volumetric matrix burners can provide the wide application of electrochemical hydrogen-based sources of electricity (fuel sells) with a power of several kilowatts to several megawatts for the reliable energy supply of remote regions and for the autonomous energy supply of housing and communal services. The use of compact 3D matrix burner–based sources for the production of hydrogen from network gas or liquid hydrocarbons directly at fuel stations will allow solving the problem of hydrogen supply for ecologically clean vehicles.

Direct Conversion of Natural Gas into Chemicals

One of the most popular and extensively studying today direct methods of converting natural gas into chemicals is the Oxidative Coupling of Methane (OCM). It is the interaction of CH_4 molecules in the presence of O_2 or other oxidizing agent to form C_2-hydrocarbons, ethane and ethylene, according to the gross reaction:

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O \qquad (5)$$

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \qquad (6)$$

In some rare cases, heavier hydrocarbons are formed, for example, benzene. The process was discovered in the early 1980^s [11, 12]. Due to a large number of works, the OCM has become one of the most thoroughly studied reactions of the oxidative conversion of methane. It's essentially heterogeneous-homogeneous nature has been experimentally demonstrated. Methyl radicals $CH_3^{\bullet}$ formed by the catalytic reaction escape into the bulk of the reactor. In the temperature range optimal for the OCM, 600-950 ºC (Fig. 3), at an oxygen concentration below 20% and atmospheric pressure, the main reaction of methyl radical is recombination to form ethane (reaction (4)). A huge number of works devoted to the process makes OCM one of the most well studied catalytic reactions. The main problems of the practical implementation of the OCM are the existence of a kinetic limit of the yield of ethane and ethylene, ~25% according both to experiments and kinetic estimates [11], and a high heat release by the reaction, which requires designing appropriate reactor systems

[12]. So far, despite the great interest in this process, and major international effort, there have been no reports on its practical implementation. In addition, it is not clear what can be an economically justified production capacity of this process, i.e., whether it is simple enough for processing small volumes of unconventional gas. Today 17 scientific and commercial organizations from 8 European countries and 1 non-European country intensively working on OCM in a frame of joint European project OCMOL [13].

The most advanced today technology for the direct conversion of natural gas into chemicals is so called Direct Methane to Methanol (DMTM) technology [11, 14]. But even for this technological processes the current state of elaboration of the of partial oxidation of hydrocarbon gases to oxygenates is far from perfect, mainly due to insufficient volume of research development. Nevertheless, it is possible to clearly identify the areas where this technology will be promising, and in some cases, the only one suitable for solving the outstanding problems.

The prevention of hydrate formation during the production and transportation of natural gas remains one of the most promising areas for application of DMTM. Hydrate formation is a very serious problem for the gas industry. By some estimates, preventive measures account for 20% of the costs of the extraction and transportation of natural gas, the total consumption of methanol for this purpose in Russia already exceeding 400,000 tons/year. The main consumers are numerous remote gas-production enterprises at large distances apart, consuming annually only a few thousand ton of methanol each. Thus, the delivery of methanol from sites of its production thousands of miles away is associated with high costs. In this case, a low-tonnage on-site production of methanol can provide tangible economic benefits. No less important is the factor of reliability of supply. In addition, raw methanol produced by DMTM, is significantly cheaper than commercial-grade methanol and is quite suitable as an inhibitor [11, 14].

Purification of natural gas from sulfur compounds can also become one of the attractive areas of commercial applications of the DMTM process. Dewatering of produced gas and purification from sulfur compounds and carbon dioxide are the most important stages of the gas production. For this purpose, a large number of industrial processes, based on various absorbents, including methanol, have been developed. Among the most well-known is the Rectisol process (the licensors are the Linde AG and Lurgi GmbH) for extracting acidic gases by organic solvents at temperatures below 0 ºC. Hydrogen sulfide, carbonyl sulfide, and carbon dioxide are normally extracted with methanol, in some cases with other solvents. After purification, the fraction of sulfur is below 10^{-6}, and that of carbon dioxide is even lower. The main advantages of the process are the use of cheap and readily available methanol, ease of technological design, and low power consumption. The Rectisol process is economical, with a significantly lower specific energy consumption compared to other purification methods, such as absorption by ethanolamines. That the solubility of H_2S in methanol is substantially higher than that of CO_2 allows, on the one hand, their selective separation and, on the other, reaching a high degree of purification from sulfur compounds in the presence of CO_2. The process is best suited for the purification of gases containing a large number of different contaminants, including organosulfur compounds, the solubility of which in methanol is high. The application of a technology, based on a combination of the DMTM and Rectisol processes enables to carry out three important operations together: to effectively and economically purify natural gas from acidic components, introduce methanol into it in the amount required for its further transportation, and obtain liquid methanol for inhibition of hydrate formation in the gas transporting system upstream of the plant [11, 14].

Processing of de-ethanization gases from gas fractionation plants can also become an area of practical applications of the DMTM process. Virtually all of the natural gas produced is processed to extract higher hydrocarbons, valuable raw materials, as well as to prevent their condensation in the cold units of the gas transporting system. This is achieved by extracting ethane, at least partially, propane, butane, and higher hydrocarbons, valuable chemical raw materials and high-calorific ecological household and motor fuel. This treatment also provides a stable composition of natural gas transported through pipelines irrespective of its origin. Despite a wide variety of technologies used for the fractionation of hydrocarbon gases, all derived products fall into four main groups: dry natural gas purified in accordance with the requirements of transportation, liquefied gases (propane-butane fraction), liquid products (gas condensate, wide fraction of light hydrocarbons), and de-ethanization gases. The first three fractions are highly marketable and relatively easily transportable commercial products. However, the last fraction, which contained most of the ethane removed from natural gas, as well as some amounts of methane and propane, in many cases cannot be used otherwise than as fuel for local needs or, in some cases, is simply flared. At the same time, this fraction is an ideal raw material for the DMTM process, readily processing at pressures below 30 atm with a high yield of products. Therefore, the integration of a partial oxidation unit with a gas fractionation plant, would allow producing valuable oxygen-containing products from otherwise waste material.

The combined production of methanol and power at thermal power plants (TPP) makes it possible to not only simplify and streamline the process of methanol production, but also to significantly reduce NOx emissions during electricity generation. Nitrogen oxides NOx are among the most dangerous anthropogenic emissions, a major component of photochemical smog. For TPP and gas-compressor stations operating on natural gas, they constitute a major hazard to ecosystems. Therefore, the reduction of NOx emissions at TPP is one of the most important global environmental issues. The reduction of NOx emissions by power plants into the atmosphere is highly expensive. Nowadays, only a small part of the power plants has equipment to remove nitrogen oxides. The dilution of natural gas with nitrogen at its partial oxidation to methanol before natural gas subsequent combustion in power plant can significantly reduce NOx emissions due to decrease of combustion temperature. To further reduce the NOx emissions, to a level of a few percent of the initial concentration, it is advantageous to use the primary (unfractionated) liquid from the DMTM process, containing ~40% methanol and ~5% formaldehyde, introduced into the flue gases at temperatures from 320 to 820 ºC. As shown in [15], the introduction of methanol and some other compounds into flue gases at these temperatures results in the oxidation of nitrogen oxide to nitrogen dioxide, which then can be removed in scrubbers.

Such a process is especially advantageous if methanol is produced directly at the power plant in an integrated chemical-power process. After standard oxidation with air and separation of the liquid oxidation products, the off-gas of the DMTM process can be used for energy generation. Steam produced in DMTM also can be utilized directly at the TPP. Thus, the efficiency of carbon use in such integrated process is expected to be close to 100%. A full use of the reaction heat and calorific value of the exhaust gas actually eliminates the two main drawbacks of the DMTM process associated with the low selectivity of methanol formation and low conversion of gas. At the same time, its benefits, such as one-step process and low capital and operating costs, make the DMTM-based integrated process of methanol production quite competitive compared with existing methods of production of commercial methanol. The integrated chemical-power production of methanol can be launched at dozens of power plants fueled by natural gas. By technical-economic assessments, the cost of methanol and specific investment expenditures will be significantly lower than the values typical of modern plants. In addition, the environmental performance of power plants will be improved without additional expenditures [11, 14].

Selective Oxycracking of Heavier Components of Natural Gas

As a very simple technology for processing small volumes of natural gas with a high content of heavy methane homologues, the selective oxycracking of these homologues can be considered. The conversion of heavy components of natural gas into lighter, higher-octane compounds less prone to detonation and soot formation makes it possible to use thus processed gas as a fuel for gas-piston and gas-turbine engines [11]. This technology [16, 17] is based on the simple fact that the temperature of the gas-phase oxidative conversion of gaseous methane homologues is substantially below the temperature of oxidative methane conversion (Fig. 7), which, under these conditions, exceed 1000 °C [18, 19]. This makes it possible to perform the selective gas phase oxidation of C_3+ alkanes in complex mixtures of hydrocarbon gases, such as natural and associated gas, practically without involving methane into the oxidation process. Moreover, the methane content even increases, since it is one of the main products of oxycracking of its heavier homologues [11, 14, 20].

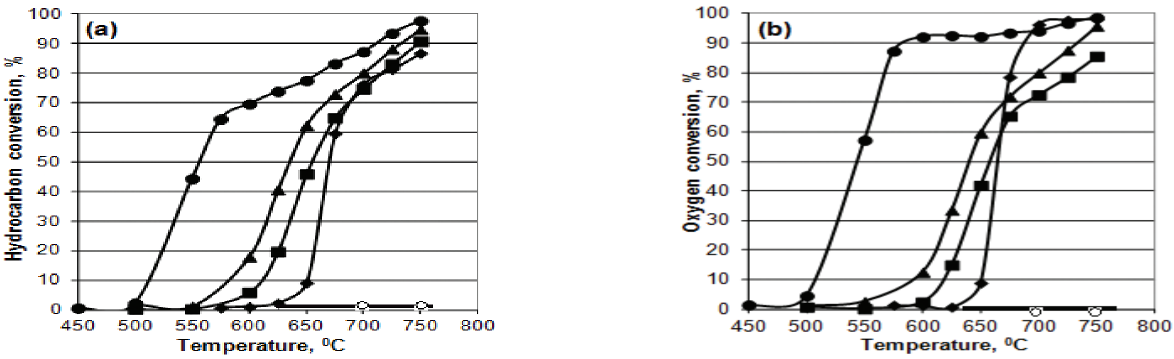

Fig. 7. Temperature dependences of the oxidative conversion of C_1-C_5 alkanes (CH_4 (o), C_2H_6 (♦), C_3H_8 (■), n-C_4H_{10} (▲) and n-C_5H_{12} (●)). ([C_nH_{2n+2}] = 5 mole %, [O_2] = 2.5 mole %, t_r = 2 s, balanced by N_2) [17].

The main products of the oxycracking of methane homologues are ethylene, methane, ethane, hydrogen, and carbon monoxide, with ethane and propylene being present in small amounts [17, 20-22]. The presence of a heterogeneous catalyst significantly accelerates the process at low temperatures, but impedes it at higher temperatures, at which an abrupt transition to the branched-chain-reaction mode occurs. The reactor surface acts in a similar manner, apparently due to the heterogeneous termination of chains. In addition, the presence of a catalyst greatly increases the formation of CO_2 and H_2O because of the deep oxidation of hydrocarbons on the catalyst surface [22]. Therefore, at these conditions, the gas-phase process is preferable.

Oxygen addition markedly increases the rate of conversion of alkanes, particularly at moderate temperatures: above the temperature of the surface catalytic process but below the thermal pyrolysis temperature [17] (Fig. 8). Furthermore, oxygen, which is consumed in the gas-phase process simultaneously with hydrocarbons, being present in a greater part of the reactor, significantly inhibits the formation of heavy condensation products, such as C_4H_6 (butadiene) and C_3H_4 (propadiene and methylacetylene), which to some extent may be considered as soot precursors [23].

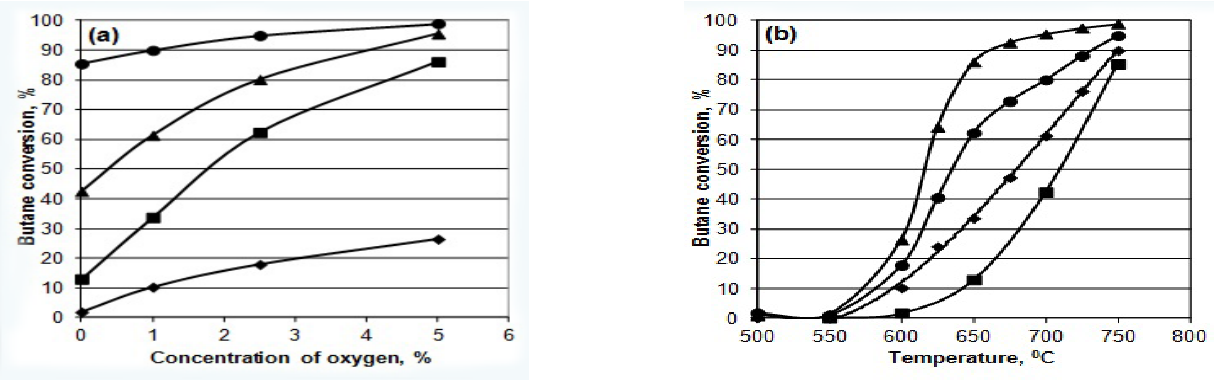

Fig. 8. Conversion of n-butane at different temperatures as a function of initial concentration of oxygen (a) (T = 600 °C (♦), 650 °C (■),700 °C (▲) and 750 °C (●)) and at different initial concentration of oxygen as a function of temperature (b) ($[O_2]$ = 0 % (■), 1% (♦), 2.5% (●) and 5% (▲)) ($[n\text{-}C_4H_{10}] = 5\%$, $t_r = 2$ s, balanced by N_2) [17].

On the base of the selective oxycracking it was developed a process of oxidative conversion of C_3+ components of associated oil gas into lighter, high-octane compounds thus making processed gas suitable for use as a fuel for gas-piston and gas-turbine power plants for local needs of oil and gas fields. The process was successfully pilot-tested, demonstrating the ability to convert up to 90% of C_5+ hydrocarbons and up to 80% of the C_3–C_4 fraction (Fig. 9). This technology can help to reduce the flaring of associated oil gas at remote and offshore oil fields by, at any rate, 20-30% by using part of it to produce energy for own needs.

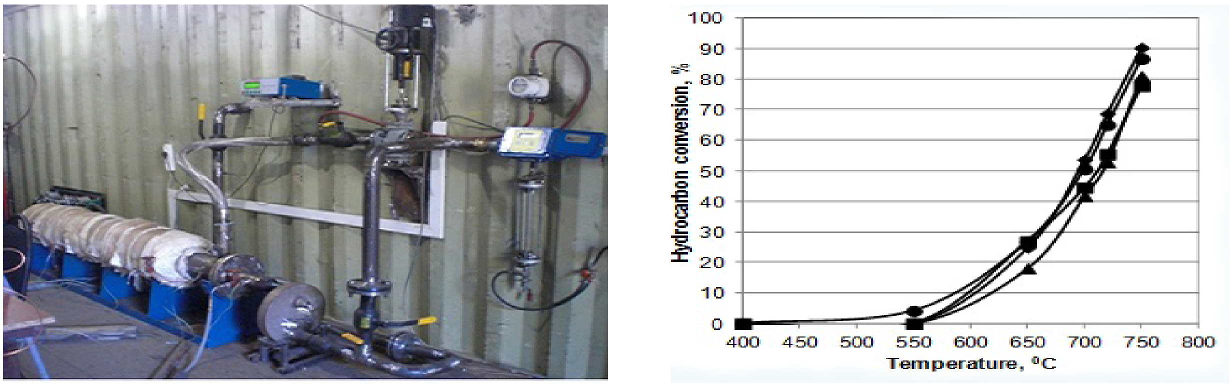

Fig. 9. Reactor part of the pilot unit for the selective oxy-cracking of heavy gas-phase hydrocarbons (a) and results of pilot testing at the conversion of the typical oil associated gas (b) (C_3H_8 (■), n-C_4H_{10} (▲), n-C_5H_{12} (●), n-C_6H_{14} (♦)). The composition of gas (mol. %): CH_4 – 81.0; C_2H_6 – 1.22; C_3H_8 – 17.0; ΣC_4H_{10} – 2.81; ΣC_5H_{12} – 1.50; n-C_6H_{14} – 1.83. The amount of added air – 15%. t_r – ~1 s.

A more interesting prospect is the creation of technologies making use of the subsequent processing of valuable oxycracking products, such as olefins, CO, and hydrogen, for example, by their catalytic co-polymerization [24] without preliminary separation from gas phase. The copolymerization of CO and ethylene, followed by the separation of resulting liquid products can considerably improve the economic attractiveness of the process.

Thus, despite the absence up to now of economically proved and industrial-scale tested small-capacity direct and indirect gas-chemical technologies, intensive efforts to develop such alternative technologies let to expect near bright future for them.

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