Non-Catalytic Gas Phase Oxidation of Hydrocarbons

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Article info	Abstract
	The predicted role of gas chemistry in meeting the global needs for fuels and petrochemicals makes it necessary to increase the efficiency of gas chemical processes and reduce their energy consumption. An important role in solving these problems can be played by non-catalytic autothermal oxidation processes that provide high energy efficiency with minimal demands on the composition of processed gases and their preliminary preparation. The paper presents the latest results of the development of two promising directions in natural gas processing. One, so called matrix conversion, belongs to the group of processes based on their preliminary conversion into syngas and demonstrates the possibility of a significant increase in specific capacity due to the transition to autothermal oxidative conversion. The other is based on the processes of direct conversion of hydrocarbon gases into chemical products – their partial oxidation and oxycracking with subsequent catalytic carbonylation of the resulting methanol and ethylene. In this case, additional advantages are achieved due to the possibility of direct processing of complex gas mixtures without their preliminary separation.

1. Introduction

The leading technological field of the last century, which gave the already familiar mobility to our way of life and allowed us to connect the whole world into a single system, making it truly global, was petrochemistry. The relative simplicity of destructive processes of oil refining (cracking, pyrolysis, dehydrogenation, isomerization) makes it possible to widely use equilibrium catalytic processes. But the oil resources in the earth's crust are limited. Huge resources of unconventional natural gas, especially gas hydrates, which account for half of the organic carbon of the earth's crust, can provide the world economy with hydrocarbons for centuries. So this century will inevitably become the century of natural gas and gas chemistry.

Gas chemistry is a petrochemistry based on methane. Its fundamental difference from traditional petrochemistry lies in the "constructive" direction of its processes. The goal of gas chemistry is to obtain from the most stable hydrocarbon molecule CH_4 the entire scope of more complex (and less stable) products of modern petrochemistry. But the conversion of methane into thermodynamically less stable products requires a lot of energy [1–3].

The most accessible and inexpensive source of energy for gas chemical processes is the oxidation of methane itself. And the most effective method of energy supply is autothermal processes since they allow avoiding the use of expensive metal-intensive heat exchange equipment and the inevitable losses in heat transfer processes. Therefore, it can be predicted that gas chemical technologies based on autothermal processes will be the most attractive [4].

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The set of products that can be obtained directly from the main component of natural gas – methane, is very limited. If we do not consider the relatively low-tonnage processes of halogenation and sulfidation of methane, then these are hydrogen, carbon black (soot), acetylene, ethylene, and simple oxygenates (methanol, formaldehyde) [4]. The most important product that can be obtained directly from methane is syngas, since it opens up the possibility to obtain from it in the Fischer-Tropsch process synthetic oil, and therefore almost all petrochemicals. The uniqueness of syngas for gas chemistry is that it is practically the only product into which methane can be converted completely and in a thermodynamically equilibrium process. But it requires very high temperatures, up to 1000 °C, and therefore a lot of energy [1–3], making autothermal gas chemical processes particularly attractive.

Existing industrial technologies of chemical conversion of natural gas are overwhelmingly based on its preliminary conversion into syngas. This complex, energy-intensive and capital-intensive process consumes up to 70% of the cost of the target products. Specific capital expenditures in existing gas chemistry reach $200 000 bpd [5], which is significantly higher than in petrochemistry, which hinders its development. The use of vast unconventional methane resources requires the creation of new cost-effective technologies for their extraction, transportation and chemical processing.

In this paper, we present our latest results of the development of the most promising, from our point of view, directions in natural gas processing. One belongs to a group of processes based on their preliminary conversion into syngas; the other is based on the processes of direct conversion of hydrocarbon gases into chemical products.

2. Matrix conversion of hydrocarbons to syngas

A number of companies and research groups around the world are actively searching for new methods of converting hydrocarbon gases into syngas. Among them, we can note such interesting processes as oxidation on ceramic membranes, processes based on short time catalysis, use of microchannel and membrane reactors, syngas production with the use of energy technologies, oxidation with metal oxides, filtration combustion and some others [6–8]. However, despite intensive long-term efforts and a number of large pilot installations,

none of these methods has yet reached the industrial level. Below we will consider in detail the method of matrix conversion of hydrocarbon gases into syngas, as the most promising, from our point of view. The basic principles of the matrix reformer are quite simple and are described in more detail in [9]. The process is based on a weakly exothermic process of partial oxidation of methane

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298} = -36 \text{ kJ/mol} \qquad (1)$$
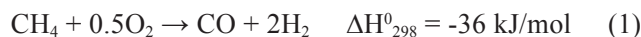
However, the heat release in this process, which requires an oxygen excess coefficient $\alpha = [O_2]/2[CH_4] = 0.25$, is too small for its stable implementation. Therefore, it is inevitably accompanied by a parallel reaction of complete oxidation of methane

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^0_{298} = -802 \text{ kJ/mol} \qquad (2)$$

which provides the necessary additional amount of heat. The goal of any technology based on the partial oxidation of methane to syngas is to minimize the contribution of the complete oxidation reaction to increase the selectivity of syngas formation and approach the value $\alpha = 0.25$.

As well as in filtration combustion [6, 8], stable conversion of very rich mixtures of hydrocarbons with an oxidizer is ensured by the recovery of part of the heat of the products into a fresh mixture of reagents. During filtration combustion, this is usually provided by heat transfer through a solid heat carrier with a countercurrent movement of the gas flow relative to it. In matrix conversion, heat transfer is performed by means of convectively and radiatively heated gas-permeable walls (matrix) forming the reactor cavity. Intensive convective and radiation heat recovery from conversion products to fresh reagents and the locking of the IR radiation of the flame front during flameless combustion near the inner surface of the permeable volumetric (3D) matrix significantly expand combustion limits and open the possibility to operate with values of oxygen excess coefficient as low, as $\alpha = 0.34$–0.36 [9]. Figure 1 shows the principle of operation of the matrix reformer. The flows of hydrocarbon gas and oxidizer (atmospheric air, enriched air or oxygen), in some cases with the addition of steam, enter the mixer and then symmetrically from both sides into a cylindrical matrix reformer. After conversion near the inner surface of two symmetrically arranged flat round matrices 6 fabricated from pre-pressed Fehral wire, the resulting syngas exits through the upper outlet pipe 3. Radiation screen 7 provides an additional reflection of the radiation energy of the flame front on the matrix.
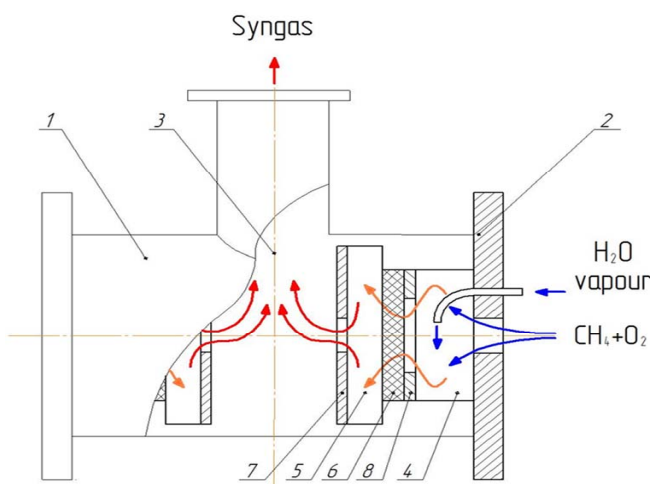
Fig. 1. The principle of operation of matrix reformer: 1 – core vessel; 2 – flange; 3 – outlet pipe; 4 – mixing chamber; 5 – combustion chamber; 6 – matrix; 7 – radiation screen; 8 – inlet aperture.

Operation with atmospheric air allowed obtain a stable conversion at $\alpha = 0.34$–0.36, providing a concentration of H_2 up to 25% and CO up to 14% in the resulting syngas. The concentration of CO_2 is ~3.6%, the rest is nitrogen. As the oxidizer is enriched with oxygen, the concentrations of syngas components increase proportionally, and the nitrogen concentration decreases. Operation with oxygen allowed to obtain the concentration of $H_2 > 54\%$ and a concentration of $CO > 31\%$ with the H_2/CO ratio in the range of 1.6–1.8. The conversion of both reagents exceeds 95%.

These results were obtained at normal pressure. Currently, the possibility of working at pressures up to 6 atm is shown, and studies are being conducted at higher pressures. However, an increase in pressure leads to a proportional increase in heat release on the surface of the matrix. Consequently, a further increase in pressure is likely to require a change in the design of the converter and methods of heat release from the matrix.

The main advantages of the matrix conversion, which make it very promising, especially for the rapidly developing small-tonnage gas chemistry [10], are listed below:
• It is autothermal process that needs no additional heat or energy;
• Process allows processing hydrocarbon gases of almost any composition, including fat natural gases, associated petroleum gases, refinery gases, biogas, etc.;
• Process provides the possibility for a wide range of possible capacities, including small-tonnage installations;
• Process is very compact with a specific volume capacity at least 10 times higher than steam reforming, which significantly reduces capital costs;
• Process is quite simple in design and operation, which significantly reduces operating costs;
• The absence of a catalyst significantly decreases the demand for the quality and purification of the feedstock.

The possibility of obtaining cheap syngas based on matrix conversion of hydrocarbon gases by atmospheric air opens up real prospects for small-tonnage conversion of natural and even associated petroleum gases directly at the field conditions [11]. As was shown by semi-industrial tests of the Fischer-Tropsch synthesis using cheap syngas obtained by the oxidation of methane with atmospheric air [12], such a process not only significantly reduces the cost of the synthetic hydrocarbons obtained, but also has some additional advantages. The most important among them are [13]:
• Significant decrease in capital costs;
• No need for recycling;
• Low partial pressure of steam, which is favorable for kinetic of the process and increases the service life of the catalyst;
• Lower specific release of heat, which makes it possible to use reactor tubes with significantly higher diameter;
• Decrease of the probability of local overheating, increase of selectivity to higher hydrocarbons;
• Safety of operating in field conditions.

The first and last points are especially important since high CAPEX and the use of oxygen in the field conditions are practically excluded. It is worth noting that the composition of syngas used in works [12, 13] and some others practically coincide with the composition of syngas obtained by the matrix conversion of natural gas by atmospheric air.

Matrix conversion allows utilizing low resources sources of inexpensive and easily obtained biogas and other renewable hydrocarbon gases for the production of liquid biofuel by their air conversion into low-cost nitrogen-rich syngas, followed by Fischer-Tropsch synthesis in a cascade of sequential reactors [14].

Matrix reforming opens up the possibility for simple small-capacity production of hydrogen directly on site of its consumption from any local gas resources, which allows bypassing the problems of storing and transporting of large volumes of hydrogen, which do not yet have practically acceptable solutions. To increase the yield of hydrogen,
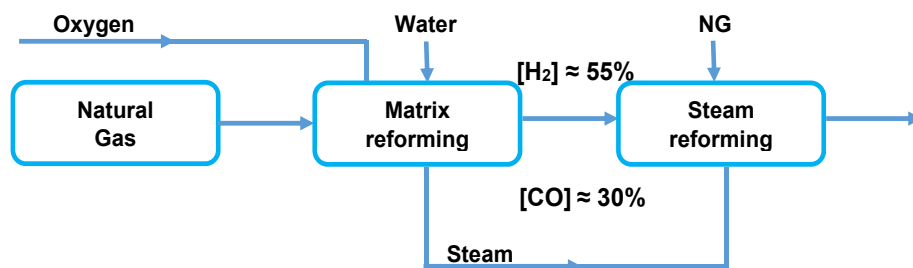
Fig. 2. Scheme of combined matrix and catalytic reforming for hydrogen production.

the gas-phase process of matrix reforming can be supplemented by a sequential catalytic process of steam conversion of the formed carbon monoxide – water gas shift reaction (WGSR). The autothermal nature of this process allows noticed reduction of carbon footprint compared to steam reforming. Figure 2 shows a scheme of combined matrix and catalytic reforming for hydrogen production, and Fig. 3 shows a demonstration unit for an input gas flow of ~2 m³/h, which was developed by the authors and successfully tested in the Institute of Problems of Chemical Physics (IPCP).

The table represents the comparison of parameters of steam and combined conversion of natural gas to hydrogen, which was obtained based on pilot tests of the IPCP installation. The technological possibilities of 10–20-fold scaling of the process are quite obvious. Further scaling, of course, requires additional study. But the modular principle of increasing productivity is also possible.

Another possibility opened by matrix reforming is the possibility of low-tonnage production of such a universal and popular product as methanol. Our experiments with syngas of the composition obtained by matrix reforming using atmospheric air have shown the possibility of stable catalytic synthesis of methanol with a CO conversion per pass through the reactor of at least 20% and a selectivity of methanol formation up to 95%. At the same time, fuel gas consumption is reduced by ~4 times, water consumption is reduced by ~5 times and capital costs are significantly reduced.

The great importance of increasing the syngas yield at matrix reforming plays the optimization of the processes occurring in the post-flame zone after the complete conversion of oxygen. Our kinetics simulation of the process revealed three characteristic stages of hydrocarbons matrix conversion (Fig. 4). In the flame zone I, in the lack of oxygen, along with CO, H_2, CO_2 and H_2O, the products of hydrocarbons pyrolysis are formed. Then, in the post-flame zone II, in the absence of oxygen, at 1400–1600 K, slow pyrolysis of residual hydrocarbons occurs together with steam and CO_2 conversion of products. Kinetic analysis shows that the pyrolysis of hydrocarbons into acetylene and the subsequent steam and dry reforming of the latter proceeds much faster than the direct interaction of hydrocarbons with H_2O and CO_2, which leads to decreasing hydrocarbons and acetylene
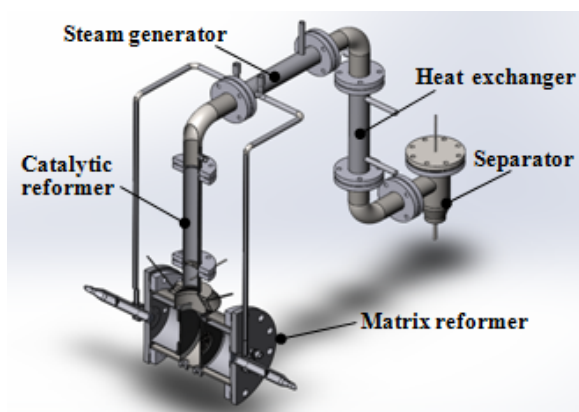
<table>
<tr><td>(a)</td><td>(b)</td></tr>
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Fig. 3. Demonstration unit for an input gas flow of ~2 m³/h. The scheme of the process (a) and its general appearance (b).

Table
The comparison of parameters of steam and combined conversion of natural gas to hydrogen

Parameter	Combined conversion (oxidizer – O_2)	Steam reforming
Specific capacity (for syngas), l/hour	65 from 1 cm^2 of matrix	3.5–4.0 from 1 cm^3 of catalyst
Fuel gas consumption for 1 m^3 of converted gas, m^3	≈0.2	0.75–0.80
Number of catalytic stages	1	2
Energy consumption	Autothermal	Requires energy
H_2O/CH_4 ratio	1.0–1.5	2.5–3.0
Concentration of H_2, %vol	70–75	>75

concentrations and increasing H_2 and CO concentration. The final composition of the products is established in zone III, in which it slowly approaches thermodynamic equilibrium. However, the time required for this significantly exceeds the time they stay in the reformer. Therefore, it is necessary to optimize conditions in the post-flame zones II and III to decrease acetylene yield and increase syngas yield [15, 16].

The processes of steam and dry reforming of hydrocarbons in the post-flame zone make it reasonable to introduce an additional amount of steam and/or CO_2 into this zone to increase the syngas yield. In the case of the introduction of an additional amount of carbon dioxide, for example, by its recycling after separation from the resulting syngas, such a process can be considered as a method of partial utilization of CO_2 [17]. According to our kinetic modeling, the non-catalytic dry reforming of hydrocarbons in the post-flame zones begins with their thermal pyrolysis, followed by the conversion

of CO_2 in interaction with radicals formed during pyrolysis. At the same time, the conversion rate of the residual hydrocarbons does not depend on the concentration of the supplied CO_2 [17].

3. Direct GTL technologies without preliminary conversion of hydrocarbons into syngas

In parallel with the development of new technologies for producing syngas, direct methods for converting natural gas into demanded petrochemicals are being actively developed. The most popular of them, of course, is the oxidative coupling of methane (OCM) into ethane and ethylene [18, 19]. But, despite many years of effort and a huge number of publications on this process, it has not yet been commercialized. The possibility of implementing processes based on the halogenation and oxyhalogenation of methane is being studied. A number of interesting new processes are being developed at the pilot plant level [20, 21].
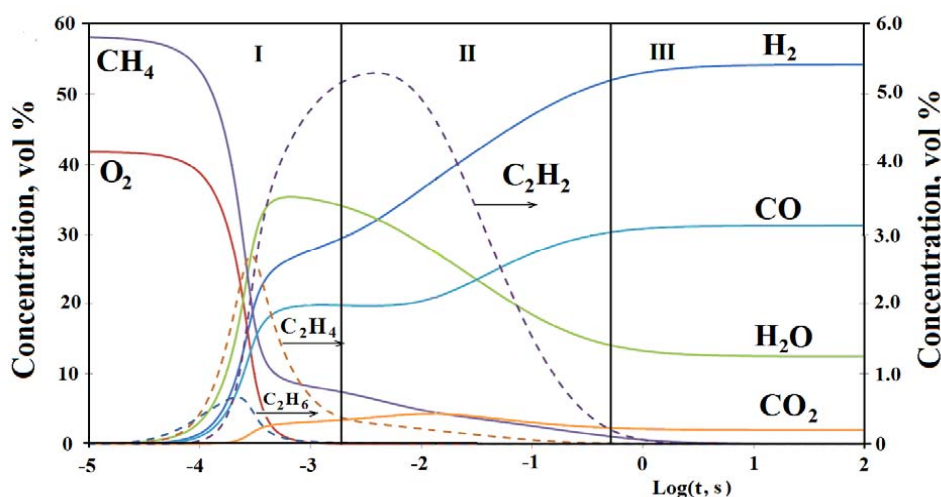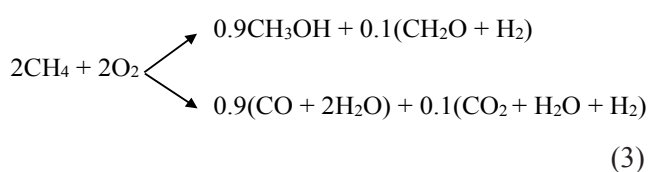

Fig. 4. Distribution of concentrations for the partial oxidation of methane at O_2: CH_4 = 0.72 : 1, T = 1700 K.

Recently, the process of partial oxidation of methane into acetylene, which has long become an industrial process, has again attracted much attention [22, 23]. Computer modeling of the process shows the possibility of achieving almost 40% selectivity of acetylene formation at the conversion of hydrocarbons above 80% [22]. We can foresee an interesting future for this process since it allows us to obtain a sufficiently high yield of such demanded and chemically versatile product as acetylene directly in one stage in a fairly well-developed technological process. In addition, modern methods of computer modeling of such processes provide an additional impetus for its improvement.

Below we will describe another possibility of developing alternative GTL technologies that do not require syngas production. Currently, in addition to the partial oxidation of natural gas to acetylene, three other processes based on partial oxidation have been developed to some extent.

Direct partial oxidation of C_1–C_5 hydrocarbons at high pressures P = 60–80 atm and relatively low temperatures T = 450–550 °C with principal products CH_3OH and CO (DMTM) [24]

$$2CH_4 + 2O_2 \Big\langle \begin{array}{l} 0.9CH_3OH + 0.1(CH_2O + H_2) \\ \\ 0.9(CO + 2H_2O) + 0.1(CO_2 + H_2O + H_2) \end{array}$$

$$(3)$$

Selective oxidation (oxycracking) of C_2–C_5 hydrocarbons at low pressure P = 1–5 atm and high temperatures T = 700–750 °C with principal products C_2H_4 and CO [25]

$$C_nH_{2n+2} + mO_2 \rightarrow xC_2H_4 + yCO + zCH_4 + \text{other}$$
minor products   (4)
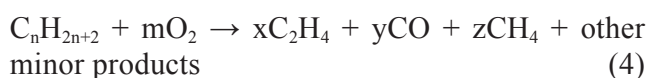
Oxidative coupling of methane at P = 1–5 atm, T = 700–900 °C with principal products C_2H_4 and CO [18, 19]

$$nCH_4 + mO_2 \rightarrow xC_2H_4 + yC_2H_6 + zCO + \text{other}$$
minor products   (5)
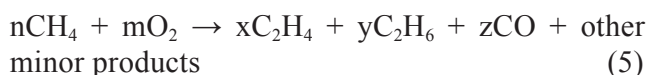
By combining these processes in the processing of raw natural, associated petroleum, refinery and other hydrocarbon gases, it is possible to obtain in controlled ratios three main components: methanol, ethylene and carbon monoxide. The possession of these three fundamentally important components in controlled ratios allow us to carry out

many well-developed industrial catalytic processes using metal-based catalysts to obtain a variety of high-margin products [26].

Carbonylation of methanol or alkenes to obtain the corresponding acids and aldehydes is an industrially developed and proven process [27]. Hydroformilation of ethylene makes it possible to obtain propanal or diethyl ketone by the interaction of CO and ethylene with platinum group metal catalysts [28]. The studied catalyst systems can be correlated with a process in which the stage of the combined conversion of refinery gases to oxygenates can be implemented with the highest efficiency and the lowest costs. It has been found that in the hydroformylation of hydrogen-enriched mixtures in the presence of rhodium–phosphine catalysts, propanal is formed as the main product (up to 99%), while the formation of diethyl ketone (up to 20%) occurs if ethylene is present in the mixture in a molar excess relative to CO. Subsequent condensation of carbonylation products produces valuable petrochemicals and high-octane components of motor fuels [29].

Figure 5 shows a possible scheme for processing hydrocarbon gases, including stages of oxidative conversion, followed by hydroformylation and aldol condensation with the production of valuable petrochemical products and high-octane components of motor fuels.

The simplest and most obvious of this group of processes is the carbonylation of methanol obtained by direct oxidation of methane with carbon monoxide formed in the same process [30]. Carbonylation of ethylene makes it possible to obtain methyl propanoate and diethyl ketone as green solvents by the interaction of CO and ethylene in the presence of methanol and platinum group catalysts. At the methoxy carbonylation of ethylene (Lucite Alpha process) the first stage is the interaction of methanol, ethylene and CO with the formation of methyl propionate. The second stage is the interaction of methyl propionate with formaldehyde with the production of methyl methacrylate [31].

Very interesting opportunities for the development of new processes for the production, first of all, olefins are opened by the still poorly investigated processes of oxidative pyrolysis and conjugated oxidation of various saturated and unsaturated hydrocarbons [32]. For example, oxidative pyrolysis of propane can significantly decrease the temperature of reaching the maximum yield of propylene and increase its relative yield in comparison with
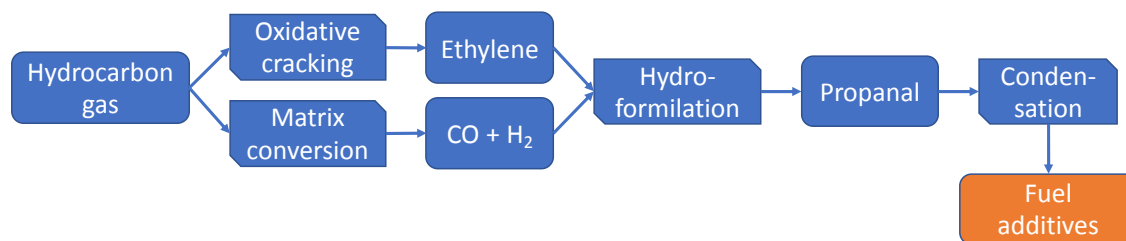
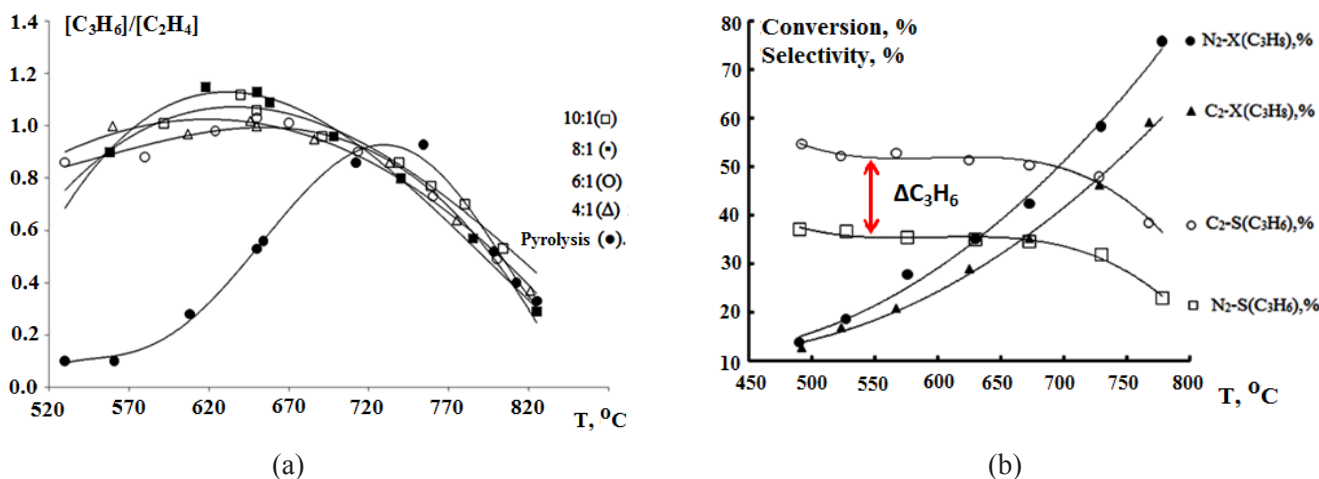Fig. 5. Possible scheme for processing hydrocarbon gases.

|(a)|(b)|

Fig. 6. (a) – Temperature dependence of the [C$_3$H$_6$]/[C$_2$H$_4$] ratio for C$_3$H$_8$:O$_2$ = 10:1 (□), 8:1 (■), 6:1 (o), and 4:1 (Δ) mixtures and for the pyrolysis of propane (•). P = 650 Torr, τ = 2 s. (b) – Temperature dependences of the propane conversion X(C$_3$H$_8$) and the selectivity of propylene formation S(C$_3$H$_6$) for the oxidation of N$_2$:C$_3$H$_8$:O$_2$ = 4.5:8:1 and C$_2$H$_4$:C$_3$H$_8$:O$_2$ = 4.5:8:1 mixtures; P = 660 Torr, t = 4.5 s. According to [32].

its thermal pyrolysis (Fig. 6a). And the addition of ethylene during the partial oxidation of propane increases the selectivity of the formation of propylene (Fig. 6b). Moreover, such conditions can be selected that the concentration of the supplied ethylene and ethylene at the outlet of the reactor, which is one of the products of propane oxidation, will be almost equal. That is, in this case ethylene plays the role of a homogeneous catalyst for the formation of propylene [32].

4. Conclusions

Non-catalytic processes based on partial oxidation and oxidative cracking of hydrocarbons open up a number of promising opportunities for the conversion of various hydrocarbon gases into petrochemicals and fuels. The main advantages of these processes are high energy efficiency and low capital costs, which opens up the possibility of using low-resources hydrocarbons from various, including unconventional sources. The non-cata-

lytic nature of these processes makes it possible to significantly reduce the requirements for the composition of the gas and the costs of its preparation. The absence of a catalyst greatly simplifies the computer modeling of such processes and their subsequent scaling. Among the priority problems that can be solved on the basis of these processes are the processing of small streams of associated petroleum gases, which are still flared all over the world, as well as the distributed production of hydrogen directly at the places of its consumption, which makes it possible to bypass still unresolved problems of its storage and transportation.

Acknowledgements

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