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Perspective tendencies in development of small scale processing of gas resources

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Abstract: This paper analyses alternative routes for production of chemicals from different hydrocarbon gases by their direct, without syngas production, oxidative conversion to oxygenates or ethylene. Main of these routes are direct oxidation of methane to methanol (DMTM) and selective oxy-cracking of heavier natural or associated petroleum gas components which can be used for production of high value-added petrochemicals (in combination with carbonylation processes) and fuel gases, useful for gas piston engines. The advantages and practical capabilities of such technologies are discussed.

Keywords: associated petroleum gas; carbonylation; fuel gas; gas to liquids; Mendeleev XX; natural gas; oxidation.

Introduction

One of the main causes of low profitability of modern gas chemistry technologies is that they are based on traditional methods of syngas production with high capital and energy consumption. Traditional technologies for syngas production consume up to 70 % of total expenditures for conversion of natural gas to methanol or synthetic liquid hydrocarbons (GTL-products). To a more wide use of natural gas as a raw chemical material new technologies for its conversion into chemicals and motor fuels are necessary. Two possible alternatives for the development of new generation of GTL processes are possible. The first one is the decreasing expenditures for the stage of syngas production by developing of new technologies of its production from natural gas. The second is the development of alternative technologies which do not need the use of syngas.

Alternative GTL technologies that did not need the preliminary production of syngas are very attractive. As a base of such technologies can be used the processes of partial oxidation of hydrocarbons, such as direct oxidation of methane to methanol (DMTM), selective oxy-cracking of heavier natural or associated petroleum gas components, or oxidative coupling of methane (OCM) to ethylene with subsequent catalytic carbonylation and/or oligomerization of oxidation products. The main products of these processes are methanol and CO (DMTM) and ethylene and CO (selective oxy-cracking and OCM). The ratio between obtained products can be varied in a wide range by changing the process parameters and initial ratio of reagents. This let to enlarge the assortment of obtainable products by subsequent carbonylation and/or oligomerization of oxidation products basing on the already existing industrial processes.

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Scientific foundations of processes of partial oxidation of methane to methanol and oxycracking of hydrocarbons

The main peculiarity of methane oxidation, because of which the respective study is so difficult, is the nonlinear character of almost all major stages of this process with respect to concentrations of the starting reagents. Nonlinearity with respect to the starting reagents of nearly all significant reactions, a low accuracy (lower than 15 %) of the data on the rate constants of even most studied reactions, variety of parallel routes of the formation and consumption of the most part of intermediate and final products, a strong dependence of many rate constants on the temperature, pressure, and even composition of the reagents, many multichannel reactions, and other factors so far do not allow one to imagine the possibility of any complete and reliable quantitative and even qualitative analysis of these processes. The inevitable presence of heavier hydrocarbons in the real gas makes this problem more complicated.

A large group of promising processes of direct conversion of natural gas to chemical products is based on the partial (i.e. incomplete, at the oxygen concentration lower than the value necessary for complete oxidation) oxidation in the medium-temperature range from ~250 to 1200 °C. In this case, oxygenates (methanol, ethanol, formaldehyde, and other) are formed at temperatures from 400 to 600 °C, olefins are formed at 800–900 °C, and syngas is formed at 800–1200 °C.

Unlike high-temperature methane oxidation in which radicals $OH^\cdot$, $H^\cdot$, $CH^\cdot$, $CH_2^\cdot$, and others play an important role, the key radicals in processes of medium-temperature methane oxidation are methyl radical $CH_3^\cdot$ and methyl peroxide radical $CH_3OO^\cdot$, which is readily formed from methyl radical in the presence of even minor concentrations of oxygen in the reversible reaction

$$CH_3^\bullet + O_2 \leftrightarrow CH_3OO^\bullet \tag{1}$$

At the temperatures lower than 600 °C, especially under elevated pressures, the equilibrium in reaction (1) is shifted to the right, which initiates the chain of subsequent transformations resulting in the formation of oxygenates. From the viewpoint of production of such a large scale product as methanol, the range of elevated pressures of 50–100 atm and temperatures from 400 to 600 °C is most interesting. The mechanism of methane oxidation in this range is fairly well studied nowadays [1, 2] and demonstrates a series of interesting features. The major reactions determining the most striking peculiarities of the mechanism of methane oxidation in this temperature range are presented below in Scheme 1.

According to N.N. Semenov's definition, this is a typical degenerate branched process, since branching proceeds via the formation and subsequent decomposition of the relatively stable saturated compound methyl hydroperoxide. However, under the conditions indicated, methyl hydroperoxide decomposes very rapidly, providing a high intensity of branching in this reaction.

The main peculiarities of partial oxidation of methane to methanol (POMM) are governed by the fact that it is a degenerate branched chain process with very intensive branching but a very short chain.

$CH_4 + O_2 \rightarrow CH_3^\bullet + HO_2^\bullet$ Initiation

$CH_3^\bullet + O_2 \leftrightarrow CH_3OO^\bullet$

$CH_3OO^\bullet + CH_4\ (CH_3OH, CH_2O, HOOH, \text{etc.}) \rightarrow$

$\rightarrow CH_3OOH \rightarrow CH_3O^\bullet + OH^\bullet$ Branching

$CH_3OO^\bullet + CH_3OO^\bullet \rightarrow CH_3OH + CH_2O + O_2$ Termination

$\rightarrow CH_3OOCH_3 + O_2$

$$\left.\begin{array}{l} CH_3OO^\bullet + CH_3OO^\bullet \rightarrow 2CH_3O^\bullet + O_2 \\ CH_3O^\bullet + CH_4 \rightarrow CH_3OH + CH_3^\bullet \\ CH_3O^\bullet + O_2 \rightarrow CH_2O + HO_2^\bullet \\ HO_2^\bullet + HO_2^\bullet \rightarrow HOOH + O_2 \end{array}\right\} \text{Formation of products}$$

Scheme 1: The major reactions of the mechanism of methane oxidation.

The presence of heavier methane homologues usually promotes methane oxidation due to a higher rate of radical generation in the reaction

$$C_nH_{2n+2} + O_2 \rightarrow C_nH_{2n+1}^{\bullet} + HO_2^{\bullet} \qquad (2)$$

compared to a similar reaction of methane itself. However, there are some paradoxes of the oxidation of light alkanes: under certain conditions, the conjugated oxidation of more stable methane could promote the oxidation of its less stable homologues [2]. This effect is related to a higher branching efficiency of methane (compared to its homologues) for the oxidation in the medium-temperature range provided by the formation and decomposition of methyl peroxide radicals in the reaction sequence

$$CH_3^{\bullet} \rightarrow CH_3OO^{\bullet} \rightarrow CH_3OOH \rightarrow CH_3O^{\bullet} + OH^{\bullet} \qquad (3)$$

In addition, the oxidation of heavier alkanes can be accompanied by the decomposition of the corresponding alkyl peroxide radicals to olefin and radical $HO_2^{\cdot}$ relatively poorly reactive under these conditions

$$C_nH_{2n+1}^{\bullet} \rightarrow C_nH_{2n+1}OO^{\bullet} \rightarrow C_nH_{2n} + HO_2^{\bullet}, \qquad (4)$$

which is equivalent to the switching off branching and the appearance of an additional termination channel.

The presently attained level of the understanding of the kinetics of this process and the related kinetic modeling qualitatively (and even quantitatively to some extent) shows the main regularities of the POMM process. The fundamental foundations of the partial oxidation of natural gas to methanol were developed on the basis of experimental studies and kinetic modeling of the process and allowed one to propose new principles for its organization. Although a low concentration of oxygen is required to provide a high selectivity of methanol formation, which results in a low conversion of methane, an increase in the conversion with retention of a low current concentration of oxygen and temperature of the process can be attained due to the distributed oxidant supply with elimination of excessive heat prior to the supply of each next portion. The latter is especially important, since each percent of oxygen in the mixture increases warming by approximately 40 °C, and it is easy to overstep the optimum equilibrium conditions in reaction (1) at the oxygen concentration higher than 4 %.

Two types of reactors providing a high methane conversion within one cycle were proposed on the basis of analysis of peculiarities of the mechanism of the process: reactor of partial oxidation of natural gas with fractional air supply and gas cooling of a reaction mixture and reactor-generator with fractional air supply and reaction mixture cooling due to energy vapor generation between oxidation steps [3].

The methods for increasing conversion due to the partial recirculation of reaction gases were developed. This makes it possible to obtain more than 60 kg per 1000 m^3 of passed gas in the simplest variant when using atmospheric air as an oxidant. When air enriched in oxygen up to 50 % is used, recirculation makes it possible to obtain more than 200 kg per 1000 m^3 of passed gas. In both cases, the “dry,” i.e. containing no heavy hydrocarbons, methane gas with a high methane number is obtained as the second product. Presently it seems promising to develop field small scale setup with the productivity with respect to methanol from two to thousands of tons annually on the basis of this process.

Experimental

The scheme of the experimental setup is shown in Fig. 1. The setup included tubular flow reactor (8), system of flow regulation, control, and analysis. The starting gases, hydrocarbons mixture (C_1–C_4) and oxygen were fed from cylinders (1) through pressure regulator (2). Pentane was fed from peristaltic pump (12) through evaporator and heated pipeline (7). The consumption of the starting gases and their ratio were controlled and specified by gas mass flow controllers (3). The temperature at different points inside the reformer was

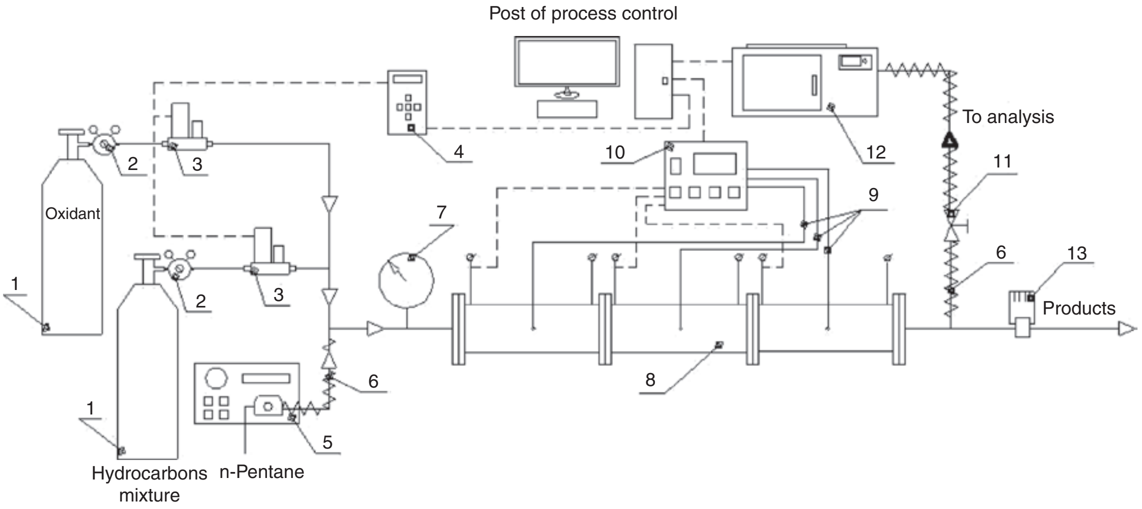


Fig. 1: Scheme of the laboratory experimental stage.
1 – gas cylinders; 2 – pressure regulator; 3 – mass flow controller; 4 – mass flow control module; 5 – peristaltic pump; 6 – heating tubing; 7 – manometer; 8 – tubular flow reactor; 9 – thermocouple; 10 – PID controller; 11 – sample valve; 12 – gas chromatograph; 13 – back-pressure regulator.

measured by thermocouples (10). Some portion of the reaction products flow was taken on-line to chromatographic analysis. The gas composition (O_2, N_2, CH_4, CO, CO_2, C_{2+}, C_{3+}, C_{4+}) was analyzed using a GC instrument equipped with TC and FID detectors.

Partial oxidation of mixtures of methane and its homologues

For the processing of natural and casing-head gases with a high content of heavy methane homologues, the working pressure and temperature can be lower than those for methane oxidation.

The homogeneous oxidation of mixtures of alkanes C_1–C_4 starts already at 10 atm. At pressures $P<40$ atm, methane in the composition of the mixture is not oxidized and its conversion under these conditions has formally a negative value because of methane formation due to the oxidation of heavier hydrocarbons. An increase in the oxygen content in the initial mixture substantially increases the conversion of hydrocarbons C_3–C_4 (Fig. 2).

At the higher pressures $P>40$ atm, methane is already involved in the oxidation process and its conversion becomes appreciable.

The oxidation of ethane starts under a pressure of 30 atm. The further pressure increase results in an increase in the conversion of ethane. As the initial oxygen concentration increases, the ethane concentration in the mixture increases and its conversion become formally negative (Fig. 2).

The major oxidation products are methanol, formaldehyde, water and CO. The concentrations of CO and methanol increase with the pressure increase, and these products are formed in approximately equal amounts in the whole pressure range. Ethanol and propanol (1–2 wt.%) and minor amounts of formic and acetic acids (0.1–0.3 wt.%) were also observed among the liquid-phase products of oxidation of mixtures of C_1–C_4 alkanes. In addition to CO, methane, and ethane, CO_2 and insignificant amounts of hydrogen, ethylene, and propylene are gas-phase oxidation products. Note that the partial oxidation of ethane results in higher yields of formaldehyde and ethanol, whereas the oxidation of other alkanes leads to the predominant formation of methanol [2, 4].

Since the partial oxidation of C_{2+} hydrocarbons occurs much more rapidly than the oxidation of methane, this provides a possibility of selective oxidation of C_{2+} alkanes directly in the casing-head petroleum gas.

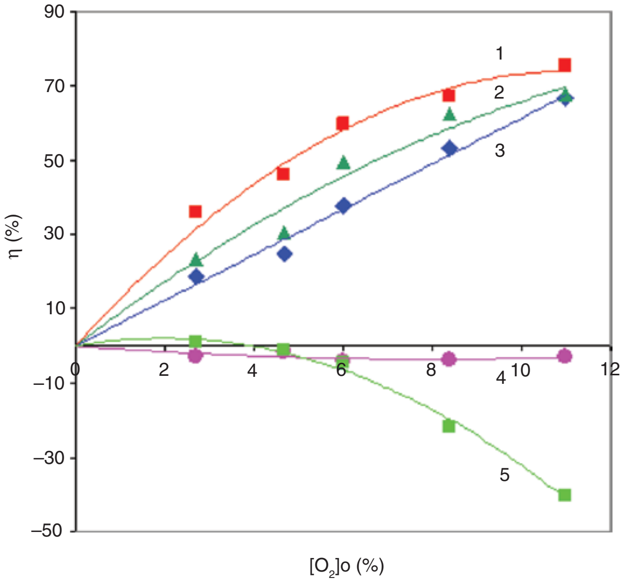


Fig. 2: Conversion of hydrocarbons vs. initial oxygen concentration: *1*, butane; *2*, isobutane; *3*, propane; *4*, methane and *5*, ethane; $P = 20$ atm, $T_0 = 370$ °C. Composition of the mixture: 93.6 % CH_4, 1.1 % C_2H_6, 4.5 % C_3H_8, 0.5 % *iso*-C_4H_{10}, and 0.5 % C_4H_{10}.

Oxycracking

Selective oxycracking of hydrocarbon gases at 700–750 °C and normal pressure is another developed method of simple and flexible processing of mixture of hydrocarbon gases, in particular, casing-head gas that would allow their utilization directly in the fields [5]. Only C_{2+} hydrocarbons undergo oxycracking under these conditions, and the oxycracking products are compounds less prone to resin and soot formation and detonation, namely, ethylene and other olefins, methane, CO, and H_2. The data on the compositions of gas mixtures obtained by the oxycracking of mixtures of methane with C_{2+} hydrocarbons are presented in the Table 1.

It was shown [5] for the oxycracking of *n*-alkanes C_2–C_5 that the temperature of the onset of noticeable conversion of the reagents decreased by ~100 °C on going from ethane to pentane (Fig. 3). An increase in the reactivity in the series of *n*-alkanes is primarily related to a decrease in the energy of the C–H bond in the molecule. The cleavage of this bond upon hydrogen atom detachment with oxygen is the rate-determining step of the process under the studied conditions. An increase in the number of carbon atoms in the alkane molecule results in a fast decrease in the selectivity of the formation of the primary hydrogenation products. However, the overall selectivity of formation of lower olefins in the series of alkanes C_2–C_5 at the alkane/oxygen ratio equal to 2:1 under other equivalent conditions (temperature and resistance time) changes insignificantly.

Advantages of direct partial oxidation and oxycracking of hydrocarbon gases compared to processes based on initial production of syngas

The following advantages of the direct partial oxidation of hydrocarbon gases and oxycracking of heavy components of casing-head gases compared to the processing processes including the stage of syngas production should be mentioned:

- the one-step character of the processes, technological simplicity, and the possibility to construct module automated setups that do not require numerous and highly qualified staff;
- the gas-phase noncatalytic character of the process making it easily controllable, requiring no supply and periodical recovery of the catalyst, and insensitive to minor impurities of catalytic poisons, for example, sulfur;

Table 1: Composition of gas mixtures obtained by the oxycracking of hydrocarbon gases at 750 °C.

No.	Oxycracking of mixture	Supply of O_2, L/h per 1000 L/h of starting gas	Starting gas				Gas after cracking				
			CH_4, vol.%	C_3H_8, vol.%	C_4H_{10}, vol.%	C_5H_{12}, vol.%	CH_4, vol.%	CO, vol.%	C_2H_4, vol.%	C_{3+}, vol.%	N_2, vol.%
1	Methane + butane, oxygen as oxidant	27	95.1	–	4.9	–	89.7	1.4	3.7	1.8	–
2	Methane + butane, oxygen as oxidant	10	95.3	–	4.7	–	91.1	0.6	3.3	2.1	–
3	Methane + pentane, 60 % O_2 +40 % N_2 as oxidant	56	94.1	–	–	5.9	81.3	4.0	5.2	1.7	3.2
4	Methane + pentane, air as oxidant	67	94.1	–	–	5.9	66.9	2.1	4.5	2.5	19.0
5	Methane + propane + pentane, 60 % O_2 + 40 % N_2 as oxidant	96	88.0	6.0	–	6.0	72.6	6.6	7.4	2.9	4.8
6	Methane + ethane (6 %) + propane + butane, oxygen as oxidant	162	82.0	8.0	4.0	–	71.2	9.4	7.6	1.7	0.7

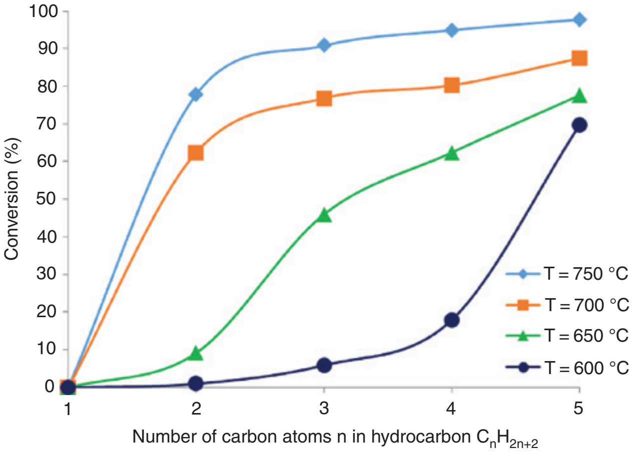


Fig. 3: Temperature dependences of the conversion of hydrocarbons C_1–C_5.

- a high flexibility toward raw materials and the possibility of using alternative, nontranditional, and poorly resource sources of hydrocarbon raw materials, including those with a high content of heavy methane homologues;
- a relatively weak dependence of economics of the process on the scale of the production, which makes it possible to profitably exploit small scale setups;
- the possibility of functioning in the composition of energochemical complexes.

Control of the ratio of products of partial oxidation and oxycracking for further use in carbonylation processes

The major products of partial gas-phase oxidation of hydrocarbon gases are oxygenates, *viz.*, methanol and formaldehydes, as well as carbon monoxide. An approximate yield of the products of partial methane oxidation can be presented by the following scheme:

$$2CH_4 + 2O_2 \begin{array}{l} \nearrow 0.9CH_3OH + 0.1(CH_2O + H_2) \\ \searrow 0.9(CO + 2H_2O) + 0.1(CO_2 + H_2O + H_2) \end{array} \tag{5}$$

For the partial oxidation of methane homologues that are found in the composition of casing-head petroleum and fatty natural gases, only 50 % or less of the starting hydrocarbon raw materials are processed to oxygenates, and the rest amount is transformed into CO, CO_2, and C_{2+} hydrocarbons. Less than 25 % of oxygen are consumed to the formation of oxygenates, and the rest amount is consumed to the formation of CO and water, and an aqueous solution of methanol is always formed.

For oxidative cracking of C_{2+} hydrocarbons, the selectivity of ethylene formation to carbon is lower than 50 %, and other reaction products are CO, CH_4, and olefins C_{3+}.

Although a certain change in the ratio between the main channels and between the products in each channel can be attained by a change in the parameters of the process, a principal moment is the simultaneous formation of the key target product (methanol, formaldehyde, or ethylene) and carbon monoxide as a secondary, often undemanded product. Both liquid oxygenate or ethylene and formed CO should be used to enhance the degree of use of hydrocarbon raw materials, *viz.*, selectivity of formation of target products to carbon. The use of the wide and well studied chemistry of carbonylation processes can provide a possibility of developing basically new small scale alternative GTL processes for processing natural and casing-head petroleum gases that do not require the formation of syngas. The products obtained by carbonylation can be used directly under field conditions (methyl acetate, dimethyl carbonate, diethyl ketone, and others) and for the synthesis of valuable chemicals (methyl glycolate, methyl propionate, ethylene diacetate, etc.).

Of course, the direct involvement in the carbonylation process of the reaction mixture, which is obtained by the partial oxidation or oxycracking of light hydrocarbons and containing oxygenates and CO or ethylene and CO without separating the mixture into the components is of greatest interest. The conditions of these processes differ strongly from the earlier studied interaction of individual components and, therefore, require serious additional studies, which are being performed by us presently.

In order to develop alternative GTL processes based on carbonylation of products of the oxidative processing of hydrocarbon gases, it was necessary to establish what parameters of the process exert the maximum effect on the component distribution and ratio of concentrations of methanol, ethylene, and carbon monoxide, since reagents in different ratios are required for the syntheses of the target carbonylation products.

For the direct partial oxidation of "dry" methane performed under a pressure of 70–80 bar, temperatures 450–550 °C, and an oxygen concentration in the initial gas mixture of 3 %, the ratio of methanol to CO, as follows from the scheme presented above (5), is about 1. The change in the oxidation conditions can only enhance the CO fraction in the obtained vapor–gas mixture, which increases with an increase in the temperature and oxygen concentration. The technological organization of the process with three oxidation steps or with the recirculation of the unreacted gas favoring an increase in the yield of methanol based on passed methane also decreases the methanol to CO ratio. At the same time, the stoichiometric ratio of methanol to CO in various syntheses based on methanol carbonylation is 2:1 or 1:1, i.e. in all cases, the complete utilization of CO cannot be attained. However, as will be shown below, the enhanced CO content does not substantially decrease the fuel characteristics after the condensation of the carbonylation products when using the waste gas as a fuel mixture for power setups.

The partial oxidation of methane mixtures with heavier homologues under a pressure of 20–40 bar favors the situation where pentane, butane, and propane primarily undergo oxidation in this process with the predominant formation of methanol, methane, and CO. The concentration of oxygen in the starting mixture supplied to oxidation exerts the maximum effect on the change in the distribution of oxidation products. The product distribution for the partial oxidation of a hydrocarbon mixture consisting of 92 % methane, 1.3 % ethane, 5.6 % propane, and 1.1 % butanes at different initial concentrations of oxygen is presented in Fig. 4 [6]. As can be seen, the methanol to CO ratio can vary in a wide range depending on the initial oxygen concentration. The CO concentration increases with an increase in the O_2 concentration, whereas the methanol content in the product does not change so substantially and attains a maximum at 6–7 % O_2. Therefore, the

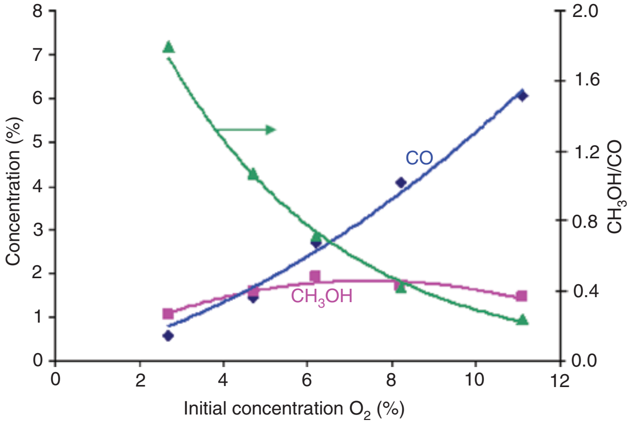


Fig. 4: Dependences of the concentrations of CH_3OH and CO in the reaction mixture and their ratio for the partial oxidation of a hydrocarbon mixture (92 % methane, 1.3 % ethane, 5.6 % propane, and 1.1 % butanes) on the initial oxygen concentration at $T_{init} = 370$ °C and $P = 20$ bar [6].

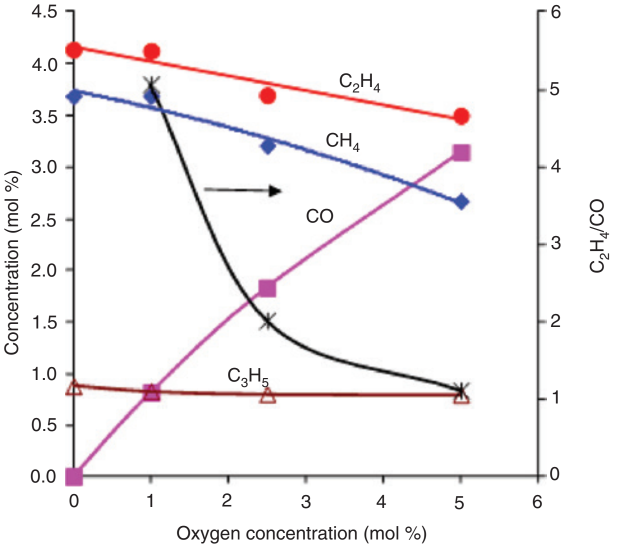


Fig. 5: Influence of the oxygen concentration on the distribution of products of the oxidative cracking of *n*-butane at 750 °C [7].

CH_3OH/CO ratio decreases with an increase in the oxygen concentration. To obtain methanol and CO in a ratio of 1:1, the initial oxygen concentration should be ~5 %, while it should be at a level of ~2 % for the CH_3OH/CO ratio equal to 2:1.

Many processes are known for the preparation of valuable chemicals based on ethylene and CO. These are oxycarbonylation, methoxycarbonylation, and syntheses of diethyl ketone, oligoketones, and polyketones. These reactions occur at the molar ratios of ethylene to CO from 1:1 to 2:1. The mixtures indicated can be obtained by oxidative cracking in the temperature range 700–750 °C.

The C_2H_4 to CO ratio can be optimized by a change in the parameters of the process and the initial oxygen concentration, and the oxygen concentration in the mixture supplied to oxidation exerts the maximum effect (Fig. 5) [7]. The data presented in Fig. 5 show that the CO content substantially increases with an increase in the oxygen concentration in the initial gas mixture, whereas the content of ethylene decreases insignificantly. As a result, the C_2H_4/CO ratio varies in wide ranges (in this experimental series, from 5 to 1). The optimum ratio equal to 1 is achieved the oxygen concentration about 5 %.

Thus, the degree of use of the starting raw materials can be increased by controlling the distribution of products obtained by the oxidative conversion of hydrocarbon gases, and a high efficiency of the processes than require no stage of syngas preparation can be achieved.

Processes of carbonylation of products of oxidative processing of hydrocarbon gases

A concept of using processes of homogeneous partial oxidation of hydrocarbon gases in chemical industry is a part of the presently developed GTC (gas-to-chemicals) approach [8]. Many reaction are known that potentially involve products of partial oxidation of hydrocarbon gases, including methanol, ethylene, and CO, resulting in the production of valuable chemicals.

Synthesis of acetic acid from methanol and CO

The synthesis of acetic acid is a well known and industrially mastered process involving CO and methanol:

$$CH_3OH + CO \rightarrow CH_3COOH$$

The basis of the modern methods for acetic acid preparation is the Monsanto process based on the carbonylation of methanol at a low pressure with the iodide-promoted rhodium-containing catalyst exhibiting higher selectivity and activity than the cobalt-based catalysts. This makes it possible to decrease the temperature and pressure of the synthesis to 175–185 °C and 3 MPa, respectively [9]. The selectivity of the process to methanol is about 99 %, which is caused by the occurrence of a specific molecular catalytic mechanism on the rhodium active sites.

The selectivity of the process to CO is 85 %, which is related, first of all, to the occurrence of the undesirable reaction of "water gas" (WGSR, Water Gas Shift Reaction):

$$CO + H_2O \rightarrow CO_2 + H_2$$

This reaction is also catalyzed by the rhodium complexes and, hence, it is impossible to avoid it due to a change in the conditions of the process. The catalysts based on the iridium complexes are free of this drawback.

In 1983 the Eastman Chemical company developed the process of preparation of acetic anhydride by the carbonylation of methyl acetate. The carbonylation occurs on the rhodium catalysts with promotion by the lithium salts (LiI). The powder of the built setup is 320 thousands of tons annually [10]. The production of methyl acetate is carried out according to a standard procedure of acetic acid synthesis supplemented by the step of esterification with a methanol excess under the conditions of reaction distillation.

Another variant of methanol carbonylation with the formation of acetic acid is the Cativa process developed in the 1990s by the BP Chemicals Co. The Cativa process combines the use of the iridium and ruthenium catalysts and differs from the Monsanto process as follows. The oxidative addition of methyl iodide on the iridium catalysts is 150 times faster than that on the rhodium catalysts, which determines an increase in the total rate of the process [11], and the selectivity to acetic acid can exceed 99 % (the iridium catalyst makes it possible to avoid the formation of propionic acid as a side product).

The method for acetic acid synthesis by methanol carbonylation is considered to be most economic among industrial methods (oxidation of acetaldehyde, oxidation of hydrocarbons C_4–C_7, and other). All plants that are being built at present using this technology are designed to the productivity with respect to acetic acid at a level of 0.5 mln. tons annually, and the capital outlays to the building of this production are estimated as 500 mln. $US.

Oxidative carbonylation of methanol with formation of dimethyl carbonate

The reaction of methanol with carbon monoxide in the presence of oxygen on the copper-containing catalyst (CuCl) affords dimethyl carbonate

$$2\ CH_3OH + CO + O_2 \rightarrow (CH_3O)_2CO$$

The process was first implemented in industry by the EniChem Company [12] and differs from the earlier used method of methanol phosgenation by the absence of toxic and corrosive reagents and products. It was proved later than the systems similar to the catalytic system of the Wacker process containing $PdCl_2$ and $CuCl_2$ can be used as efficient catalysts for this process [13]. The presence of palladium in these catalytic systems facilitates the activation of CO and favors an increase in the activity and productivity of the catalytic system. Dimethyl carbonate can be used as a "green" solvent for the preparation of dye compositions, is one of popular electrolytes for lithium rechargeable batteries, and can be used as an additive to moor fuel: it has a high octane number (105) and a high oxygen content, which favors a decrease in the emission of CO, SO_x, and NO_x by engine [14]. Dimethyl carbonate is also a promising raw materials for the preparation of aromatic polycarbonates through diphenyl carbonate. At the moment the world production of dimethyl carbonate does not satisfy the existing demand for it [14].

Preparation of ethylidene diacetate

As mentioned above, methyl acetate can be obtained along with acetic acid by the carbonylation in a methanol excess [15]. The further reductive carbonylation of the latter affords ethylidene diacetate [16], from which vinyl acetate monomer, one of the most important petrochemical products, can be obtained [17]:

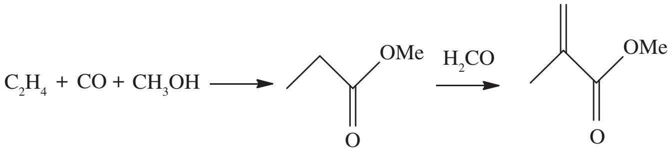
$$2CH_3COOCH_3 + 2CO + H_2 \rightarrow CH_3CH(OCOCH_3)_2 + CH_3COOH,$$
$$CH_3CH(OCOCH_3)_2 \rightarrow CH_2 = CHOCOCH_3 + CH_3COOH.$$

The described syntheses are more economic than the traditional ones by 30–40 % and, hence, numerous modifications of carbonylation processes with the formation of both methyl acetate and ethylidene diacetate were patented in different companies in different countries of the world.

Carbomethoxylation of ethylene

Methyl propionate is one of the low-molecular-weight products, which can be formed by the cooligomerization of ethylene and CO in the presence of methanol involving the stage of isomerization of the active site. The reaction of methyl propionate formation (carbomethoxylation of ethylene) requires the participation of equimolar amounts of ethylene, methanol, and CO and occurs in the presence of the palladium complexes with sterically loaded bidentate phosphine ligands.

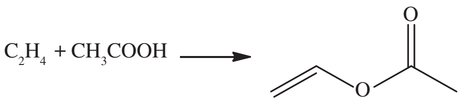
Carbomethoxylation of ethylene was commercialized in 2008 when the Lucite Alpha process was developed [18]. At the first stage of the process, ethylene, CO, and methanol react to form methyl propionate, which reacts at the second stage with formaldehyde to transform into methyl methacrylate.



The carbomethoxylation stage proceeds *via* a complicated mechanism including two types of catalytic cycles [19] involving the catalysts being adducts of the palladium salts with diphosphine ligands bearing tertiary substituents at the phosphorus atom (to suppress polymerization). In the case of the industrial Alpha Lucite process, this is 1,2-bis(di-*tert*-butylphosphinomethyl)benzene.

Production of vinyl acetate

Vinyl acetate is one of the most important monomers (a component for polymer production) in industrial organic synthesis. The world production of vinyl acetate reaches 6.5 mln. tons annually. Along with the mentioned above method for its production from ethylidene diacetate, which, in turn, can be obtained by the reductive carbonylation of methyl acetate, there is another way. Ethylene that replaced the acetylene technology was acknowledged to be the most profitable raw materials for the preparation of vinyl acetate. At present the main technology of vinyl acetate production is the reaction of ethylene with acetic acid in the presence of the palladium catalyst and oxygen.



The reaction can be conducted under the action of the homogeneous $PdCl_2/CuCl_2$ catalyst at the temperatures from 110 to 130 °C and pressures of 30–40 atm. However, these conditions are very corrosive toward the technological equipment. The developments of recent years led to the preparation of heterogeneous Pd/

Au catalysts without the drawbacks indicated that allow one to attain selectivity up to 94 % to ethylene and 98–99 % to acetic acid. The use in these technologies of fluidized bed reactors makes it possible to decrease capital outlays by 30 %. Several large plants on the production of vinyl acetate using the indicated method have been built during several recent years in China, India, Iran, and Saudi Arabia.

The most promising processes for processing production of the oxidative conversion of natural gases by catalytic carbonylation methods are the processes the products of which have the highest value added and are characterized by high demand in the world market. Among these products are first of all dimethyl carbonate and methyl methacrylate used for the production of highly marginal polymers and in a series of other high-tech areas of industry.

Our preliminary experiments using as raw materials for carbonylation of model gas mixtures imitating the composition of products of methane partial oxidation to methanol and products of hydrocarbon oxy-cracking showed technological affinity of these processes.

Dimethyl carbonate was obtained in the yield up to 17 % per one cycle (reaction temperature 150 °C, pressure 15 atm) by the oxidative carbonylation of vapor–gas mixtures containing methanol, up to 10 % CO, and up to 10 % O_2 on the heterogeneous catalyst prepared by supporting 10 wt.% $CuCl_2$ on active carbon.

Ethylene methoxycarbonylation in a vapor–gas mixture containing 10 % ethylene and 50 % CO on the original heterogeneous catalysts being the palladium complex on the sulfate cation-exchange resin at a temperature of 200 °C and a pressure of 20 atm makes it possible to obtain methyl propionate (intermediate product of methyl methacrylate synthesis) in the yield up to 40 % per one cycle.

Oxidative conversion of hydrocarbon gases to fuel gas with high methane number for power plants

“Fatty” natural and casing-head petroleum gases are inappropriate for direct use in many types of modern power plants, in particular, those based on gas piston engines (GPE), because they contain heavy fractions of C_{3+} hydrocarbons with low methane numbers. The studies performed show [20] that the presence of even 1 % alkanes C_3–C_5 significantly decreases the delay time of spontaneous ignition of methane. The admissible content of heavy components C_{5+} in the gas motor fuel at which their influence on the detonation stability of the fuel is rather low and estimated by the value of 0.5 % only.

The high content of C_{3+} hydrocarbons in the gas mixture results in knocking (detonation) in the engine and does not allow it to achieve the nominal power. In addition, carbonization and wear of engine parts increase, and the operation source decreases. Therefore, producers of GRM specify certain requirements on the fuel gas quality to provide the operation of the equipment under normal conditions and the achievement of the declared characteristics. Although these requirements can somewhat differ depending on the type and structure of the engine, the most typical ones are the following requirements [21]:

- content of methane higher than 70 vol.%,
- lowest heating value (LHV) 30–36 MJ/m^3,
- density 0.7–1.2 kg/m^3.

Methane number MN is the most important parameter of the gas fuel characterizing its antidetonation properties [22]. For example, the Cummins Westport Company requires the use of gas mixtures with MN higher than 65 for the normal operation of engines [23]. The producers warrant the operation of GRM with nominal values of power and efficiency only if these requirements are fulfilled.

“Fatty” natural and casing-head petroleum gases usually have MN lower than 52 and LHV higher than 40 MJ/m^3. The most popular method of their preparation for use in power plants is the extraction of liquid C_{3+} hydrocarbons by the deep cooling method using expensive and power-consuming setups. Placing of these setups in sites of hydrocarbon raw materials mining can be economically reasonable only in rare cases. We considered the possibility of achieving higher (than the initial values) fuel parameters of complicated hydrocarbon gas mixtures by the method of their preliminary partial oxidation. The partial oxidation of

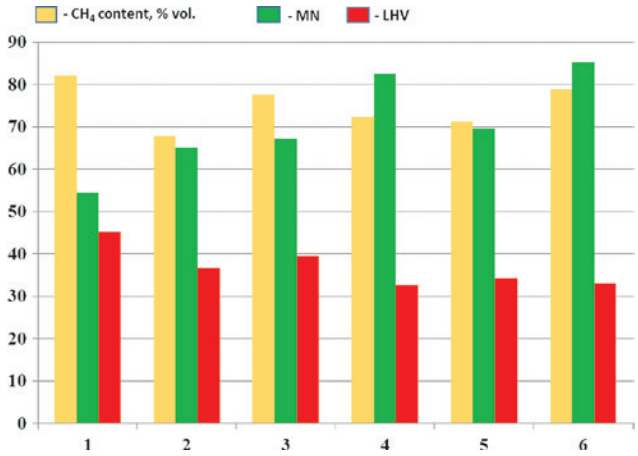


Fig. 6: Changes in the fuel characteristics of a mixture of hydrocarbon gases of the composition 82 vol.% CH_4, 6 vol.% C_2H_6, 8 vol.% C_3H_8, and 4 vol.% C_4H_{10} at different methods of oxidative processing.

hydrocarbon gas mixtures, including along with methane its homologues, at a pressure of 25–40 atm and temperatures 500–650 °C in a flow reactor at the initial oxygen concentration higher than 5 % results in an efficient decrease in the concentration of C_3–C_4 hydrocarbons having low MN with the simultaneous formation of CO and an increase in the methane concentration in the mixture [24]. As a result, the MN of the obtained gas increases and the inclusion of this process into the procedure of preparation of the initial hydrocarbon gas can lead to the enhancement of its antidetonation properties.

One more method for processing heavy GRM components with the formation of methane as one of the products is oxidative cracking under normal pressure and at temperatures about 750 °C. Among the compounds formed along with methane there are some products less prone to detonation than converted saturated hydrocarbons C_{3+} (ethylene, CO, CO_2), as well as H_2 manifesting a higher affinity to detonation [5]. These compounds act in different directions on the values of MN and LHV. Gas mixtures with various fuel characteristics can be obtained by the variation of the oxygen concentration. Note that the influence of ethylene and other olefins on the characteristics of power plants is yet studied insufficiently.

The fuel characteristics of the starting hydrocarbon mixtures can be enhance more by the introduction of an additional stage of carbonylation, since carbon monoxide is one of the products of the oxidative processing of the hydrocarbon mixtures. Owing to the involvement of CO into the carbonylation reaction with the compounds also obtained by this oxidative processing, methanol and/or formaldehyde, at the partial oxidation under pressure or with ethylene obtained by oxycracking at temperatures about 750 °C, their content in the gas mixture decreases and the methane concentration thus increases [25]. The simultaneous production of fuel gas with required optimum characteristics and valuable petrochemical products with high value added, such as methyl acetate, dimethyl carbonate, methyl propionate, ethylidene diacetate, diethyl ketone, oligoketones, polyketones, and others, becomes possible.

The data on a change in the fuel characteristics of a mixture of hydrocarbon gases with a composition of 82 vol.% CH_4, 6 vol.% C_2H_6, 8 vol.% C_3H_8, and 4 vol.% C_4H_{10}, the starting fuel characteristics MN = 54.3 and LHV = 45.2 MJ/m^3, and different methods of oxidative processing are presented in Fig. 6.

1. Starting hydrocarbon mixture.
2. One-step partial oxidation with air under a pressure of 30 bar at a temperature of 470 °C and an air flow rate of 250 m^3 per 1000 m^3 of the starting gas.
3. Three-step oxidation with technical oxygen (95 %) under a pressure of 30 bar at a temperature of 500 °C and a technical oxygen flow rate of 150 m^3 per 1000 m^3 of the starting gas.
4. Partial oxidation with technical oxygen (95 %) in the circulation process (circulation multiplicity 1:5) under a pressure of 30 bar at a temperature of 500 °C and a and a technical oxygen flow rate of 350 m^3 per 1000 m^3 of the starting gas.

5. Oxycracking at 750 °C and a technical oxygen flow rate of 170 m^3 per 1000 m^3 of the starting gas.
6. Combined process: oxycracking at 750 °C, partial oxidation under a pressure of 30 bar and at a temperature of 500 °C, and carbonylation to obtain methyl propionate (170 kg per 1000 m^3) and fuel gas. The flow rate of technical oxygen was 250 m^3 per 1000 m^3 of the starting gas.

The experimental data on the composition of reaction mixtures obtained from the partial gas-phase oxidation and oxidative cracking of the mixture in a flow reactor were used for calculations. The methane number and lowest heating value were determined from the data on the composition of gas mixtures using the AVL method (developed by the AVL List GmbH [26]).

As can be seen from Fig. 6, the fuel characteristics of the gas mixture obtained by partial oxidation under pressure or oxidative cracking correspond, as a rule, to the requirements imposed on the fuel for GRM.

The described methods for the improvement of fuel characteristics of "fatty" natural or casing head petroleum gases are characterized by technological simplicity and a higher flexibility toward raw materials. This makes it possible to use hydrocarbon gases of various compositions, including those with a high content of heavy methane homologues and the gas from alternative, nontraditional, and poor-resource source, and to develop simple in exploitation and cheap module automated setups for the preparation of hydrocarbon gases under the conditions of small deposits and deposits remote from power supply sources.

Conclusions

Therefore, the processes of partial oxidation of natural gas and other types of hydrocarbon gases can be a real base for effective alternative technologies for natural gas conversion into a wide assortment of highly demanded chemicals with high added value. Such technologies are much simpler and in some cases can turned out be more effective than multi-stage traditional technologies via production of syngas and provide possibility to obtain high value-added petrochemical products and fuel gases simultaneously.

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References

[1] V. S. Arutyunov, V. M. Shmelev, A. N. Rakhmetov, O. V. Shapovalova. *Ind. Eng. Chem. Res*. **53**, 1754 (2014).

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

[3] V. Arutyunov. *Catal. Today*, **215**, 243 (2013).

[4] E. V. Sheverdenkin, V. S. Arutyunov, V. M. Rudakov, V. I. Savchenko, O. V. Sokolov. *Theor. Found. Chem. Eng*. **38**, 311 (2004).

[5] V. S. Arutyunov, R. N. Magomedov, A. Yu. Proshina, L. N. Strekova. *Chem. Eng. J.* **238**, 9 (2014).

[6] I. G. Fokin, V. I. Savchenko, V. S. Arutyunov. *Russ. J. Phys. Chem. B*. **8**, 148 (2014).

[7] R. N. Magomedov, A. V. Nikitin, V. I. Savchenko, V. S. Arutyunov. *Kinet. Catal*. **55**, 556 (2014).

[8] I. Makaryan, I. Sedov, V. Savchenko. *Johnson Matthey Technol. Rev*. **59**, 14 (2015).

[9] A. Behr, P. Neubert. *Applied Homogeneous Catalysis*, Wiley-VCH, Weinheim (2014).

[10] S. W. Polichnowski. *J. Chem. Ed*. **63**, 206 (1986).

[11] A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers, R. J. Watt. *J. Am. Chem. Soc*. **126**, 2847 (2004).

[12] U. Romano, R. Tesel, M. M. Mauri, P. Rebora. *Ind. Eng. Chem. Prod. Res. Dev*. **19**, 396 (1980).

[13] X. Ding, X. Dong, D. Kuang, S. Wang, X. Zhao, Y. Wang. *Chem Eng. J.* **240**, 221 (2014).

[14] B. A. V. Santos, V. M. T. M. Silva, J. M. Loureiro, A. E. Rodrigues. *ChemBioEng Rev*. **1**, 214 (2014).

[15] P. Cheung, A. Bhan, G. J. Sunley, E. Iglesia. *Angew. Chem. Int. Ed*. **45**, 1617 (2006).

[16] D. Liu, X. Huang, L. Hu, D. Fang, W. Ying. *J. Nat. Gas Chem*. **19**, 165 (2010).

[17] N. Rizkalla, R. Vale EP 2138093 (Halcon) (1982).

[18] http://www.luciteinternational.com/our-technologies-innovation-130/ (accessed September 2016).

[19] W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman, S. Zacchini. *J. Chem. Soc. Dalton Trans*. 3300 (2002).

[20] K. Ya. Troshin, A. V. Nikitin, A. A. Borisov, V. S. Arutyunov. *Combust. Explos. Shock Waves* **52**, 386 (2016).

[21] S. S. Ivanov, M. Yu. Tarasov. *Neftyanoe Khozyaistvo (in Russian)* **1**, 102 (2011).

[22] S.B. Gupta, M. Biruduganti, B. Bihari, R. Sekar. in *Natural Gas – Extraction to End Use*, S. B. Gupta (Ed.), pp. 211–234, InTech Publishing, Rijeka (2012).

[23] Natural gas as fuel. Fuel Quality Calculator http://www.cumminswestport.com/fuel-quality-calculator (accessed 01.12.16).

[24] V. S. Arutyunov, V. M. Rudakov, V. I. Savchenko, E. V. Sheverdenkin. *Theor. Found. Chem. Eng*. **39**, 487 (2005).

[25] V. S. Arutyunov, V. I. Savchenko, I. V. Sedov, I. G. Fokin, A. V. Nikitin, L. N. Strekova. *Chem. Eng. J*. **282**, 206 (2015).

[26] M. Leiker, K. Christoph, M. Rankl, W. Cantellieri. Evaluation of anti-knocking property of gaseous fuels by means of methane number and its practical application to gas engines. Pfeifer U. (AVL, Graz, Austria), ASME-72-DGP-4 (1972).