Energochemical technologies: energy and bulk/basic chemicals in a single process*

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The exoergic reactions, which underlie the production of large-scale basic chemicals for organic industry, can be used for one-pot generation of energy and chemical products. Typical examples include methane oxidative conversion to produce synthesis gas and methane oxidative dimerization to give ethylene and ethane.

Key words: exoergic reactions, exothermal reactions, oxidative dimerization of methane, oxidative conversion of methane.

The mankind got acquainted with exoergic reactions in those distant past when people stopped being afraid of fire and learned to control burning and to utilize it for heating places of their habitation and for cooking. Since then, despite the appearance of alternative energy sources (water, nuclear, solar, wind, and geothermal energy, *etc.*), oxidation of, initially, organic substances and, later, fossil fuel still predominates in the world energy balance.[1]

For a long time, oxidation processes have also been used for the production of chemical compounds. Starting from the XVIII century, oxidative methods have been developed for the manufacture of basic chemicals. Nowadays, oxidation processes are used for the industrial production of chemicals whose volume amounts to millions of tons and the range covers more than 100 names.

With rare exception (for example, the reaction of nitrogen with oxygen), oxidation processes are exothermic. Indeed, substantial heat evolution accompanies the reactions that underlie the production of a number of basic chemical products including

sulfuric acid:

$$SO_{2(g)} + 1/2\ O_{2(g)} \longrightarrow SO_{3(g)}, \qquad (1)$$

$\Delta H^\circ_{298} = -98.95$ kJ mol^{-1},

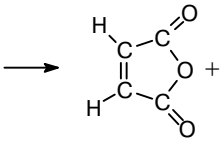
nitric acid:

$$2\ NH_{3(g)} + 2.5\ O_{2(g)} \longrightarrow 2\ NO_{(g)} + 3\ H_{2(g)}, \qquad (2)$$

$\Delta H^\circ_{298} = -422.57$ kJ mol^{-1},

maleic anhydride:

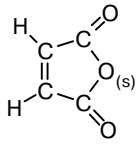
$$C_6H_{6(g)} + 4^1/_2\ O_{2(g)} \longrightarrow$$



$$+ 2\ CO_{2(g)} + 2\ H_2O_{(g)}, \qquad (3)$$

$\Delta H^\circ_{298} = -1658.12$ kJ mol^{-1},

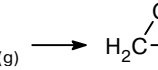
$$n\text{-}C_4H_{10(g)} + 4^1/_2\ O_{2(g)} \longrightarrow$$



$$+ 4\ H_2O_{(g)}, \qquad (4)$$

$\Delta H^\circ_{298} = -1311.53$ kJ mol^{-1},

ethylene oxide:



$$C_2H_{4(g)} + 1/2\ O_{2(g)} \longrightarrow H_2C{-}CH_{2(g)}, \qquad (5)$$

$\Delta H^\circ_{298} = -104.93$ kJ mol^{-1},

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acetaldehyde:

$$C_2H_{4(g)} + 1/2O_{2(g)} \longrightarrow CH_3—CHO_{(g)} \quad (6)$$

$\Delta H°_{298} = -218.66$ kJ mol^{-1}.

Complete combustion of a carbon-containing fuel (natural gas, oil, *etc.*) resulting in the formation of thermodynamically stable products, *i.e.*, carbon dioxide and water, is accompanied by the greatest heat evolution. Heat-and-power units such as boilers of thermal stations or internal combustion engines of vehicles are designed to achieve complete fuel combustion. The formation of partial oxidation products (CO, aromatic hydrocarbons, *etc.*) not only decreases the efficiency but also cause environment pollution.

A chemical reactor serves a different purpose: the task is to perform incomplete combustion of the feedstock, while maximizing the yield of one of the possible products and minimizing the proportion of side reactions of more extensive oxidation. Currently, oxidation of ethylene into ethylene oxide, acetaldehyde, vinyl acetate, and some other chemicals is carried out on an industrial scale with a selectivity approaching 90—100%.

The chemical industry as a whole is an energy-consuming branch. Before 1990, about 15% of all energy generated in the USSR was spent for the production of chemicals. Of the factors responsible for the high energy inputs into chemical industry, the poor utilization of the heat evolved in a chemical reaction comes among the first. Although it should hardly be expected that chemical industry would cease to be an energy-consuming branch, the need to design the ways of reducing energy consumption factors is obvious.

The utilization of the heat of exothermal reactions to counterbalance the losses that cannot yet be avoided, has become the directrix line of the development of chemical technology in recent years. A number of effective cases when this was successfully accomplished are known in the industrial practice. Thus in the production of elemental sulfur from hydrogen sulfide as a component of natural gas ("gas sulfur"), the reaction heat is utilized both for the industrial and public needs. The heat evolved upon carbon oxide hydrogenation in the methanol production can also be recovered.

The attempts to use the heat of chemical reactions for decreasing the energy expenditure have persisted and, by the end of the last century, they resulted in a pronounced decrease in the consumption factors and in the production cost.

This is especially efficient if the following conditions are met:

(1) the heat of the reaction is rather high;

(2) the scale of production of this chemical is sufficiently large, so that the capital outlays for heat recovery can be repaid over a short period.

As promising examples of energochemical technologies of this type, one can mention two processes being developed in Russia, namely, oxidative conversion of methane to synthesis gas (a mixture of carbon monoxide with hydrogen) and oxidative dimerization of methane to give a mixture of ethylene and ethane.

Currently, the industry uses a series of large-scale processes based on reactions involving carbon monoxide:[2] production of hydrogen, production of methanol, Fischer—Tropsch process (synthesis of higher hydrocarbons, alcohols, and alkenes), alkene hydroformylation and related processes (production of higher aldehydes and alcohols used as plasticizers, extractants), production of acetic acid, Gattermann—Koch synthesis (preparation of carboxylic acid halides) and related processes, production of formic acid, phosgene and dimethyl carbonate syntheses, synthesis of polyketones (promising biodegradable polymers, which may prove suitable for replacing polyethylene), and methyl methacrylate (the monomer for the manufacture of Plexiglass).

The so-called steam methane reforming is used most often for the production of synthesis gas in industry:

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2, \quad (7)$$

$\Delta H°_{298} = 206$ kJ mol^{-1}.

Carbone dioxide conversion is used to a substantially lesser degree

$$CH_4 + CO_2 \longrightarrow 2\ CO + 2H_2, \quad (8)$$

$\Delta H°_{298} = 247$ kJ mol^{-1}.

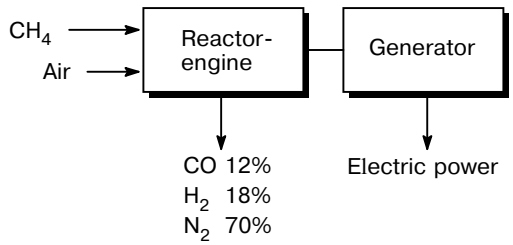
Synthesis gas can also be obtained by partial combustion of methane

$$CH_4 + O_2 \longrightarrow 2\ CO + 2H_2, \quad (9)$$

$\Delta H°_{298} = -35.72$ kJ mol^{-1}.

Only the last-mentioned reaction proceeds with heat evolution; moreover, the reaction is exoergic even at 298 K (the standard decrease in the free energy is -86.32 kJ mol^{-1}). It was proposed to use this reaction for the production of synthesis gas with simultaneous electric power generation.[3,4] This was done using a modified diesel engine or a compression engine, which served simultaneously as the chemical reactor. This process, implemented in 1998 on a synthesis gas unit with a capacity of 10000 m^3 per hour, is characterized by a high productivity of unit volume of the reaction space.

The functional diagram of such a process is shown below.



Low-pressure natural gas unsuitable for conventional utilization can be employed here as the feedstock. Oxidation of natural gas in this process is performed by air. On the one hand, this improves the economic characteristics of the process (oxygen production is not required) but, on the other hand, the quality of the resulting synthesis gas is reduced due to the high content of nitrogen (~70%). Nevertheless, even such a synthesis gas can, in principle, be used to produce both gasoline and a promising diesel fuel, dimethyl ether.

Power generation coupled with production of synthesis gas ensures a decrease in the production costs of the methane conversion and, hence, a decrease in the cost of the resulting hydrogen and synthesis gas. The significance of this result can hardly be overestimated if one recalls that these products are used as feedstocks for the manufacture of basic chemicals such as ammonia, methanol, and so on. A reduction of price of synthesis gas can change crucially the situation with synthetic liquid fuel for motor transport. Indeed, the cost of synthesis gas accounts for up to 60% of the cost of the Fischer—Tropsch manufacture of liquid hydrocarbons. With inexpensive synthesis gas, chemically produced fuel may become competitive.

Yet another route in the development of energo-chemical industrial processes based on methane is performing the methane conversion into carbon monoxide in a fuel cell.[5,6] However, the productivity of these systems is still relatively low and their technical prospects are obscure.

One more widely used important product of heavy organic synthesis (apart from CO) is ethylene. The production volume of ethylene is constantly increasing: in 1989, the world output was 52 million tons of ethylene; according to the data for January 1, 2000, the scale of production reached 92.7 million tons per year, and by 2010, the output is predicted to reach 147 million tons per year. Nevertheless, the demand for ethylene in recent years has exceeded the gain in production.

It is known that ethylene is used in the production of important products and intermediate materials such as polyethylene (up to 61%), styrene, vinyl chloride, ethylene oxide, ethylene glycol, acetaldehyde, vinyl acetate, *etc*. The volume of ethylene production is an important indicator of the economic development of a country, while the demand for ethylene reflects the state of the petrochemical industry.

Unlike carbon monoxide, which can be produced from any carbon-containing feedstock, ethylene is synthesized only from hydrocarbons. The processes are based almost exclusively on endothermic reactions such as pyrolysis of hydrocarbons or hydrocarbon fractions ranging from ethane to gas oils. For example, up to 80% of the total amount of ethylene made in the USA is produced by ethane pyrolysis, whereas in Europe, ethylene is mainly synthesized by the pyrolysis of liquid hydrocarbons. The proportions of condensed gases and so-called natural gas liquids in the feedstock constantly increase. In Russia, the main bulk of ethylene is produced by pyrolysis of straight-run gasolines isolated from petroleum refinement, while the proportion of ethylene made by ethane pyrolysis does not exceed 10% of the total output.

All production processes based on the pyrolysis of hydrocarbons (from ethane to gasoline hydrocarbons) are inherently energy-consuming, which is related to the necessity of cleavage of very strong C—C bonds (345—355 kJ mol^{-1}) and/or C—H bonds (400—415 kJ mol^{-1}).

Several approaches to the development of ethylene production from methane are known; one variant is methane transformation into synthesis gas followed by Fischer—Tropsch hydrogenation of carbon monoxide

$$2\ CO + 4\ H_2 \longrightarrow CH_2{=}CH_2 + 2\ H_2O,$$

and another route includes the intermediate synthesis of methanol, whose production from synthesis gas is among the most efficient industrial processes from the economic standpoint

$$CO + 2\ H_2 \longrightarrow CH_3OH,$$

$$2\ CH_3OH \longrightarrow CH_2{=}CH_2 + 2\ H_2O.$$

For several years, specialists have also been attracted by the possibility of ethylene synthesis from methane *via* the steps of methane chlorination and pyrolysis of methyl chloride with subsequent oxidation of the resulting hydrogen chloride (Benson process). However, at present, this approach is not regarded as a real alternative to the pyrolysis of higher alkanes because of its multistage character and complexity of industrial implementation.

All the above-mentioned routes from methane to ethylene are, at the minimum, two-stage processes. A process for direct conversion of natural gas to ethylene actively studied in recent years is catalytic oxidative dimerization of methane (ODM):[7]

$$4\ CH_4 + O_2 \longrightarrow 2\ CH_3{-}CH_3 + 2\ H_2O, \qquad (10)$$

$$\Delta H^\circ_{298} = -177\ \text{kJ mol}^{-1},$$

$$2\ CH_4 + O_2 \longrightarrow CH_2{=}CH_2 + 2\ H_2O, \qquad (11)$$

$$\Delta H^\circ_{298} = -281.6\ \text{kJ mol}^{-1},$$

$$CH_3{-}CH_3 \longrightarrow CH_2{=}CH_2 + H_2, \qquad (12)$$

$$\Delta H^\circ_{298} = 137.2\ \text{kJ mol}^{-1},$$

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O, \qquad (13)$$

$$\Delta H^\circ_{298} = -802.4\ \text{kJ mol}^{-1}.$$

Extensive studies of this process started in the early 1980s, the peak of publications devoted to investigations

of ODM catalysts fell at 1988—1992. The materials proposed as catalysts were mainly oxides of metals of almost all groups of the Periodic System, in some cases, with addition of alkali metal halides. The results attained for each catalyst under the optimal conditions are close, which is apparently due to specific features of the reaction mechanism. The highest yields of C_2 hydrocarbons per pass are normally 17—20% for a degree of methane conversion of up to 30% and the selectivity of formation of C_2 hydrocarbons exceeding 50—60%. The main by-products formed in the process apart from hydrogen are CO and CO_2, resulting from more extensive oxidation of methane.

In the last several years, the growth of the number of publications devoted to the ODM in the literature has markedly decreased. This is mainly due to the fact that the price of natural gas in Europe and the USA makes the process of ethylene production from methane noncompetitive compared to traditional pyrolysis of methane homologs. However, in the countries that possess substantial natural gas resources and have a developed gas transmission pipeline network, the interest in the ODM is rather high.

The situation in Russia in which the natural gas resources are substantial and oil production is rather expensive differs from that observed in the USA or Europe: the price of natural gas is \$20—23 per ton, while the price of 1 ton of ethylene reaches \$100—140. Meanwhile, in the Western Europe, the price of natural gas is in the range of \$84—170 per ton and the price of ethylene is \$450—500 per ton. Thus, the ethylene/natural gas price ratio in Russia is 4.3 to 7.0, whereas in the Western Europe, this ratio is 2.6—6.0. These figures point to a higher profitability of the ethylene production from natural gas in Russia compared to that in Western Europe. The manufacture of polyethylene on the basis of natural gas in Russia appears even more promising. The price of polyethylene in Russia amounts to \$700—1000 per ton, while that in Europe is \$780—840, *i.e.*, the polyethylene/natural gas price ratio in Russia is 30—50, while in Western Europe, this value is 4.6—10.0.

The chemical processing of methane, the major component of natural gas, is an important reserve for the extension of the raw material base in the ethylene production. The growth of prices of crude oil and petroleum products serves as an extra incentive for the development of research along this line.

A driving force for the structural changes for the raw material base of petrochemistry is a decrease in the number of stages that separate production of the target product from the raw material production. A greater number of stages required to convert the raw material to the product not only decreases the process selectivity but also increases the total energy expenditure.

Research into the process of ethylene production from natural gas by catalytic oxidative dimerization of methane is carried out in a number of Russian scientific centers (I. M. Gubkin Russian State Oil and Gas University, Institute of General and Inorganic Chemistry of the RAS, All-Russian Research Institute of Organic Synthesis, N. D. Zelinsky Institute of Organic Chemistry of the RAS, Institute of Chemical Physics of the RAS, Institute of Catalysis of the Siberian Branch of the RAS, *etc.*).

Thus catalysts for the ODM process based on mixtures of lanthanide oxides have been studied at the I. M. Gubkin Russian State Oil and Gas University.[8] Testing of the proposed catalysts in an enlarged unit showed characteristics acceptable for the industrial use (the degree of methane conversion was up to 20% per pass, the selectivity relative to dimerization products was 80%, and that for ethylene was up to 60%), which opens up obvious prospects for industrial use of these materials.[9]

Methane containing ethane, carbon dioxide, and nitrogen impurities can also be used as the feedstock for oxidative dimerization.

It is assumed to produce polymerization grade ethylene as the target product. The carbon dioxide formed as a by-product would be isolated by monoethanolamine treatment and discharged to the atmosphere. Utilization of carbon dioxide in the production of urea, in methane reforming furnaces, or for process requirements could improve the economic and environmental parameters of the process as a whole.

The mixture of oxygen with hydrogen, carbon monoxide, and other combustible substances produced upon gas separation can be utilized by being added to the fuel in pyrolysis furnaces and steam generators. This would decrease the total energy expenditure.

Calculations showed that even taking into account that the specific capital investment for the ODM is much greater than that for the ethane pyrolysis, the net cost of ethylene can be 1.4 times lower in the former case.

Since both the main (reactions (10), (11)) and side reactions (reactions (9) and (13)) involved in ODM are exothermic, the whole process is accompanied by substantial heat evolution. For a total selectivity of methane conversion into C_2 products equal to 80% (the content of ethylene is 60% of the sum of products), ~400 kJ of energy per mole of reacted methane is evolved. Therefore, the reactor section is assembled as a cascade of adiabatic reactors with the heat remove between them. According to the process flowchart designed at the public joint-stock company Research Institute of Organic Synthesis and the Gazprom, this heat is utilized for steam generation. The amount of steam produced in this way not only covers the process requirements for a production capacity of 25 thousand tons per year but also can be used for other needs in a quantity of 30 tons per hour. It is also possible to eliminate additional water consumption by this process because water formed in the reaction is condensed during the separation of products and, after purification, it can be used as make-up water in the steam generation and water circulation systems.

Thus, according to tentative technological and economic estimates, the technology of ethylene and polyethylene from natural gas by oxidative dimerization of methane developed by Russian scientists (for the state-of-the-art economic situation and the process characteristics attained) can be promising and profitable even at present. Naturally, the search for new, more efficient catalysts and design elements in the implementation of the ODM process remains topical.

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