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THE MAIN DIRECTIONS OF NATURAL GAS PROCESSING IN THE CHEMICAL INDUSTRY

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Astract

The chemical industry is one of the main consumers of natural gas. Natural gas is used in the chemical industry, on the one hand, as a source of energy, on the other hand, as a source of raw materials for a large number of chemical industries. The main part of natural gas is used as a source of raw materials, converted into synthesis gas, which includes carbon monoxide and dioxide, hydrogen, unreacted methane and a small amount of impurities contained in natural gas (nitrogen, argon, etc.).

Keywords: *gas, gas chemistry, methanol, Fischer-Tropsch, synthesis gas, adsorption, absorption*

Introduction

Currently, all natural hydrocarbon gases go through two stages of primary processing:

- preparation of gas for processing, including their purification from mechanical impurities, from undesirable chemical compounds, primarily acidic, and drying. When cleaning gases from chemical impurities, various sorption (absorption, adsorption, chemisorption), catalytic (hydrogenation, hydrolysis, oxidation) and membrane cleaning methods are used. After the extraction of hydrogen sulfide, it is processed into elemental sulfur by the Claus method. Gas dehydration can be carried out by various methods: direct cooling, absorption, adsorption or their combination;
- separation of gases, starting with the separation of suspended liquids by low-temperature separation, extraction of liquid hydrocarbon components by compression and oil absorption, as well as various low-temperature methods (low-temperature absorption – LTA, low-temperature condensation – LTC, low-temperature rectification – LTR, low-temperature adsorption – LT-adsorption) leading to the production of unstable gas gasoline and reflux – raw materials for the production of liquefied gases and individual hydrocarbons.

The next stages of the physical processing of hydrocarbon gases are the separation of hydrocarbon gases into individual hydrocarbons and the separation of helium, mainly by cryogenic means, followed by concentration and liquefaction, as well as the stabilization of gas gasoline and gas condensate carried by gas from the well.

These processes make it possible to obtain commercial products that meet the necessary requirements. As a result of the primary processing of natural hydrocarbon gases, commercial gas, fuels (motor gasoline, diesel and boiler fuel), stable gas condensate, liquefied gas, gas sulfur, odorant, carbon black, helium are obtained, individual hydrocarbons are isolated for further processing.

However, at present, the use of useful gas components in our country does not meet the potential of the resource base and does not correspond to world practice. Therefore, the concept of gas feedstock processing is fundamentally reviewed, taking into account possible directions for its chemical processing, based on an analysis of the state of operation and loading of existing capacities for processing gas resources and gas condensate feedstock in Russia.

Hydrocarbons released from gas are a valuable raw material for the production of various chemical products. Chemical processing of natural gases makes it possible to obtain a wide range of valuable products: motor fuels, medical and agricultural preparations, polymeric materials, large-capacity products such as methanol, ammonia, acetylene, and halogen derivatives. In turn, dozens of chemical compounds are produced on the basis of ammonia, methanol, acetylene: urea, formaldehyde, urea-formaldehyde resins, high-octane gasoline components; methyl tert-butyl ether, melamine and resins based on it, nitrogen fertilizers.

Thus, the problem of complex chemical processing of natural gas, which provides for the qualified use of all its components, is very relevant.

The most important practical use of the chemical processing of natural gases has two directions (Konovalov, N. M., Voinov, N. A., Markov, V. A., Nikolaev, N. A., 1993):

1. Thermal and thermocatalytic transformations of natural gas components. These are the processes of pyrolysis and dehydrogenation, leading to the formation of unsaturated hydrocarbons – acetylene, olefins, dienes, which are widely used for the production of various macromolecular compounds and oxygen-containing products. A new process being developed within this direction is the production of aromatic hydrocarbons from gas components $C_3 – C_4$.

2. Oxidative transformations of light hydrocarbons – components of natural gases, primarily the conversion of methane into synthesis gas and the production of such important chemical products as methanol, formaldehyde, dimethyl ether, acetic acid and other carboxylic acids, aliphatic alcohols, synthetic hydrocarbons. This trend also includes a new process, the oxidative dimerization of methane to ethylene.

The development of new industrial technologies for thermal and thermal catalytic transformations of natural gas components was aimed at developing pyrolysis technology in the presence of heterogeneous catalysts (catalytic pyrolysis) and initiating additives; creation of new types of pyrolysis – hydropyrolysis, oxypyrolysis and pyrolysis in the melt of metals and their salts; electrocracking, plasma pyrolysis. Unfortunately, success in these areas has been achieved only on the scale of enlarged laboratory and pilot plants, but not on industrial scale.

Of great interest is the one-stage catalytic synthesis of aromatic hydrocarbons from $C_2 – C_5$ alkanes, components of natural gas. This way of obtaining aromatic compounds – valuable intermediates for the production of polymers, synthetic fibers, dyes and pharmaceuticals – is an alternative to the process of catalytic reforming of petroleum fractions. Studies of the catalytic transformations of low molecular weight paraffinic hydrocarbons have been intensively carried out in recent years in many research centers both here and abroad. The work carried out under the direction of A. L. Lapidus revealed the most promising catalytic systems – zeolites of the pentasil family (Konovalov, N. M., Voinov, N. A., Markov, V. A., Nikolaev, N. A. 1993; Ershov A. I., 1975).

Oxidative transformations of lower paraffinic hydrocarbons, taking into account the complexity and low selectivity of their direct oxidation, are aimed at obtaining valuable chemical products based on synthesis gas (a mixture of carbon monoxide and hydrogen in various proportions) obtained by methane conversion.

Syngas production

The main modern methods for producing synthesis gas from methane are as follows (Konovalov, N.M., Voinov, N.A., Markov, V.A., Nikolaev, N.A. 1993):

1. Steam conversion:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2,$$

2. Carbon dioxide conversion:

$$CH_4 + H_2O \rightleftharpoons 2CO + 2H_2,$$

3. Partial oxidation:

$$CH_4 + 1/2O_2 \rightleftharpoons CO + 2H_2,$$

A new direction is the combination of endothermic processes (1 and 2) with the exothermic reaction of methane oxidation.

The most promising technologies for the production of synthesis gas are currently considered the so-called Tandem process – a two-stage steam-oxygen conversion of natural gas in two tubular reactors, and for large-capacity production – autothermal reforming (ATR) in the reactor, in which the partial combustion of the feedstock is accompanied by thermal and catalytic steam reforming of the feedstock. The latter process makes it possible to optimize the composition of the synthesis gas, taking into account its further processing into liquid hydrocarbons, methanol or dimethyl ether. Membrane methods for controlling the CO: H ratio in synthesis gas using polymeric membranes selectively permeable to hydrogen have been developed and are being implemented.

In Russia, NPO "Energomash" them. V.P. Glushko in collaboration with the Institute of Chemical Science of the Russian Academy of Sciences and NIFKhI im. L. Ya. Karpov developed a technology for producing synthesis gas using liquid-propellant rocket engines. This process requires the use of commercially pure oxygen and elevated pressure, but allows for high productivity, smaller reactor dimensions, its mass, metal consumption, and capital intensity compared to other technologies for producing synthesis gas. INHS RAS and ICT RAS proposed a process for obtaining synthesis gas from methane in a diesel engine. A set of studies on the conversion of methane to syngas in plasma and stationary microwave discharge has been carried out at the RRC "Kurchatov Institute" (Ershov, A.I. 1975).

Tropsch process

The process of obtaining hydrocarbons based on carbon monoxide and hydrogen on iron and cobalt catalysts was developed long before the era of the appearance of cheap oil – in 1923 – by Fischer and Tropsch. The first industrial plants were commissioned in Germany. With the advent of cheap oil on the world market, the production of artificial fuel was almost universally discontinued. Recently, interest in this process has increased in many countries, including Russia.

The main direction of the process can be represented by a diagram (Klein, H., Schmidt, P., 1971):

$$CO + H_2 \longrightarrow C_nH_{2n+2} + C_nH_{2n} + H_2O$$

Very important factors for the development of this process are the increase in the productivity of LCL synthesis units, the selectivity of the process for liquid hydrocarbons, as well as an increase in the octane number of gasoline and cetane – diesel fractions. For this process, an increase in the productivity of plants is primarily associated with an increase in the activity of catalysts and an improvement in heat removal. Scientists from the Institute of Chemical Physics of the Russian Academy of Sciences and the Department of Gas Chemistry of the Russian State University of Oil and Gas are successfully developing new efficient catalysts for this process under the guidance of Corresponding Member. RAS A.L. Lapidus.

Production of methanol and chemical products based on it

Methanol is a valuable large-capacity product that is widely used in various industries. The volume of methanol consumption in the world is continuously increasing. At present, its world production exceeds 40 million tons/year. Almost the only industrial method for the production of methanol at present is to obtain it from synthesis gas by the reaction:

$$CO + 2H_2 \longrightarrow CH_3OH$$

The synthesis of methanol is a well-established process in industry, however, in the late 1970s, new prospects for improving the technology opened up when copper-containing catalysts were developed that were effective at low pressure. As a result, methanol synthesis is currently carried out at pressures of 50–100 atm in almost all industries.

Methanol consumers are the production of formaldehyde, monomers (for example, methyl methacrylate and dimethyl terephthalate), methyl tertiary butyl ether (MTBE), dimethyl ether (DME), acetic acid. Methanol is widely used as a solvent and extractant, and a process has been developed to produce gasoline from methanol. Pilot work is being carried out on the processing of methanol into olefins, the oligomerization and hydrogenation of which make it possible to organize the production of motor fuels.

A new direction in the production of formaldehyde instead of the industrial process of oxidative conversion of methanol is the one developed by Mitsubishi Gas methanol dehydrogenation process on a copper-zinc- selenium catalyst at 600 °C (Melnikov, E.P., 1975):

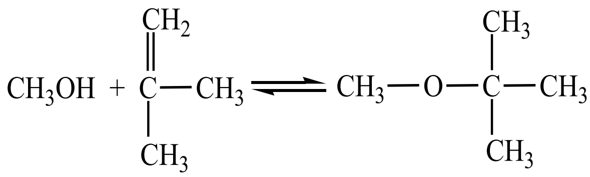
$$CH_3OH \rightleftharpoons H_2CO + H_2$$

The process of methanol dehydrogenation has not yet been implemented in industry, but it is very promising, as it makes it possible to obtain water-free formaldehyde and hydrogen. In addition, the methanol-formaldehyde mixture formed in the process can be processed without separation. Therefore, scientific research is currently being intensively conducted to find effective catalytic systems for this process.

DME, considered as a promising environmentally friendly diesel fuel, is obtained in three stages: the production of synthesis gas from natural gas, then methanol, and at the third stage, dimethyl ether is obtained by dehydration of methanol. Such a three-stage process is complicated and expensive, but the fundamental possibility of obtaining DME from synthesis gas in one stage under mild conditions and with high ether selectivity has been shown. DME is a promising raw material for the production of hydrogen-containing gas to power fuel cells (FCs). Currently, the object of intensive research is the study of catalytic methods for producing hydrogen from DME for its production and use directly in car engines.

Obtaining methyl tertiary butyl ether (MTBE)

An important place among the new methanol processing processes implemented in the industry is occupied by the production of methyl tertiary butyl ether (MTBE). It is used as a high-octane component of motor fuels. MTBE is produced from methanol and isobutylene by the reaction



Given the limited resources of isobutylene, a process has also been developed for the production of methyltretamyl ether (MTAE) from isoamylenes and methanol. The octane number of MTAE is 6 points lower than that of MTBE, but the involvement of isoamylenes makes it possible to expand the production of high-octane gasoline components.

Oxidative dimerization of methane (ODM)

This direction makes it possible to carry out the chemical processing of natural gas with the formation of ethylene and ethane, bypassing the stage of obtaining synthesis gas. The main ODM reactions leading to the formation of target products are the following (Isakov, V. P., Sugak, E. V., 1982):

$$4CH_4 + O_2 \longrightarrow 2CH_3\text{-}CH_3 + 2H_2O$$
$$2CH_4 + O \longrightarrow CH_2{=}CH_2 + 2H_2O$$
$$CH_3\text{-}CH_3 \longrightarrow CH_2{=}CH_2 + H_2$$

The course of the reaction is complicated by a significant non-selective consumption of methane for the formation of carbon oxides. Therefore, an important scientific and practical task facing researchers is the development of new affordable, stable catalysts that provide high selectivity for ethane and ethylene at a sufficiently high methane conversion. Efficient catalytic systems for this process are being successfully developed at

VNIIOS (V.A. Menshov), at the Institute of Organic Chemistry of the Russian Academy of Sciences (N. Ya. Usachev), and at the Russian State University of Oil and Gas (A.G. Dedov, A.S. Loktev).

Of great interest is also the processing of lower unsaturated hydrocarbons obtained by pyrolysis or dehydrogenation of natural gas hydrocarbons into polymeric materials: polyolefins and plastics based on them, synthetic rubbers.

We focused only on the development of gas-chemical industrial technologies for the processing of hydrocarbon components of natural gases; in recent years, much has been done to develop rational technologies for the processing of hydrogen sulfide, mercaptans, carbon dioxide, and the use of helium.

Already now, a number of gas processing plants are considering promising areas for the chemical processing of gas and gas condensate raw materials to obtain valuable products.

The development of gas chemical production facilities makes it possible to obtain a variety of chemical products that are widely used in a number of industries: mechanical engineering and automotive, construction, electronics, as well as medicine, agricultural complexes, and the production of household goods.

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