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Catalytic Methods for Associated Petroleum Gas Pretreatment and Processing

V. N. Parmon and A. S. Noskov

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences,
pr. Akad. Lavrent'eva 5, Novosibirsk, 630090 Russia
phone: +7(383)3308269
e-mail: parmon@catalysis.ru

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Abstract—Two groups of technologies, specifically those for pretreatment and for processing of associated petroleum gases, were described. One group includes technologies based on deep adsorptive drying and desulfurization. The other group integrates technologies used for processing of associated petroleum gas into aromatic hydrocarbons, synthetic motor fuel (the Fischer–Tropsch process), and carbon nanomaterials. Basic process parameters were indicated for each of the technologies. The results of pilot (semicommercial) testing were presented for some of the processes.

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According to various estimates, from 20 to 50 billion m^3 of associated gas resulted from oil and gas production is flared in Russia annually, which leads to a loss of about 1 trillion rubles and to CO_2 venting in amount of 100–150 million ton per annum. Though characterized by variable composition, associated petroleum gases typically contain, vol %: methane ~80, ethane 4–6, and propane and butane, ~15. In some cases, associated petroleum gases are contaminated with hydrogen sulfide and contain water vapor.

Here, we present the technologies proposed by the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, which were subdivided into two groups:

(A) Technologies for pretreatment of associated petroleum gases (APG): processes for deep adsorptive drying and removal of hydrogen sulfide from APG.

(B) Technologies for deep conversion of APG to high added-value chemical products: aromatic hydrocarbons, synthetic liquid fuels, and carbon nanomaterials.

Technologies for Associated Petroleum Gas Pretreatment

The task of pretreatment of associated petroleum gas to remove hydrogen sulfide, whose importance was already mentioned, can be accomplished by selective oxidation of hydrogen sulfide to sulfur [1, 2]:

$$H_2S + 1/2O_2 \rightarrow S + H_2O.$$

The main advantages offered by this process are those in terms of its continuous nature and implementability at temperatures of 200–250°C, under which "mild" conditions other APG components do not undergo transformations, as facilitated by the use of special oxide catalysts. Depending on the content of hydrogen sulfide, the process may be implemented either in fluidized-bed catalytic reactors (Fig. 1a) at high (15–80 vol %) content of hydrogen sulfide in APG or in catalytic reactors with monolith honeycomb catalyst at H_2S concentrations under 10–15 vol % (Fig. 1b). The above-described technology is patented in Russia, the US, Canada, France, and other countries.

Presently, this technology is implemented with pilot-plant equipment of different capacities exploited at a number of gas processing plants (GPPs) and at APG pretreatment facilities; its application allows removal of 98–99% hydrogen sulfide from APG. Figure 2 shows a photograph of this type of unit operated at the Bavly associated gas pretreatment installation (Tatarstan).

Prior to transportation, APG requires deep drying to remove water vapor, for which purpose it was

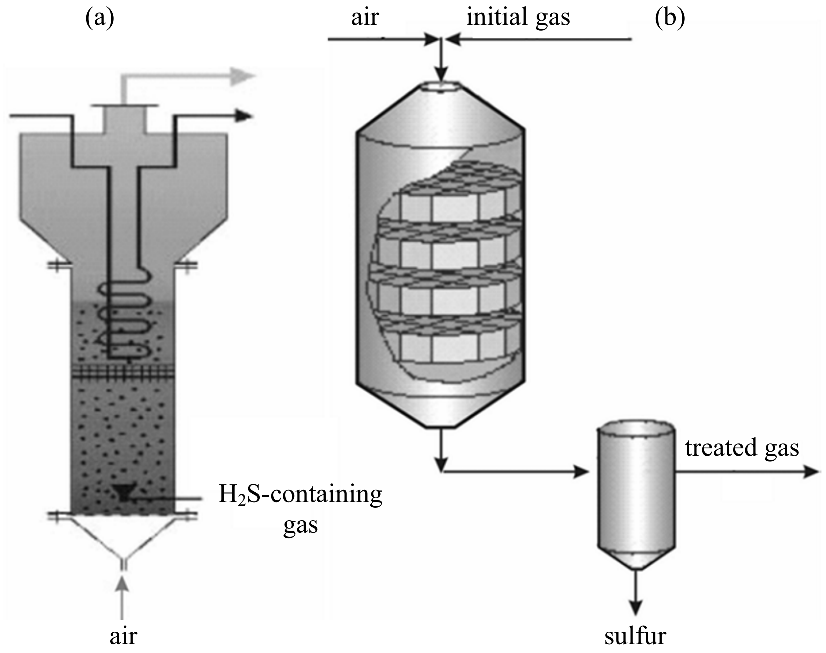


Fig. 1. Technology of catalytic pretreatment of gases to remove hydrogen sulfide: (a) a fluidized-bed reactor for pretreatment of high-concentrated gases containing up to 80% H_2S and (b) a honeycomb monolith catalyst reactor for pretreatment of low-concentrated gases.

suggested [3] to use composite nanoporous adsorbents. Passing a water vapor-containing APG through a granular layer of the nanoporous material, e.g., alumina containing an anhydrous salt ($CaCl_2$) in its pore space, causes active moisture sorption via formation of solid crystal hydrates $CaCl_2{\cdot}nH_2O$ inside the pores. The resulting “salt in nanoporous matrix” composite materials have a very high sorption capacity

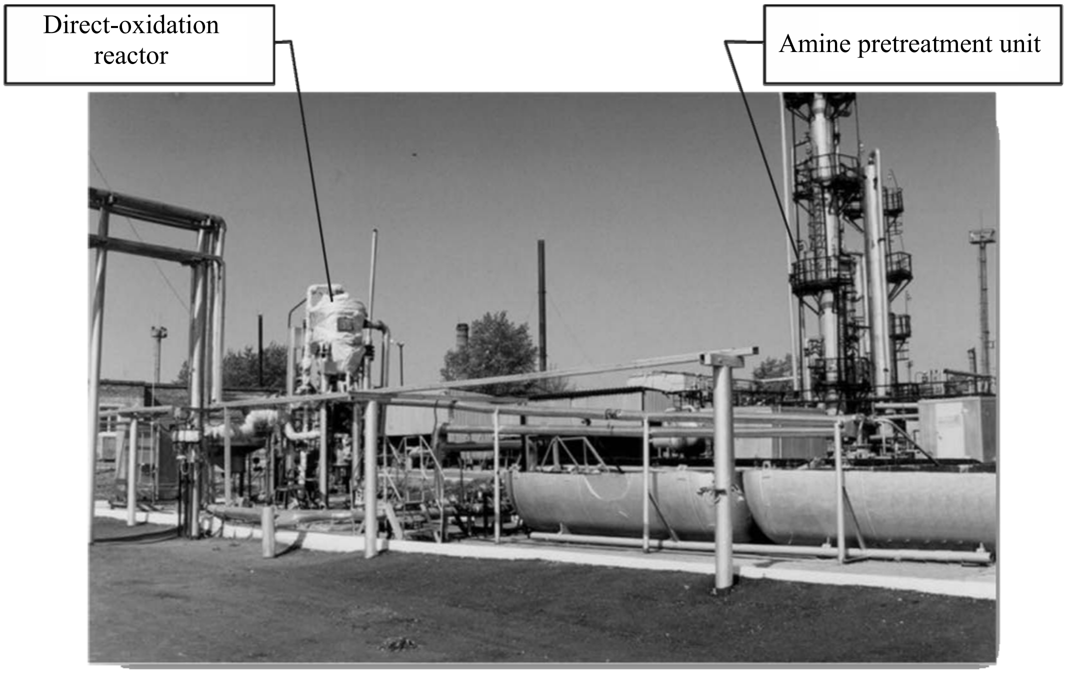


Fig. 2. Installation for associated petroleum gas pretreatment involving hydrogen sulfide utilization [Bavly associated gas pretreatment unit (mini GPP)].

Fig. 3. A semicommercial installation for associated gas aromatization (C_2–C_{4+} hydrocarbons) with the capacity of 1000 ton year^{-1} (Krasnodar).

of 0.6–1.0 H_2O g (material g)$^{-1}$ and remain loose even after sorption of this large amount of moisture. Good sorption properties of such materials can be restored by heating them to 100–130°C, which leads to decomposition of the crystal hydrates and makes the composite sorbent materials suitable for reuse.

Using such composite sorbents it is possible to remove water vapor to the dew point equivalent to the temperature of –70–80°C. A pilot production facility established in Omsk supplies composite sorbents to Russia's refineries (for technical air drying) and a number of enterprises, e.g., Omskkauchuk Open Joint-Stock Company, Salavatnefteorgsintez Open Joint-Stock Company (for deep drying of hydrocarbons).

Table 1. The component content and level for the propane–butane fraction aromatization feedstock and products

Feedstock		Product mixture	
component	wt %	component	wt %
Ethane	3.5	C_1. C_2+H_2	31.5
Propane	40.9	C_3	21.6
i-Butane	22.1	C_4	6
n-Butane	23.8	C_5	0.9
Butylenes	0.3	Benzene	8.9
i-Pentane	5.9	Toluene	18.5
n-Pentane	3.1	Xylenes	9.2
Hexanes	0.4	C_{9+}	3.4
Total	100	Total	100

Technologies For Deep APG Processing into Chemical Products

Oil and gas production yields significant amount of light hydrocarbons, primarily C_1–C_5 which, for a variety of reasons, do not find efficient on-site application. Their transportation in the gaseous state is troublesome, and often these gases are eventually flared.

One possible route to use C_1–C_5 gases is their processing into much more easily transportable liquid hydrocarbons.

This task can be accomplished with reasonable facility via C_1–C_5 gas processing into aromatic compounds (benzene, toluene, xylenes). This process may involve the following reactions:

	T^*, K
$6CH_4 \leftrightarrow C_6H_6 + 9H_2$	1630
$2C_3H_8 \leftrightarrow C_6H_6 + 5H_2$	760
$2n\text{-}C_4H_{10} \leftrightarrow p\text{-}C_6H_4(CH_3)_2 + 5H_2$	800
$C_3H_8 + n\text{-}C_4H_{10} \leftrightarrow C_6H_5CH_3 + 5H_2$	710
$3C_2H_6 \leftrightarrow C_6H_6 + 6H_2$	930
$CH_4 + 2C_3H_8 \leftrightarrow C_6H_5CH_3 + 6H_2$	880

Table 2. Laboratory testing parameters for the conversion of associated gases into aromatic hydrocarbons

Parameter	Value
Natural gas composition, vol %	
methane	80
ethane	4
propane + butane	12
nitrogen	4
Process temperature, °C	540–570
Space velocity, h^{-1}	800–1400
C_3 conversion, wt %	80.5
C_4 conversion, wt %	100
Yield of aromatics with respect to the C_3–C_4 fraction converted, wt %	85.5
Liquid product mixture components, wt %	
benzene	36.7
toluene	38.9
C_8 fraction	7.1
C_{9+} fraction	17.3

Table 3. The Fischer–Tropsch reaction product mixture, wt %, in relation to the catalyst and process temperature

Synthesis products	Cobalt, 220°C	Iron, suspended layer	
		240°C	340°C
C_5–C_{12} fraction			
paraffins	60	29	13
olefins	39	6	70
aromatic hydrocarbons	0	5	5
oxygen-containing compounds	1	7	12
C_{13}–C_{18} fraction			
paraffins	95	44	13
olefins	5	50	60
aromatic hydrocarbons	0	0	13
oxygen-containing compounds	< 1	6	10

	T^*, K
$CH_4 + C_3H_8 + n\text{-}C_4H_{10} \leftrightarrow p\text{-}C_6H_4(CH_3)_2 + 6H_2$	1060
$CH_4 + C_2H_6 + C_3H_8 \leftrightarrow C_6H_6 + 6H_2$	940
$CH_4 + 3C_3H_8 \leftrightarrow C_{10}H_8 + 10H_2$	830
$CH_4 + 3C_3H_8 \leftrightarrow C_{10}H_{18} + 5H_2$	730

It should be noted that these reactions may proceed from left to right, as desired, at $T > T^*$ only (T^* is the equilibrium shift temperature).

Such reactions are carried out with the use of medium-porous high-silica ZSM-5 and ZSM-11 zeolites with Cu, Pd, Zn, and Ge metal and other additions, the main challenge being to ensure the necessary activity and stability of these catalysts.

Zeolite-based catalysts of this type, developed at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences [4], have been produced since 2006 in amount of up to 150 ton year^{-1} on the basis of Novosibirsk Chemical Concentrates Plant, Open Joint-Stock Company.

These catalysts are used in the technique which was developed and implemented on a pilot (semicommercial) scale for processing associated gases from oil and gas production into an aromatic concentrate, a mixture of benzene, toluene, and xylenes [5]. Pilot testing of the process and the catalyst was carried out on a complex of semicommercial installations operated at the Scientific Research and Design Institute for Gas Processing (*NIPIgazpererabotka),* Open Joint-Stock Company (Krasnodar) (Fig. 3). The installation consists of two consecutive flow reactors with the total effective volume of 470 l. The catalyst loading was 120 l (40 l in the first and 80 l in the second reactor). Under the optimal conditions, the service cycle was 10 day, and the catalyst is expected to have a service life of at least 1 year. Table 1 lists the main process parameters. The selectivity of the conversion of the propane-butane fraction to aromatic hydrocarbons is 70–72%, and the yield of aromatic hydrocarbons, 40% per pass.

The research efforts needed for organizing the production of the zeolite catalysts at the Novosibirsk Chemical Concentrates Plant, Open Joint-Stock

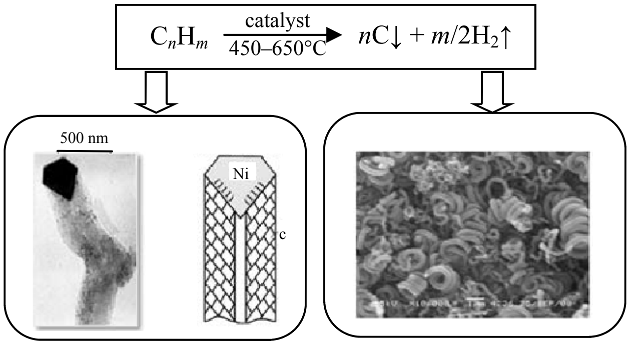
Table 4. Characteristics of the catalytic reactors used for Fischer–Tropsch synthesis process

Reactor type	Specific capacity, product ton (reactor m^3)$^{-1}$ year^{-1}
Tubular reactor	400–450
Fluidized-bed reactor	450–500
“Slurry” reactor	240–250
Membrane (laboratory) reactor	1100–1200

Company, as well as the development and pilot (semicommercial) testing of the technology for APG processing into aromatic hydrocarbons, were undertaken in the framework of the “Development of the Basic Resource- and Energy-Saving Technology and Designs of Nanoporous Catalytic Membrane Reactors for Light Hydrocarbon Feedstock Processing” project in 2005–2007. This was an important innova-tion project, with Russian Federal Agency for Science and Innovation as State Customer, and Aspekt Association, Moscow, as Leading Executor. Based on the organized catalyst production process it is possible to process APG in amounts of up to 2 billion m^3 year^{-1} and additionally produce aromatic hydrocarbons (benzene) in amounts of up to 300 thousand ton year^{-1}, which is equivalent to 10 billion rubles year^{-1} in monetary terms.

In this context, of special interest are the new data on coprocessing of methane, ethane, and propane-butane, i.e., all the APG components. Table 2 summarizes the results of the laboratory tests of this process, which were carried out at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences.

It should be noted that C_3–C_4 hydrocarbons are converted nearly exhaustively, and there are C_{9+} hydrocarbons among the liquid products. Further efforts dedicated to this process will open wide prospects for development of new lines of APG processing.



(a) (b)

Fig. 4. Nanocarbon materials for production of composite polymers: (a) formation of carbon nanofibers on a nickel metal particle and (b) carbon nanohelices.

An alternative procedure for chemical processing of APG is that based on the Fischer–Tropsch (FT) process. The latter was developed in the 1920s in Germany for diesel fuel production from coal gasification products. The amount of diesel fuel produced in Germany with the use of the FT process reached 600 thousand ton year^{-1} (1944).

The main stages of the FT process are the APG conversion to synthesis gas (CO + H_2), FT synthesis proper, and separation of the synthesized products. Depending on the catalyst used, the FT synthesis process yields different liquid hydrocarbons (Table 3).

The FT process is carried out under the pressure of 1–3 MPa in various types of reactors (Table 4). The production per unit reactor volume is relatively low, which necessitates the use of large reactors. A significant advance in this respect was made via reducing the size of the membrane reactors recently developed at Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences [6], whose production per unit reactor volume is nearly 3 times that of the known types of reactors. Porous catalytic membranes deal with several weak points inherent in conventional reactors used for FT; specifically, they ensure isothermal reaction volume and avoid limiting the gas-liquid mass transfer and intradiffusion inhibition. A unit element of the FT synthesis reactor based on porous catalytic membranes, designed for production of liquid hydrocarbons in amount 20 ton year^{-1}, is represented by a reactor block, 120 mm in diameter and 400 mm in length. The use of porous catalytic membranes allows development of cost-effective installations with a relatively low unit capacity of 50–100 ton year^{-1}. The resulting liquid hydrocarbons can be combined with oil to be jointly transported through existing pipelines to the areas of consumption.

It should be noted, however, that the development of FT installations is a highly capital intensive option: Typical investment costs for plants with capacity for synthetic liquid fuels (synthetic oil) of 350–700 ton year^{-1} are (500–1000) thousand US dollars (thousand ton)$^{-1}$ (installed capacity year)$^{-1}$ (Table 4).

A new direction in APG processing is catalytic conversion into nanocarbon fibrous materials (Fig. 4). At temperatures of 450–650°C the C_1–C_4 hydrocarbons undergo decomposition on the metal catalyst particles into fibrous carbon materials with hydrogen evolution (Fig. 4a). Depending on the method of preparation and the composition of the catalyst, the resulting nanocarbon materials have different shapes and structures: threads, fibers, nanohelices. Figure 4b shows helically shaped nanocarbon materials formed on the nickel metal particles. The amount of the resulting nanocarbon materials reaches 300–400 g (catalyst g)$^{-1}$.

Of much interest are possible applications, above all, large-scale applications in road and construction activities, for such nanocarbon materials. The introduction of <1 wt % nanocarbon materials into concrete causes its strength to increase by 40–50%. This will, accordingly, lighten the structural units and reduce the prime cost of the construction work. The carbon materials of interest are promising for manufacture of polymer composite materials with new qualities: electrical conductivity, frost-resistance, and mechanical strength.

To summarize, a scientific framework was developed for the catalytic pretreatment and processing of associated gases from oil extraction into commercial products, which processes successfully passed pilot (semicommercial) tests. To really solve the APG problem in Russia it is necessary to make a further step: to move from research and development to creation of the first production units for catalytic processing of APG into high-value-added products that are in high demand at the market: aromatic hydrocarbons, motor fuels, and nanocarbon materials.

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