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Economically Attractive Technologies of Deep Conversion of Associated Petroleum Gas

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Abstract—Six industrial and emerging catalytic technologies suitable for complete processing of all the components of associated petroleum gas, including methane and ethane, were reviewed. Process schemes for methanol, olefins, synthetic crude oil, gasoline, aromatics, and polymers were considered. A comparative analysis of the technologies in terms of demand for gas feedstock, potential markets for products, capital costs, and other economic indicators was carried out for the associated petroleum gas volumes typical for small and medium-sized oil fields.

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INTRODUCTION

Utilization of associated petroleum gas (APG) remains one of the most pressing economic problems faced by oil-producing industries and regions of the Russian Federation, as repeatedly noted by the Government of the Russian Federation [1].

According to the RF Ministry of Natural Resources and Environment, 55–60 billion m^3 of APG is annually produced today in Russia, of which 26% is flared and another 30% goes for satisfying the technological needs of oil fields. Thus, according to official statistical data, ca. 15 billion m^3 of APG is burned and vented into the atmosphere. Independent expert estimates suggest that the real situation is even worse: Those 16–18 billion m^3 that are supposed to be reinjected into the reservoir or used to meet the needs of oil fields in fact are also flared.

Oil companies are undertaking efforts aimed to achieve the statutory level of ≥95% set for utilization of APG in the third year of oil field development, but the APG utilization plans that they announced do not allow accomplishing this task in the foreseeable future. Table 1 presents the amount of "free gas" that is not utilized in the framework of the target programs of oil producers in Russia in 2008, as estimated by Federal Service for Ecological, Technological, and Nuclear Supervision (Rostekhnadzor) experts [2].

It should be noted that the "free" associated petroleum gas resources are available for the most part from small and medium-sized fields, as well as from fields distant from pipelines system and gas processing sites [4]. As a result, APG utilization by ~240 fields will allow conversion of >70% of "free" APG, or 15–

Table 1. Calculated annual resource of APG suitable for processing

Oil companies in Russia	Investments in 2009–2011, million US $	Planned APG utilization, billion m^3
Rosneft	1355	3.5
LUKOIL	406	1.6
Surgutneftegaz	177	0.8
TNK-BP	1114	3.4
Gazprom Neft	257	1.0
Slavneft	93	0.3
RussNeft	180	0.5
Other	133	0.6
SIBUR Holding	–	7.5
Total for oil companies	3716	19.2
Total APG burned in Russia [3]		48
Unprocessed "free" APG		28.8

Table 2. Effect of the DLG processing parameters on the characteristics of the APG utilization project for 600 million m^3 year^{-1}

APG processing product name	Ex-works price per unit, thousand rubles	Amount of product	
		DLG delivery to the main pipeline	on-site DLG processing
Commercial propane–butane mixture (CPBM), ton year^{-1}	6	85000	85000
Dry lean gas (DLG), thousand m^3 year^{-1}	1.2	430000	0
Stable natural gasoline (SNG), ton year^{-1}	6	40000	40000
BTX fraction, ton year^{-1}	21	0	110000
Basic economic indicators			
Gross revenue, mln rubles	–	1266	3060
Capital expenditures, including infrastructure, mln rubles	–	7260[a]	10970
Capital productivity, ruble ruble^{-1}	–	0.174	0.279

[a] Distance to the main gas pipeline junction 220 km.

20 billion m^3 annually (the potential cost of the processing products is 4–6 billion US $).

In the low-temperature separation technologies used at gas processing plants (GPPs), the main APG component, methane, is separated as dry lean gas (DLG) and is used exclusively as fuel gas or is flared. The same concerns ethane, whose content in oil gases is 15–20%. Liquid commodity products are repressented by the C_{3+} fraction (broad fraction of light hydrocarbons, BFLH) and other components (stable natural gasoline). The experience of the existing GPPs suggests that, considering the rising feedstock prices, there is a need in processing of 1.2–7.2 billion m^3 of APG annually in order to achieve an acceptable profitability [5].

Because of high demand for gas and substantial costs, full-scale GPPs are to be constructed with a view to servicing of several fields, which will require creation of gas-collecting networks, compression stations, and gas pipelines for DLG, thereby significantly increasing the capital costs associated with APG utilization to be borne by an oil company. Low rates of return on investments into large-scale infrastructure projects do not allow construction of GPPs at small and medium-sized fields.

Oil companies cannot organize total reinjection of APG into the reservoir or utilization of the entire APG volume via power generation (because oil companies have limited access to Gazprom pipelines for gas delivery to combined heat and power plants), which is, apparently, the major factor responsible for burning of tens of billions of cubic meters of APG.

Requirements Posed on In-Field APG Processing Technologies

In view of the above-said, an urgent task consists in complete APG processing by gas chemical means directly in the field or at main compressor stations (booster pump station, booster compressor station, and gas processing station). As a result, the need in delivering APG to the processing site would be eliminated, and construction of gas pipelines could be avoided because there would be no DLG in the range of products. Liquid products could be supplied to consumers in a more viable, in particular, combined trans-shipment, ways.

Moreover, the involvement of not only BFLH but also of methane and ethane into gas-chemical processing causes the feedstock utilization rate in production of marketable products to increase, thereby improving the financial viability of gas utilization projects. Table 2 shows how the depth of processing affects the characteristics of the project on utilization of APG in amount of 600 million m^3 year^{-1}, with the Maiskaya group of fields (“Rosneft”) taken as an example. Gas-chemical processing of DLG, e.g., into *p*-xylene, increases the return on assets of a company engaged in APG utilization by ≥60%.

In choosing an appropriate processing technology, account should be taken of the following major

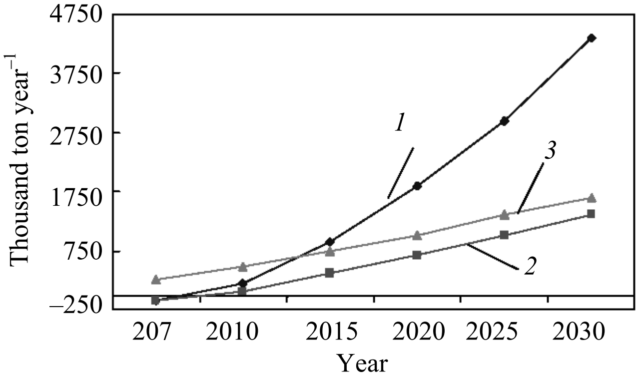

Fig. 1. Forecast of nationwide shortage in (*1*) PE, (*2*) PP, and (*3*) PET in Russia.

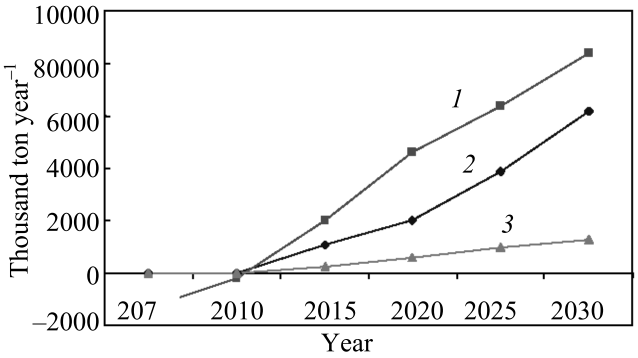

Fig. 2. Forecast of nationwide shortage in (*1*) ammonia, (*2*) methanol, and (*3*) monoethylene glycol in Russia.

restrictions posed on implementation of in-field processing with APG as feedstock.

There is a need to solve the "DLG problem," i.e., to maximize the use of all the APG components for preparation of target commercial products and to exclude combustion of gas or BFLH in cases when DLG cannot be supplied to local consumers or into the main gas pipeline.

High-margin products are to be obtained in order to ensure the economic efficiency of processing of relatively small APG volumes (100–600 million m^3 year^{-1}).

The number of products obtained on the APG processing sites is to be minimized; a preferred option will consist in obtaining a monoproduct which will allow reducing the capital costs for construction of storage facilities, as well as for storage and exports of the product from the field.

Whatever changes in its yield and composition the growing extent of field development will bring, the entire APG volume is to be processed so as to avoid flaring of excess gas or downtimes.

It should be noted that this second condition is critical for oil fields characterized by low gas to oil ratios (GORs), i.e., the ratios of the volume of gas obtained from well, in cubic meters, to that of oil extracted during the same period, in tons or cubic meters, converted to standard conditions [6]). According to official information sources, the GOR in Russia as a whole is 112 m^3 ton^{-1} (2008), with the highest GOR value characteristic for the Yamalo-Nenets Autonomous District (130 m^3 ton^{-1}, on the average).

Thus, the average increase in production due to APG conversion into synthetic oil by the Fischer–Tropsch process will not exceed 5% of the production of mineral oil. Synthetic oil is undoubtedly the best APG conversion product from both the sales (with the oil company, APG producer, as consumer) and logistics (with the existing mineral oil transport infrastructure to be used) perspectives.

However, the existing technologies are intended for consumption of large gas amounts (3–12 billion m^3) in order to achieve economically efficient and profitable gas to liquid (GTL) production. Small amounts of APG entail extremely high specific capital costs for such GTL projects [7]. Coupled with low profitability (6–8%) and long payback periods (over 10 years) this APG utilization method seems to be little attractive both for extracting and service companies operating at the associated gas conversion market.

Russian engineering companies, in cooperation with Russian Academy of Sciences institutions and foreign licensers, can offer a number of process schemes of complex facilities for deep APG processsing in oil fields, based on which an economically viable solution could be found to the above-mentioned problems, including the infamous "DLG problem."

Below, possible end products of deep conversion of APG and the efficiency of the corresponding gas-chemical facilities will be discussed.

Market of Gas Chemical Products

Despite the recession that began in 2008, Russia will experience shortages in basic chemical products [8], including polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), methanol, ammonia, and other products, according to forecasts till 2030.

Table 3. Cost of production from APG and market price of methanol, high-octane gasoline, olefins, and aromatic compounds [10][a]

Product	US \$ ton^{-1}					
	Russia		Rotterdam, Europe (FOB)	South Korea (FOB)	Japan (FOB)	China (CFR)
	Cost of production from APG[b]	Ex-works[c] price (EXW)				
Methanol	60–120	240–280	330–340	320–325	380–390	380–385
High-octane gasoline (RON 95)	630–640	670–700	1600–1700	1450–1500	1370–1400	940–960
Ethylene	550–570	570–900	1120–1125	1000–1020	1050–1060	1000–1030
Propylene	550–570	570–1000	900–940	1190–1195	1190–1200	1200–1210
Butadiene	–	1500–1600	1830–1840	2070–2072	2070–2072	2079–2081
Benzene	270–290	670–700	1090–1100	830–840	980–985	950–970
Toluene	–	600–620	890–900	870–880	870–980	850–960
Commercial xylene (mixture of isomeric xylenes)	270–290	600–630	895–905	–	–	–
p-Xylene	350–360	670–700	930–950	1053–1057	–	1150–1170
Terephthalic acid (TPA)	540–560	1100–1200	–	–	1100–1150	1110–1120
Poly(ethylene terephthalate) (PET)	710–730	1550–1650	1590–1650	–	–	–

[a] EXW: The seller makes the goods available at its premises; FOB: The sellers load themselves the goods on board the vessel nominated by the buyer and pay the export customs duties. [b] APG is delivered directly from the field at 600 rubles per 1000 m^{-3}. [c] Average market price of products obtained from conventional raw materials (oil, natural gas) as of third-quarter of 2010.

The shortage in basic polymers at domestic and foreign markets may reach 1.0–4.2 million ton year^{-1}, and that in methanol and carbamide, 6–8.5 million ton year^{-1} (Figs. 1 and 2).

Russia periodically experiences shortages in benzene whose availability for domestic processors depends on the world market for benzene derivatives (caprolactam, phenol). Increase in the world market

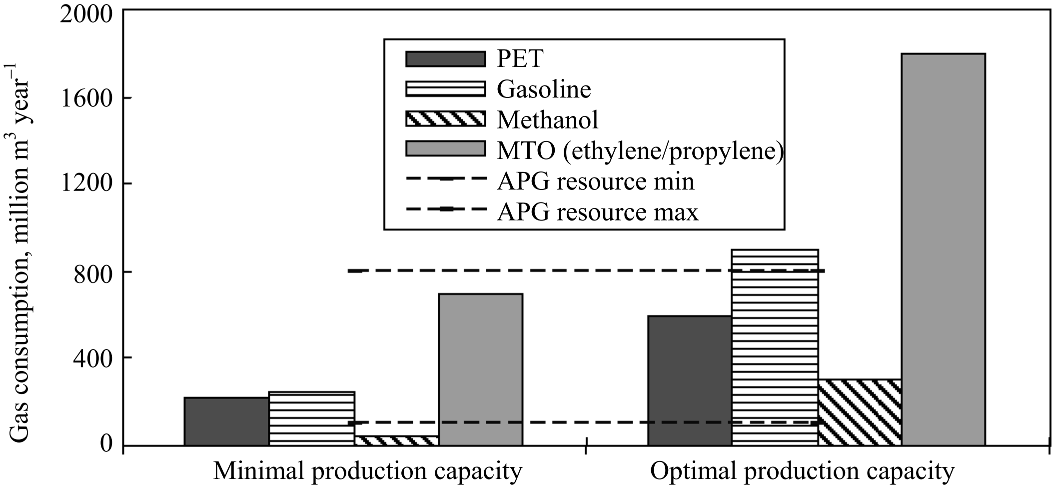

Fig. 3. Ratio of the minimally cost-effective (IRR ~ 10%) and optimal (IRR > 25–35%) facilities for APG processing into a variety of products at the APG yield typical for mineral resources users (100–800 million m^3 year^{-1}, dotted lines).

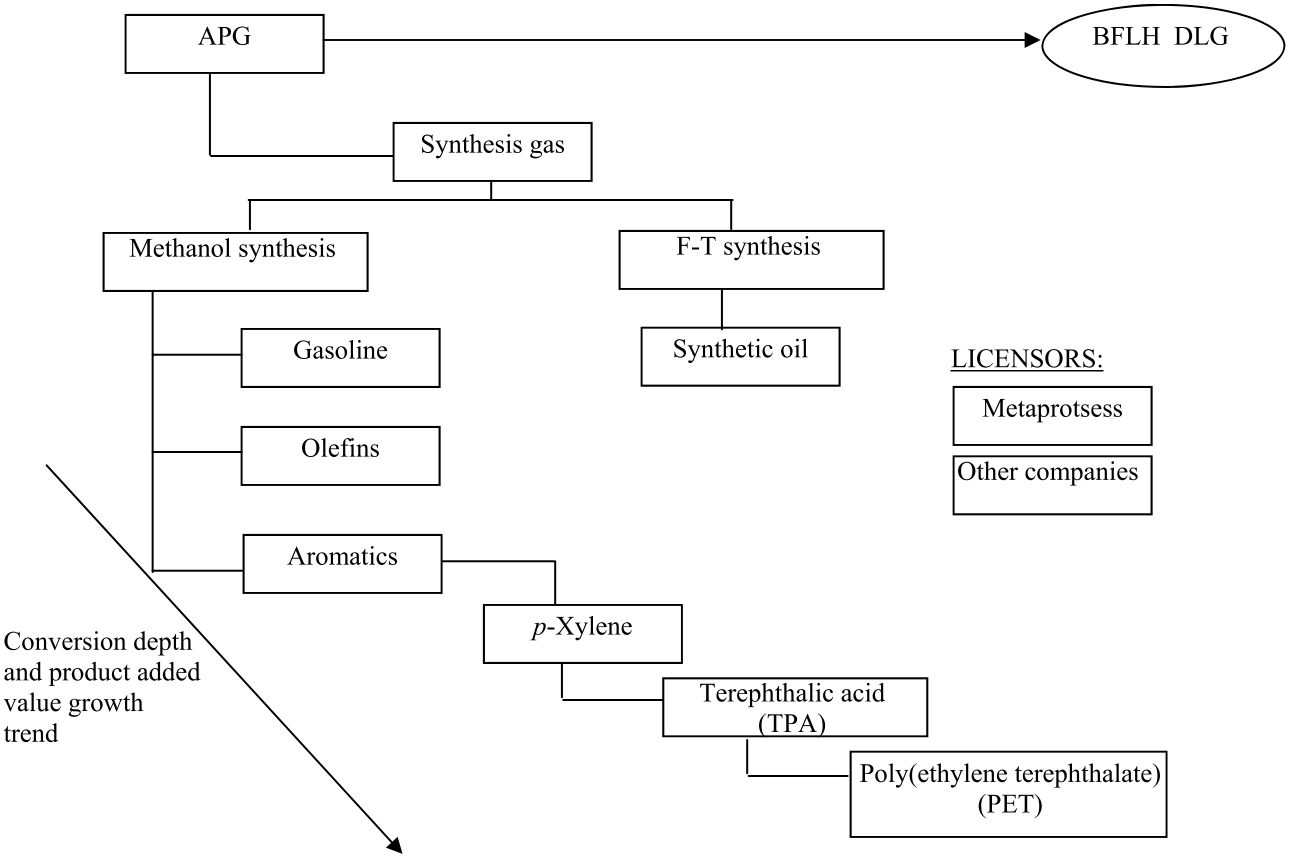

Fig. 4. Directions of APG processing via synthesis gas production stage with the "DLG problem" eliminated.

prices for these products makes it virtually impossible to purchase benzene from Russian producers. This situation is due to the export-oriented behavior demonstrated by Russian producers of aromatic hydrocarbons.

In 2006, 1035 thousand tons of benzene was produced in Russia [9], including 149.7 thousand tons derived from coal and 884.8 thousand tons, from crude oil. Russia' domestic consumption of benzene in that period was 520 thousand tons (50.2%), and the balance went for intra-deliveries, in-plant consumption, and exports. Today, the growth in benzene consumption in Russia is kept down by the lack of its production, but, according to forecasts for 2011, the situation would change and benzene consumption in Russia would grow to 800–1025 thousand tons.

In the Asia-Pacific region characterized by the rapidly growing production of polymers the demand for olefins and aromatic hydrocarbons increases as previously at high rates (4–8 and 9–25% year^{-1} in China and India, respectively). This offers good prospects for exports of gas and chemical products from Russia to that region, even taking into account the transport costs of 45–55 US \$ ton^{-1} (Table 3).

Comparison of the above estimates of the amounts of "free" APG (28.8 billion m^3 year^{-1}) and forecasted shortages in basic gas and chemical products may mislead one into believing that the petroleum gas processing would cover all the needs of Russian consumers, but in reality the locally available APG resources will be limited by the capacity of a specific production facility.

Figure 3 shows the APG consumption in relation to the minimal viable and optimal production capacities that provide for high investment attractiveness of APG utilization projects. Dotted lines show the estimated average yield of APG for users of mineral resources.

It is seen that small APG resources characteristic for small fields (30–150 million m^3 year^{-1}) in most cases will prevent creation of cost-effective gas-chemical complexes.

Table 4. Comparative efficiency of the technologies for gas conversion via synthesis gas production stage

Technology	Energy efficiency, %	Average calorific value of product, GJ ton^{-1}
Fischer–Tropsch synthesis	57	43.1
Methanol synthesis	61	20.0
Hydrocarbon synthesis via methanol	60	43.3

A certain exception is provided by methanol which is delivered to remote northern regions of Russia in amount of ~400 thousand tons year^{-1}. High costs of methanol delivery to fields and the availability of local consumers lead to the commercial viability of small-scale gas chemistry. For example, an installation for methanol production from natural gas with the rated capacity of 12.5 thousand tons year^{-1}, designed and put into operation in 2007 by "Methanol and Nitrogen Processes" Closed Joint-Stock Company in the Yamalo-Nenets Autonomous District (Novyi Urengoi) has paid for itself in just three years of operation, and another plant with the capacity of 40 thousand tons year^{-1} was constructed in 2010 and put into operation a short distance away.

At the same time, in the region producing ca. 67% APG (Khanty-Mansiisk Autonomous District-Yugra) methanol is in poor demand, and its exports from a distant field for sales outside the region is little profitable. Hence, as concerns APG conversion specifically to methanol, there is a need to analyze options for on-site methanol processing into locally marketable products, e.g., formaldehyde for carbamide-formaldehyde resins, or to increase the degree of feedstock conversion with the aim to obtain high added value competitive products.

Deep APG Conversion Technologies Offered by Metaprotses Closed Joint-Stock Company

Technologies developed and offered for complete APG processing (without DLG formation) include those intended for:

(1) production of methanol [technical-grade methanol complaint with appropriate technical specifications or rectified methanol compliant with GOST (State Standard) 2222-95]: pre-reforming of APG, production of synthesis gas, and conversion of synthesis gas to methanol over commercial copper-based catalysts (licensor Metaprotsess Closed Joint-Stock Company);

(2) production of high-octane gasoline (a Mobil process modification proposed by Metaprotsess): preparation of an intermediate, fortified crude methanol (92–94%), followed by its conversion to crude gasoline; separation of the latter into light and heavy (durene-containing) fractions; hydrogenation of the heavy fraction, and compounding of the resulting hydrocarbon fractions with additions into finished gasoline compliant with GOST R 51866-2002 (EN 228-2004) (Licensor Metaprotsess Closed Joint-Stock Company);

(3) production of C_6–C_8 aromatic hydrocarbons: production of an intermediate, fortified crude methanol (92–94%), followed by conversion of the latter into a concentrate of benzene and alkylaromatic hydrocarbons C_6–C_{9+} (aromatics concentrate), and isolation from the latter of commercial BTX (benzene-toluene-xylenes) fraction (Licensor Metaprotsess Closed Joint-Stock Company);

(4) production of *p*-xylene, terephthalic acid, and poly(ethylene terephthalate): production of an intermediate, an aromatics concentrate from fortified methanol, followed by conversion of the aromatics concentrate to *p*-xylene, oxidation of *p*-xylene to terephthalic acid, and polycondensation of terephthalic acid with monoethylene glycol (MEG) to poly (ethylene terephthalate) (Licensors Metaprotsess Closed Joint-Stock Company, UOP, Lurgi, and Uhde Inventa-Fischer);

(5) production of olefins (with ethylene/propylene as target products): production of an intermediate, fortified crude methanol (92–94%), followed by conversion of the latter to a C_2–C_4 olefin mixture, and isolation of commercial ethylene and propylene. Optionally: conversion of butenes and a part of ethylene to propylene by the metathesis reaction to control the propylene yield (up to 90–96%) (Licensors Metaprotsess Closed Joint-Stock Company, CBI Lummus); and

(6) the Fischer–Tropsch synthesis procedure: production of synthesis gas to be converted to a mixture of synthetic paraffins C_5–C_{30} (synthetic oil) (Licensor Metaprotsess Closed Joint-Stock Company).

Fig. 5. (a) Cylindrical and (b) box-shaped (“Penthouse” type) reformers available from Metaprotsess Closed Joint-Stock Company, installed at mineral resources user’s site beyond the Arctic Circle: reaction temperature 850°C; number of tubes: (a) 26 and (b) 48; number of burners: (a) 7 + 3 and (b) 32 +8; gas capacity: (a) 2200 and (b) 7500 Nm^3 h^{-1}; and congas capacity: (a) 7900 and (b) 27300 Nm^3 h^{-1}.

Figure 4 shows the general scheme of gas-chemical technologies suitable for APG conversion without DLG formation.

A feature shared by all the above-mentioned technologies consists in that, in the first stage of production, all of the hydrocarbons contained in APG are converted to synthesis gas, i.e., a mixture of hydrogen, carbon oxides, and residual methane. Synthesis gas is subsequently used for synthesis of hydrocarbons or methanol and its conversion products.

Synthesis gas is produced via the following process stages:

(1) hydrogenation of organosulfur compounds contained in the initial associated gas to H_2S, as well as of unsaturated to saturated hydrocarbons over an alumina-cobalt-molybdenum commercial catalyst;

(2) adsorption of H_2S contained in the gas that resulted from hydrogenation of organosulfur compounds over a commercial catalyst containing reactive zinc oxide ZnO;

(3) adiabatic steam low-temperature pre-reforming of the gas over a commercial nickel catalyst to decompose higher hydrocarbons to methane mixed with hydrogen, CO, and CO_2. Pre-reforming of hydrocarbon feedstock is a procedure traditionally applied by plants engaged in production of synthesis gas and in processing of relatively heavy hydrocarbon feedstock (e.g., naphtha) or a feedstock characterized by a variable hydrocarbon composition. The pre-reforming reactor is the simplest one-shelf axial-flow adiabatic reactor. The pre-reforming catalyst has been for several decades available at the market from foreign manufacturers, e.g., BASF, Johnson Matthey;

(4) steam or steam/carbon dioxide catalytic reforming of gas over a commercial nickel catalyst into converted gas, a mixture of hydrogen, carbon

monoxide, carbon dioxide, water vapor, and residual methane at ~860°C and 1.8–2.2 MPa. The reforming furnace designed and constructed by Metaprotsess Closed Joint-Stock Company employs catalysts available from Johnson Matthey;

(5) cooling and drying (water condensation) of the converted gas to synthesis gas;

(6) compression of hydrogen-containing gas (a process traditional for petrochemistry and gas chemistry);

(7) removal of CO_2 from synthesis gas (in the case of the Fischer–Tropsch process): absorption by the commercial process scheme on commercial aMDEA (activated methyldiethanolamine); removal of carbon dioxide from aMDEA by the standard separation procedure and gas stream desorption; and

(8) adjustment of the synthesis gas composition (elimination of hydrogen excess in the case of the Fischer–Tropsch process). Gas mixtures are separated by the membrane method which offers advantages over the adsorption method in terms of easy process automation and control and increased equipment service life. Hydrogen is eliminated on commercial membrane gas separators (Air Products, Air Liquid, MTR, UOP).

The synthesis gas preparation process has been refined over decades; it employs natural gas, associated petroleum gas, BFLH, light gasoline, coal, and other carbon-containing materials as feedstock. Variously designed gasifiers and reformers, as well as commercial desulfurization, reforming, and pre-reforming catalysts are offered by leading foreign and Russian producers.

Metaprotsess Closed Joint-Stock Company, in turn, has considerable practical experience in designing, manufacturing, installing, and launching compact reformers and synthesis gas processing facilities to be placed directly on the mineral user sites, including those beyond the Arctic Circle (Fig. 5).

Virtually every combustible carbon-containing substances such as, e.g., exhaust gases, process vents, or byproducts are suitable as fuel for modern commercial reformers. The achievable reforming efficiency exceeds 80% (on carbon basis) at the total energy efficiency of feedstock processing of >60% (for efficiency with respect to the calorific value of the feed gas and the resulting commercial products, see Table 4).

Thus, no extra technological problems and risks are associated with production of synthesis gas from APG. Moreover, the use of reformers allows carbon-containing gases (H_2, C_1–C_4), carbon monoxide, and carbon-containing byproducts to be re-entered into the process or used as fuel in order to save APG and provide complete feedstock conversion.

The methanol synthesis process includes the following steps:

(1) Compression of synthetic gas from 1.7–1.8 to ~5 MPa and feeding of fresh gas into the synthesis loop by the compressor. For compression purposes Metaprotsess Closed Joint-Stock Company employs medium-speed reciprocating compressors available form Ariel, e.g., API 618. Owing to easy operation and serviceability, these electrically-driven compressors represent the best option for medium-tonnage facilities located in less accessible regions;

(2) Mixing of fresh gas with circulating gas of the synthesis loop;

(3) Compression of a mixture of circulating and fresh gas in a circulating gas compressor;

(4) Gas mixture heating in a regenerative heat exchanger which uses the heat of the stream leaving the synthesis reactor;

(5) Partial (under the equilibrium conditions) conversion of a mixture of hydrogen and carbon oxides to methanol in the synthesis reactor over a commercial catalyst of methanol synthesis. Methanol synthesis catalysts are available from BASF, Johnson Matthey, Süd Chemie, Haldor Topsøe, etc. Metaprotsess Closed Joint-Stock Company employs catalysts available from Johnson Matthey. The methanol production process is protected by patent for utility model “A Plant for Production of Methanol or Synthetic Oil” no. 73666 of July 14, 2006;

(6) Metaprotsess Closed Joint-Stock Company employs a multishelf reactor with cold feed bypass provision whose advantage, when applied in medium-tonnage production facilities, consists in easy operation and maintenance (catalyst loading/unloading). Furthermore, such reactors can be manufactured within a relatively short period by several Russian plants. The reactor design is protected by patent for utility model “A Universal Chemical Reactor” no. 67887 of June 21, 2006;

(7) The circulation ratio in the synthesis loop (the

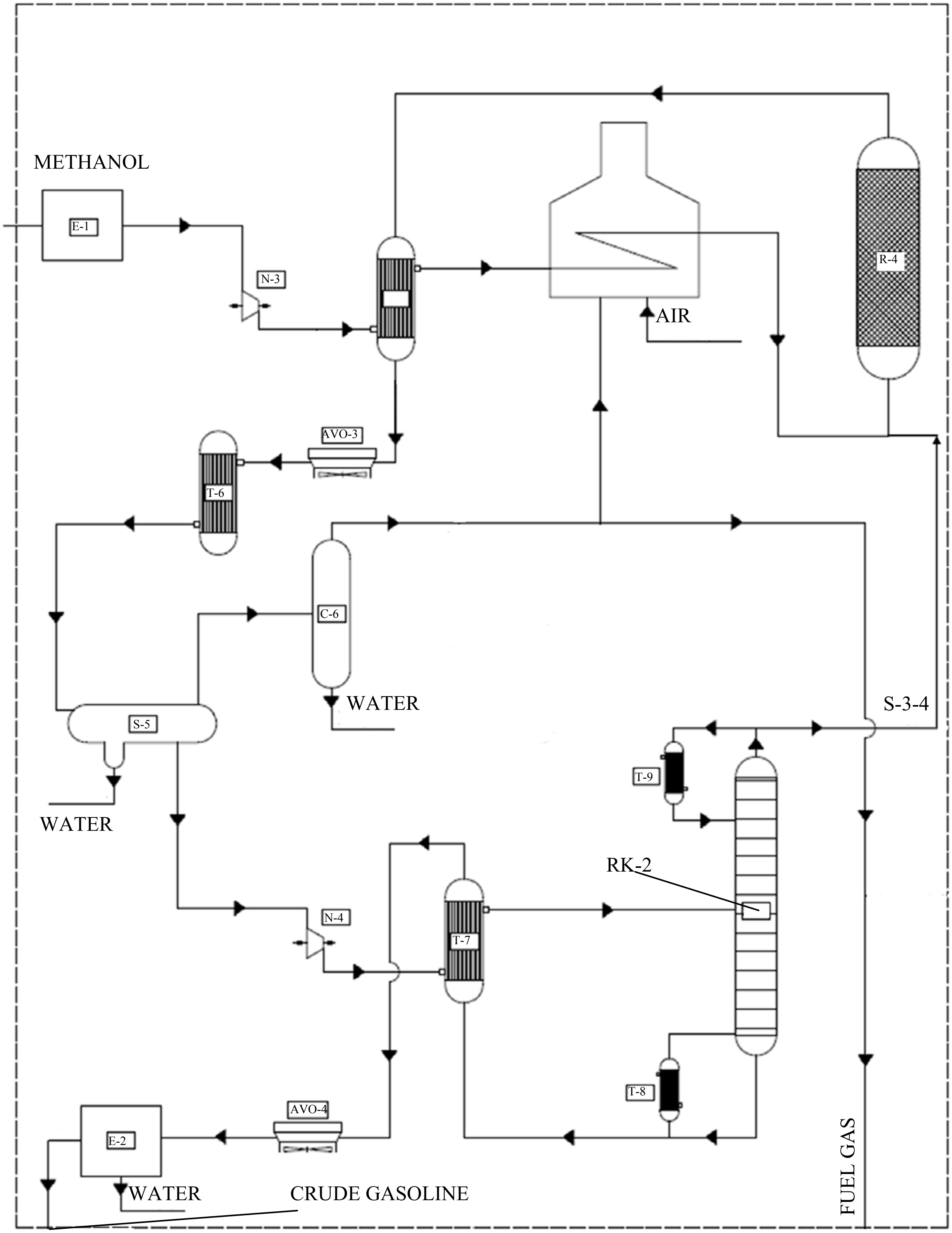

Fig. 6. Simplified flow diagram of feed methanol conversion to crude gasoline to be further processed to achieve compliance with GOST (State Standard) R 51866-2002 (EH 228-2004): (T-5, T-7) recuperative heat exchangers; (T-6, T-9) water-cooled condensers; (P-2) furnace for heating of feedstock and regeneration gases; (T-8) column bottom heater; (AVO-3 and AVO-4) air coolers; (S-5) three-phase separator; (S-6) separator; (R-4) methanol conversion reactor; (RK-2) fractionation column; (E-1, E-2) storage tanks; and (N-3, N-4) pumps.

Table 5. Commodity balance of the department for methanol conversion to a C_6–C_{11} aromatic hydrocarbon mixture

Feedstock and product component	thousand ton g^{-1}	%
Feedstock		
Methanol	400	100
Products		
Benzene	3.0	0.8
Toluene	15.0	3.5
Commercial xylene (a mixture of isomeric xylenes)	50.3	11.9
C_{9+} aromatics	43.7	10.1
Hydrogen	15.0	5.0
Dry gas and propane-butane fraction	27.0	9.0
Naphtha (nonaromatic hydrocarbons)	6.7	1.6
Water of reaction	225.2	57.9
Loss	0.6	0.2
Total	400	100

Table 6. Commodity balance of the department for synthesis of C_6–C_{11} aromatics mixture from light hydrocarbons

Feedstock and product component	thousand ton g^{-1}	%
Feedstock		
Propane–butane fraction after methanol conversion to BTX	19.6	100
Products		
Benzene	3.1	15.8
Toluene	5.0	25.5
Commercial xylene (a mixture of isomeric xylenes)	3.1	15.6
C_{9+} aromatics	1.5	7.9
Hydrogen	1.3	6.6
Dry gas and propane–butane fraction	5.0	25.5
Loss	0.6	0.3
Total	19.6	100

ratio of the flow rate of the circulation gas to that of the supply gas) being 5–7, the total conversion degree of carbon oxides to methanol is no less than 95%, despite a low degree of conversion of the reactants in a single pass;

(8) Cooling of the reacted gas in a regenerative heat exchanger and final cooling of the reacted gas in an air cooler;

(9) Separation of the condensed crude methanol in a high-pressure separator and discharge of blowdown flow circulation gas for maintaining a constant pressure in the synthesis loop (removal of inert methane, nitrogen, and excess hydrogen); and

(10) Separation of crude methanol in a low-pressure separator for degassing (flash gases: CO_2, CO, methane, hydrogen, and methanol vapor are released), and supply of crude methanol with the concentration of 82–86% for rectification or for further chemical conversion.

The Metaprotsess Closed Joint-Stock Company employs mass-transfer facilities available from Sulzer Chemtech (plates, structured packing, dispensers) and provides guarantees that the design rectification parameters will be achieved. For production of AA-grade commercial methanol, a two-column rectification scheme is used.

Technologies for Deep APG Conversion via Methanol Production Stage

Gasoline Production

The conversion of APG-derived methanol to high-octane gasoline via dimethyl ether formation stage can be represented by the following simplified scheme:

$$2CH_3OH \rightarrow CH_3OCH_3 \rightarrow \text{olefins } C_2–C_5 \\ \rightarrow \text{yhydrocarbons } C_{5+}.$$

The process is run at 0.8–0.95 MPa and 360–420°C in the presence of a high-silica zeolite-based catalyst and gives, along with hydrocarbons, abundant water and light gas fraction (hydrogen-containing gas).

The reaction mixture is separated into an aqueous layer and the gas and hydrocarbon fractions. The hydrocarbon fraction undergoes stabilization into the propane-butane fraction (C_2–C_4 olefin mixture) which is returned to the gasoline synthesis stage, with the residue represented by the main product, synthetic crude gasoline.

Crude gasoline contains up to 9 wt % durene, a hydrocarbon with a low crystallization temperature. To

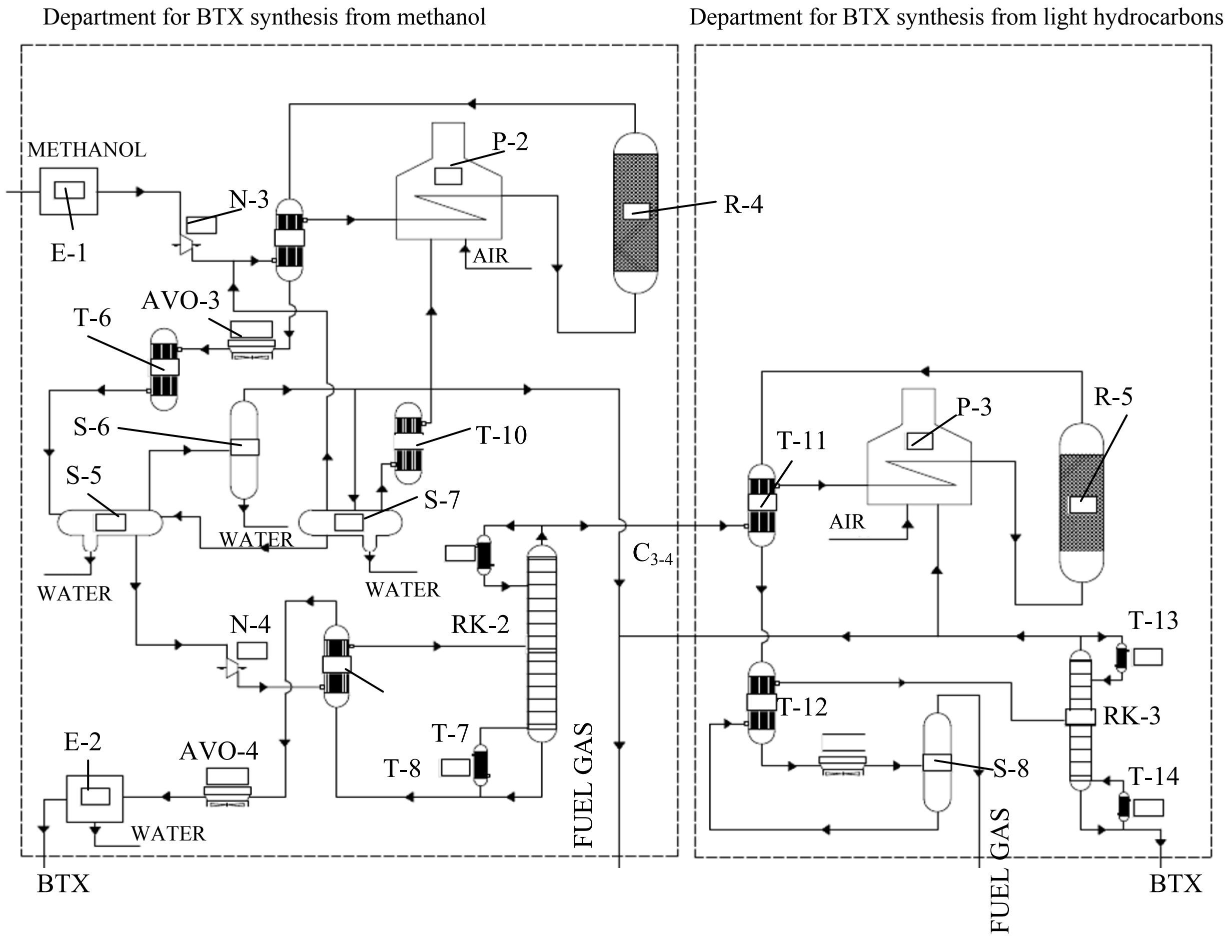

Fig. 7. Process flow diagram for the department of methanol conversion to a mixture of benzene and alkylaromatic hydrocarbons (BTX fraction): (T-5, T-7, T-11, T-12) Recuperative heat exchangers; (T-6, T-9, T-13) water-cooled condensers; (P-2, P-3) furnaces for heating of feedstock and regeneration gases, (T-8) column bottom heater; (AVO-3…AVO-5) air coolers; (S-5) three-phase separator; (S-6, S-8) separators; (R-4) methanol conversion reactor; (R-5) C_3 – C_4 hydrocarbon aromatization reactor; (RK-2, RK-3) fractionation columns; (E-1, E-2) storage tanks; and (N-3, N-4) pumps.

reduce the durene concentration, synthetic gasoline is redistilled into a heavy and a light fraction, which is followed by hydrogenation of the heavy gasoline fraction.

Heavy gasoline fraction is hydrogenated at 3.9–4.0 MPa and 240–290°C over a Pd catalyst. Hydrogen for the hydrogenation reaction is isolated from the light gas fraction on a membrane separation setup.

Commercial gasoline is obtained by mixing the light and heavy gasoline fractions with antiknock and antioxidant additions to achieve standard-compliant quality of the product. The component mixing (compounding) formula is calculated in terms of the mathematical models used for the general production planning, taking into account the changes induced in the composition of the gasoline produced by catalyst aging.

The setup for methanol conversion to crude gasoline is comprised of the following elements:

(1) a methanol evaporator;

(2) two–four parallel reactors used for methanol conversion over a domestic catalyst analogous to ZSM-5 zeolite, with zinc, cerium, and rare earth elements as promoters. The catalyst is manufactured by Nizhegorodskie Sorbenty Closed Joint-Stock Company under RF patent 2189858 “A Catalyst for Preparation of Liquid Hydrocarbons from Low-Molecular-Weight Oxygen-Containing Organic Compounds;”

(3) a circulation gas compressor and a nitrogen compressor for regeneration of the zeolite catalyst used for methanol conversion;

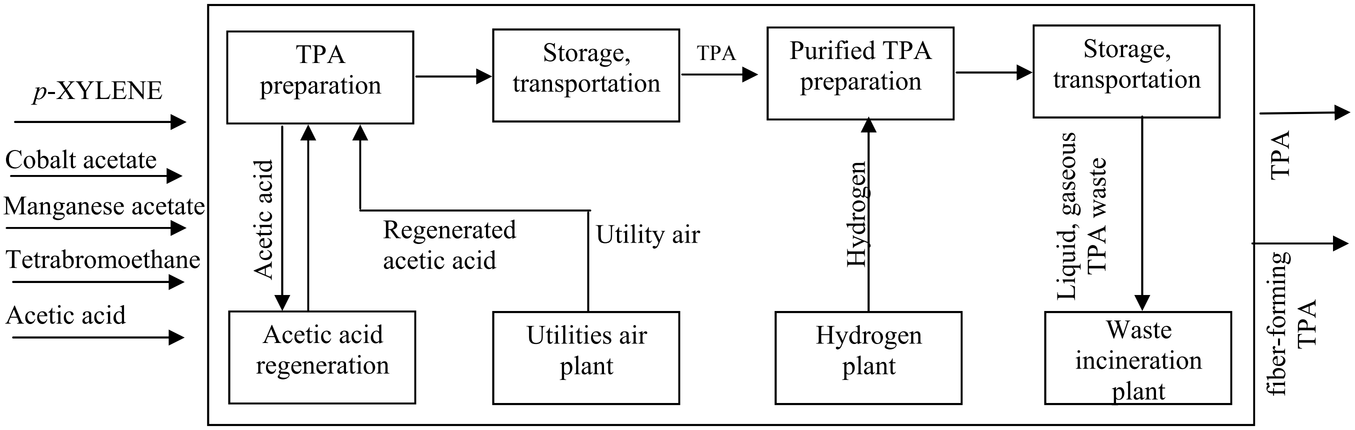

Fig. 8. Schematic block diagram of *p*-xylene conversion to terephthalic acid.

(4) a fired heater for start-up heating of the reactors and heating of the circulating nitrogen-air mixture (a regeneration mixture for coke removal from the catalyst);

(5) regenerative heat exchangers;

(6) an exhaust-heat boiler for steam generation (~4 MPa) during cooling of the reaction products;

(7) air aftercoolers for the reaction mixture prior to primary separation into liquid (water and residual unchanged methanol, liquid hydrocarbons) and gaseous reaction products; and

(8) a stabilization column.

A specific feature of the process consists in the use of rectified methanol containing up to 6–10% water, which reduces the capital and operating costs for the methanol production unit via the use of a simple one-column rectification scheme. The amount of methanol spent (based on 100% CH_3OH) is 2.65 ton per ton of Premium Euro-95 gasoline.

Figure 6 shows a simplified (no rectification, heavy gasoline hydrogenation, and compounding units) flow diagram of methanol conversion to synthetic gasoline.

Production of C_{6+} Aromatic Hydrocarbons

The APG derived from methanol at 450–550°C and 0.1–2.0 MPa is selectively converted over zinc-promoted ZSM-5-analogous zeolites to a mixture of benzene with aromatic hydrocarbons C_6–C_{11}. The possibility of this reaction has been established in the

Table 7. Mass balance for the TPA preparation from *p*-xylene according to Lurgi data for 2008

Parameter	thousand ton g^{-1}	%
Feedstock[a]		
p-Xylene	80	64.5
Oxygen (atmospheric)	44	35.5
Total:	124	100
Products		
TPA (purified)	122.5	98.9
Loss	1.5	1.1
Total:	124	100

[a] Acetic acid consumption 36 kg (TPA ton)$^{-1}$, and catalyst consumption, 0.9 kg (TPA ton)$^{-1}$.

Table 8. Mass balance for the PET preparation according to Uhde Inventa-Fischer data for 2010

Parameter	thousand ton g^{-1}	%
Feedstock		
TPA	110	68.8
Monoethylene glycol	50	31.2
Total:	160	100
Products		
PET (fiber-grade quality)	130	81.3
Water of reaction	28	17.5
Loss	2	1.2
Total:	160	100

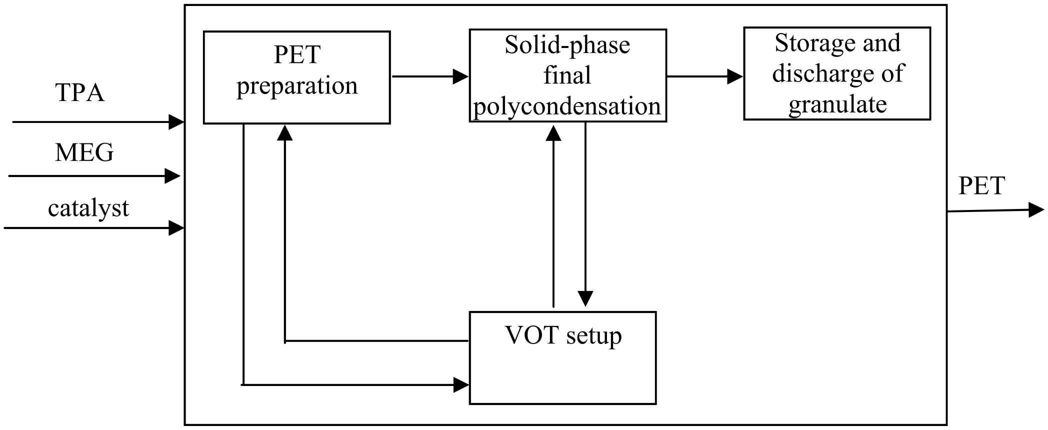

Fig. 9. Block diagram of terephthalic acid and monoethylethylene glycol conversion to poly(ethylene terephthalate). “VOT setup” is a block for evacuation, treatment of flue gas, and removal of reaction byproducts.

1980s [11]. Its commercial implementation was prevented so far, however, by a failure to solve a number of problems involved in high-temperature conversion of methanol into arenes, in particular, rapid catalyst deactivation because of increased coke formation, breakdown of the catalyst granules under water vapor exposure, etc.

Metaprotsess Closed Joint-Stock Company suggested the use in this process of a new zeolite catalyst [12] comprising a complex binder based on silica and alumina, which affords a 96% yield of alkylaromatic hydrocarbons C_{6+} at a close to 100% conversion of methanol. This catalyst owes its increased efficiency not only to the zeolite component but also to the sol-gel technique used for the binder preparation.

As shown by physicochemical analyses [X-ray diffraction, X-ray fluorescence spectroscopy, small-angle X-ray scattering, and derivatography (thermal analysis) methods], the binder is a nanostructured porous material with an average size of the primary particle of 4–8 nm and the maximum particle size not exceeding 20 nm. This catalyst is characterized by resistance to water vapor (water comes together with the feedstock and also is formed during the process), as well as by reduced coke formation owing to the shielding effect produced by the silica sol particles on the Lewis centers of alumina [13].

The process conditions are as follows: 510–530°C, 0.5–1.0 MPa, methanol feeding rate 2–4 h^{-1}, and catalyst cycle length 400–500 h.

High-temperature conversion of methanol into a mixture of C_6–C_{11} aromatic hydrocarbons leads to an appreciable amount of gaseous products which, in the course of the process, are separated into hydrogen-containing gas (H_2 and the so-called “dry gas” comprised of a mixture of CH_4, C_2H_6, CO_2, and C_{3+} hydrocarbon traces) and the propane-butane fraction. The former is used for feedstock hydrotreating and also serves as fuel gas to achieve APG saving, and the propane-butane fraction undergoes aromatization, which gives additional amounts of aromatic hydrocarbons and increases the degree of feedstock conversion.

In this procedure, the methanol conversion into arenes was for the first time combined with simultaneous conversion of the resulting light hydrocarbons into aromatic hydrocarbons, which significantly increases the yield of target products via reducing the amount of byproduct fuel gases and liquid nonaromatic products.

In this context, it is worth to mention that, in recent decades, a focus of considerable basic and applied research efforts has been on the preparation of aromatic hydrocarbons from C_{3+} hydrocarbons [14–17]. The mechanisms of the catalytic action of modified pentasils prepared by different methods are broadly similar. All of these catalysts include strong aprotic acid centers accelerating the dehydrogenation of saturated molecules, which is the key step of aromatization of lower alkanes. Relevant technologies are offered by both foreign [Asahi Chemicals (Alpha), BP/UOP (Cyclar), CP Chem (Aromax), etc.] and Russian licensors (Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Research Institute of Organic Synthesis, Zelinskii Institute of Organic Chemistry, Russian Academy of

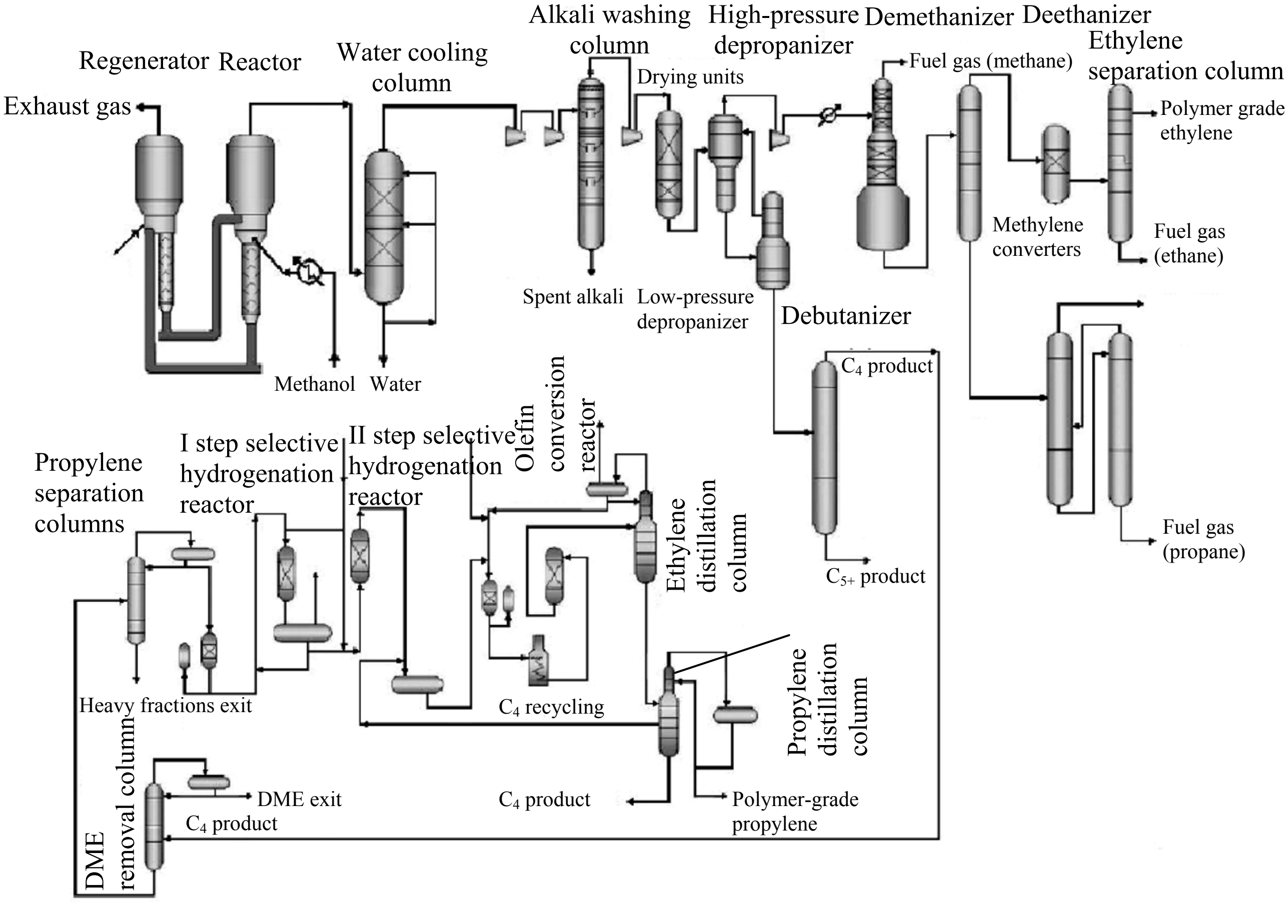

Fig. 10. Flowsheet of methanol to olefin conversion, comprising an olefin conversion stage for propylene yield increasing.

Sciences, etc.). Despite advances achieved with the pilot and commercial implementation, this method proved to be unsuitable for APG utilization because of a low yield of liquid products. The weight of the residual “dry” gas makes 60–70% of the weight of the initial APG.

Figure 7 shows a process scheme of the unit for conversion of methanol and light hydrocarbons to a C_6–C_{11} aromatic hydrocarbon mixture. Tables 5 and 6 present the commodity balance by the example of a complex facility for deep conversion of APG available from the Maiskaya group of fields, which is being created by the Yugra Gas Chemical Company.

The BTX fraction, similar to individual aromatic hydrocarbons, is a valuable petrochemical feedstock.

In particular, *p*-xylene is used for production of terephthalic acid (intermediate) and poly(ethylene terephthalate). Because *p*-xylene produced from gas feedstock does not differ in purity from that derived from oil feedstock, it can be subsequently processed with the use of modern industrial technologies and facilities.

Thus, provided sufficient amount of APG, its deeper conversion down to preparation of easily transportable and environmentally friendly polymers highly marketable at Russian market, in particular PET, may be economically justified. Figure 8 shows the block diagram of the first stage of *p*-xylene conversion to terephthalic acid (TPA) via liquid-phase oxidation with atmospheric oxygen in the presence of Co and Mn acetates.

This is a multistep process which is run in a bubble-type reactor at 110–130°C and 0.9–1.5 MPa and involves formation of intermediate oxidation products: toluic acid aldehyde, toluic acid, and carboxybenzaldehyde. Therefore, preparation of fiber-forming “purified” terephthalic acid (PTPA) requires purification by hydrogenation.

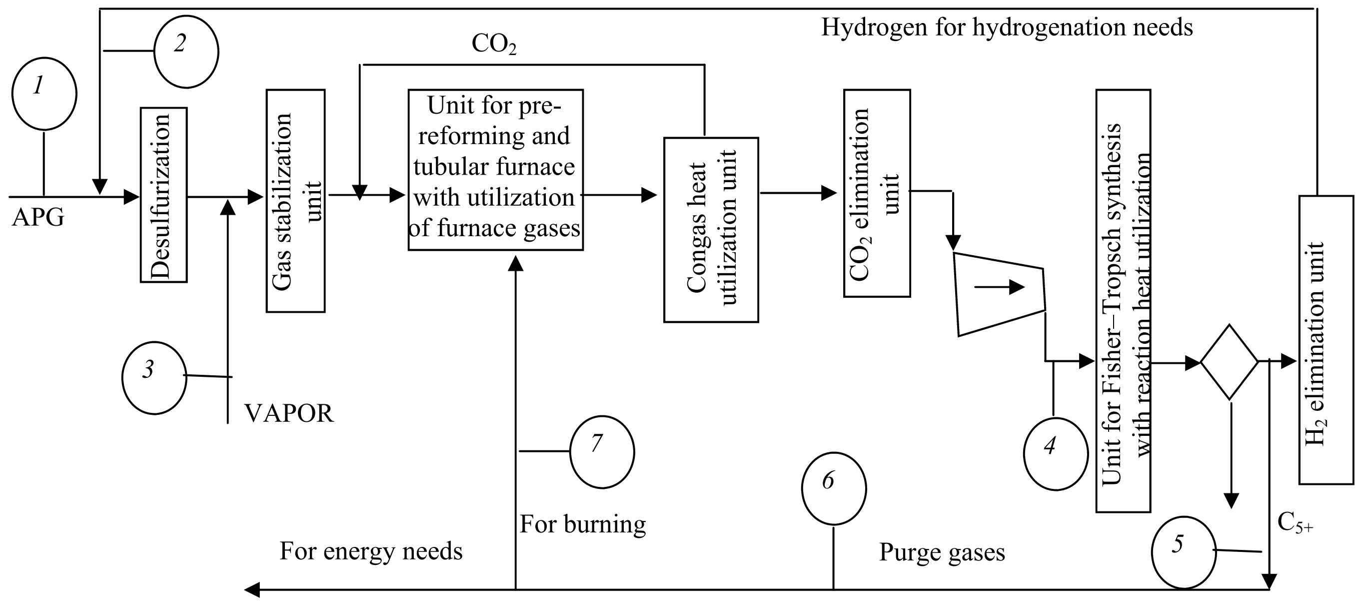

Fig. 11. Schematic diagram of APG conversion to "synthetic oil" using Fischer-Tropsch synthesis procedure: (*1*) Feed APG (pressure 0.5 MPa), (*2*) hydrogen for APG desulfurization, (*3*) process superheated steam, (*4*) compressed and pretreated synthesis gas for synthesis, (*5*) stabilized liquid synthetic C_{5+} hydrocarbons, (*6*) hydrogen-containing blowdown gases for power production, (*7*) hydrogen-containing blowdown gases to reforming furnace burners.

Licensors offer several versions of TPA preparation technologies based on *p*-xylene consumption in amount of 0.65–0.68 ton (PTPA ton)$^{-1}$. An approximate mass balance is presented in Table 7.

The resulting TPA can be further converted to poly (ethylene terephthalate) by two-stage polycondensation of the purified terephthalic acid with monoethylene glycol. In terms of the key performance characteristics, a continuous process for poly(ethylene terephthalate) preparation from terephthalic acid and monoethylene glycol is advantageous. Terephthalic acid is esterified with monoethylene glycol (molar ratio of the components ranging from 1:1.2 to 1:1.5) at 240–270°C and 0.1–0.2 MPa. The block diagram of the TPA/MEG conversion to PET is shown in Fig. 9, and the material balance is presented in Table 8.

In the second stage the resulting mixture of bis-(2-hydroxyethyl) terephthalate with its oligomers are subjected to polycondensation in several consecutive apparatuses equipped with stirrers at temperature being gradually increased from 270 to 300°C and pressure, decreased from 6600 to 66 Pa.

Table 9. Hydrocarbons composition of synthetic oil

Fractions	wt %	Groups	wt %
C_5–C_{10}	31–38	*n*-Alkanes	92–93
C_{11}–C_{18}	33–35	*i*-Alkanes +alkenes	7–8
C_{19+}	27–35		

Upon completion of the process, molten PET is extruded from the apparatus, cooled (rapid cooling gives amorphous and slow, crystalline PET), and pelletized or is used for fiber molding.

Methanol to Olefin (MTO) Process

The methanol to olefin (MTO) process is a well-understood methanol dehydration reaction run in the

Table 10. Average amount of expendables consumed in production of 1 ton of synthetic oil

Expendable	Amount
Associated petroleum gas, m^3	1800–2000
Demineralized water, m^3	5.5–6.0
Electricity, kW h	410–450
Adsorbent (zinc oxide), kg	0.4–0.7
Absorbent (MDEA), kg	0.1
Gas conversion catalyst, kg	0.02
Fischer–Tropsch catalyst, kg	0.002

presence of a solid acid catalyst [18] at 350–450°C, moderate pressure (0.1–0.3 MPa), and feedstock supply velocity 2–4 h^{-1}. The technology offered by Lummus, one of the licensors of Metaprotsess Closed Joint-Stock Company, includes methanol to olefin conversion over an aluminophosphate narrow-pored catalyst of SAPO-34 type in the first stage.

If necessary, the propylene yield in the second stage can be increased by controlling the $C_{2=}/C_{3=}$ commodity olefin ratio. To this end, excess ethylene and side butenes (2-butene and 1-butene) are converted to propylene via combining in the same apparatus the butene isomerization (1-butene is isomerized to 2-butene) and exchange (metathesis) (2-butene reacts with ethylene to form propylene) reactions.

The first commercial implementation of the above-described two-stage MTO process took place in September 2010 at Shenhua Baotou Coal Chemicals Co. Ltd. (Baotou, China). Commodity olefins were obtained within a period as brief as 72 h after raw methanol was fed. The plant constructed under Lummus license has a capacity of 600 thousand tons of ethylene and propylene per annum from 1.8 million tons of methanol and is the world's first commercial MTO plant [19].

A distinctive feature of the MTO process proposed consists in the lack of special requirements concerning the water content in methanol, which has no apparent negative effect on the methanol conversion. Theoretically, this content may be very high (70–80 wt %), but economically acceptable is the level of no higher than 20 wt%, at which crude methanol derived from APG can be used without rectification.

Table 11. Efficiency of APG processing into synthetic oil

Parameter	Option	
Volume of APG to be processed	160 million	320 million m^3 year^{-1}
Products	Synthetic oil	
amount produced,	78	152
sales price EXW[a], US $	240	240
Cost of manufacturing equipment, US $ mln	145	210
Gross revenues, $ mln	18.7	36.4
Payback period[b], year	12	10

[a] March 2010. [b] Nondiscounted payback period.

At the same time, a number of impurities in feedstock exert the key effect on the methanol conversion and olefin production selectivity. The main impact of catalyst poisons consists in the following:

(1) Alkali and alkaline-earth metals in methanol feedstock will be deposited onto the catalyst, thereby affecting its acidity and leading to its irreversible deactivation. This will reduce the olefin production selectivity and increase the yield of byproducts, e.g., aldehydes, ketones, etc., which will adversely affect further separation of olefins.

(2) Most of transition metals cause the methanol decomposition to accelerate. When occurring in crude methanol, transition metals not only irreversibly alter the acidity of the catalyst, thereby affecting the degree of methanol conversion and the olefin production selectivity, but also will accelerate the methanol decomposition, which will result in increased yield of CO and modified conditions of the reaction and of subsequent separation of olefins.

Table 12. Comparative efficiency of different directions of APG conversion (to methanol and other products)

Parameter	Processing product				
	methanol	BTX	*p*-xylene	TPA	PET
Volume of APG to be processed, mln m^3 year^{-1}	320				
Amount produced, thousand tons year^{-1}	400	125	108	153	180
Sales price EXW[a], thousand ton year^{-1}	10.78	27.52	42.06	55.04	66.83
CAPEX (accumulated total), billion rubles	8.31	10.13	11.74	14.32	16.90
Internal Rate of Return (IRR), %	19.1	15.6	16.4	28.3	25.9
Payback period[b], year	8	10	10	6	6

[a] Forecast for year 3 of the project. [b] Discounted payback period, discount rate 12%.

Table 13. Efficiency of APG conversion to olefins and high-octane gasoline

Parameter	Processing product	
	olefins	gasoline
Volume of APG to be processed, mln m^3 year^{-1}	640	
Amount produced, thousand tons year^{-1}	320	299
Sales price EXW[a], thousand ruble ton^{-1}	25.63	29.09
CAPEX, billion rubles	22.3	19.7
Internal Rate of Return (IRR), %	25	26
Payback period[b], year	7	7

[a] Forecast for year 3 of the project. [b] Discounted payback period, discount rate 12%.

(3) Excessive alkalinity of feedstock, e.g., high ammonia level, leads to only temporary poisoning of the catalyst.

Figure 10 presents the process scheme for methanol to olefin conversion unit incorporating the olefin conversion compartment.

APG Conversion to Hydrocarbons via Fischer–Tropsch Synthesis Procedure

Synthetic oil is undoubtedly the best APG conversion product both in terms of sales (with the oil company, APG producer, itself as a possible buyer) and easy logistics (the use of existing transport infrastructure for mineral oil). This APG processing option entails relatively low risks, because worldwide there are several production facilities that use natural gas for gas conversion to liquid hydrocarbons.

The technology of APG conversion through Fischer–Tropsch process consists of the following main stages:

(1) preparation of feed gas (desulfurization and pre-reforming);

(2) production of synthesis gas;

(3) adjustment of the synthesis gas composition to the H_2:CO molar ratio of 2.0 and removal of undesirable carbon dioxide;

(4) Fischer–Tropsch synthesis; and

(5) stabilization of liquid hydrocarbons into commercial “synthetic oil.”

Figure 11 shows the production flow sheet.

The unit for adjustment of the composition of synthesis gas for steam or steam/CO_2 conversion includes the following components.

There is an installation comprised of a commercial membrane gas separator (Air Products, Air Liquid, MTR, UOP) for extraction of excess hydrogen from synthesis gas to be used as fuel for the reformer furnace.

Also, there is an installation for elimination of CO_2 from synthesis gas by absorption on commercial a-MDEA. This is followed by compression of the eliminated carbon dioxide to be supplied to the inlet of the apparatus for catalytic steam reforming aimed to increase the CO content in synthesis gas.

The Fischer–Tropsch process unit includes apparatuses for gas mixture heating in a regenerative heat exchanger using the heat of the stream leaving the synthesis reactor or the heat of steam produced in the Fischer–Tropsch synthesis reactor and apparatuses for feedstock supply to the synthesis reactor, where Fischer–Tropsch synthesis process is run over the specially developed cobalt-containing catalyst. To remove the heat generated by the synthesis reaction, there is a need in a special tubular reactor in which the heat is removed by boiling water occurring in the intertubular space.

Currently, the Fischer–Tropsch synthesis procedure represents the only direct technique used for commercial production of liquid fuels from natural gas without formation of intermediates. The most commonly used catalysts are those based on Co and Fe [20]. Compared to iron catalysts, cobalt catalysts allow preparation of heavier hydrocarbons. The main byproduct formed in the presence of iron- and cobalt-containing catalysts is CO_2 and water, respectively. Metaprotsess Closed Joint-Stock Company employs cobalt-containing catalysts for the most part.

The exothermic effect of the process reaches 11–12 MJ (hydrocarbon mixture kg)$^{-1}$. Hence, there is a need to carefully choose the reactor and to control the process mode for implementation of the synthesis procedure on a commercial scale, because stable operation requires elimination of possible local increases in the synthesis temperature.

The reaction gas leaving the synthesis reactor is cooled in air or water heat exchangers and air coolers. A part of the gas stream is separated out as blowdown to be burned in a reformer furnace.

The synthesis products are to be separated immediately after the synthesis to avoid oxidation of synthetic liquid hydrocarbons with oxygen-containing compounds formed during the process. The separation follows a standard three-stage industrial scheme and yields a synthetic crude oil stream, stream of reaction water comprising oxygen-containing compounds, and a gas stream consisting of unchanged CO, H_2, CO_2, and C_1–C_4 hydrocarbon gases.

Synthetic oil can be separated into commercial fractions by distillation, which is a standard process for most of petrochemical plants. Gasoline and diesel fraction streams can be prepared by a two-column scheme with plate columns; there is a need in ca. 20 pre-distillation plates and in 80 plates in the main distillation column.

In the case of the Fischer–Tropsch synthesis run on the catalysts developed at the Zelinskii Institute of General Chemistry, Russian Academy of Sciences (RAS Corresponding Member, Prof. A.L. Lapidus) at the request of Metaprotsess Closed Joint-Stock Company, the commodity products are represented by a mixture of synthetic liquid hydrocarbons whose composition is presented in Table 9.

The resulting oil is free from sulfur- and nitrogen-containing compounds, as well as of aromatics. The consumption data for expendables per ton of synthetic oil depend on the APG composition (Table 10).

The yield of “light” fractions can be increased through the use of an installation for hydrocracking of high-boiling petroleum fractions in the process flowsheet. The octane number of the gasoline fraction can be increased via isomerization. It should be noted that production of commodity fuels complicates the production and increases its cost.

In the case of processing of small amounts of APG, the most reasonable option consists in the preparation of synthetic oil and supply of the products to consumers by pumping synthetic oil mixed with crude oil or by batching (sequential pumping of different oil grades). In the latter case, there is a need to obtain a permission for supply of synthetic oil to the main pipeline, which is issued by independent certified laboratories on the basis of the data of synthetic oil analysis.

Economic Viability of APG Conversion Options

To assess the efficiency of the different APG conversion options, the Metaprotsess Closed Joint-Stock Company performed extensive feasibility studies, including pre-investment design and engineering developments, in relation to the license areas of many of the Russian oil companies in West Siberia. For a number of projects, feasibility studies were performed with respect to an investment project on APG utilization.

Those studies demonstrated that the least viable option is APG processing via the production of synthetic oil to be transported jointly with mineral oil (Table 11).

Long payback periods are determined, above all, by low sales prices of synthetic oil, which cannot exceed the official price of mineral oil with which crude oil is mixed before being supplied to the transport pipeline.

Nevertheless, oil companies show interest in this APG conversion option because it does not require additional infrastructure for synthetic oil storage and transport.

A more economically viable option can be found in APG conversion to methanol and other products. Table 12 lists the characteristics of the project for utilization of APG in amount of 320 million m^3 $year^{-1}$ into a variety of products at the purchase gas price of 1240 rubles per 1000 m^3.

The scale factor has a moderate positive impact on the economic viability of APG processing projects. Table 13 lists the characteristics of the project on utilization of APG in amount of 640 million m^3 $year^{-1}$ to olefins and high-octane gasoline at the purchase price of gas of 1240 rubles per 1000 m^3.

Utilization of Small APG Volumes

The specific capital intensity of the above-described gas-chemical plants for APG processing is relatively high: US $ 600–700 for methanol and US $ 1400–3000 per commercial products ton for other products from processing APG in amount of 300–650 million m^3 $year^{-1}$. It is a well-known fact [21] that, for chemical production processes, reduction in the feedstock volume leads to an exponential growth of specific capital costs (by a factor of 1.5–1.7 with the plant productivity decreased by half).

Thus, cost-effective processing of small volumes (10–100 million m^3 $year^{-1}$) of APG sends development engineers in a search for new approaches and technologies to reduce the processing costs. This concerns, above all, the production of synthesis gas and decrease in the number of stages involved in its processing into commercial products.

The Metaprotsess Closed Joint-Stock Company undertakes development of two lines of synthesis gas preparation by partial oxidation of methane-containing gases. Currently, prototypes of the synthesis gas generators were developed:

– a free-piston generator for noncatalytic partial oxidation to produce compressed synthesis gas (RF Patents 2327043, 2325225, and 2325224) and

– a generator for catalytic partial oxidation on a block catalyst (jointly with Gazokhim Limited Liability Company and NAMI Scientific Centre, Federal State Unitary Enterprise).

Major benefits offered by the catalytic partial oxidation process include no need in water treatment or air separation efforts, high feedstock supply velocity (up to 50000 h^{-1}), and lower energy intensity (heat of reaction 38 kJ mol^{-1}). The gas composition is close to that corresponding to thermodynamic equilibrium, and the H_2/CO ratio lies within 1.8–2.05. As known, by varying the methane to oxidant (O_2, H_2O, and CO_2) ratio in the feed gas it is possible to obtain a synthesis gas with H_2/CO molar ratio ranging from 3 to 1 [22].

The drawbacks suffered by the processes of partial oxidation with air consist in a high content (38–52 vol %) of nitrogen ballast in synthesis gas and the need in adding steam in the case of "fat" APG or in the case of other options aimed to maintain the H_2/CO ratio at the specified level.

Compared to steam or autothermal reforming, the material consumption and capital costs for the key APG processing stage in the case of air oxidation options are by a factor of 1.5–2.2 lower.

Moreover, with air as oxidant, the operating costs were reduced by 40–60% through rejected production of oxygen (US $ 40–60 ton^{-1}) and/or of demineralized water.

Research into direct synthesis of arenes from synthesis gas on a bifunctional Fischer–Tropsch catalyst was undertaken at Zelinskii Institute of General Chemistry, Russian Academy of Sciences, under supervision by A.L. Lapidus, Corresponding Member of the Russia Academy of Sciences, Dr. Sci. (Chem.), and A.A. Dergachev, Chief Scientist, Dr. Sci. (Chem.) [23], and later on by staffmembers of an Aromagaz Limited Liability Company subsidiary company. That work was financially supported by the Russian Foundation for Small Business Support in Science and Technology (project no. 9122, Start 09 Program).

A catalyst characterized by high activity (CO conversion by 97%) and selectivity with respect to formation of liquid hydrocarbons whose yield reaches 153 g m^{-3} (80% of the theory) at a high selectivity for *p*-xylene (55%) was prepared and patented (RF Patent application nos. 2009101523 and 2009102958, positive decisions). The liquid end products consist entirely of aromatic compounds, with the proportion of C_8–C_{10} hydrocarbons being 76%. However, because of the catalyst lifetime of tens of hours, this highly promising process of direct synthesis of arenes from synthesis gas cannot be recommended for commercial application as yet.

CONCLUSIONS

The discussion above suggests the possibility of development of highly profitable (IRR 25–28%) gas-chemical production facilities based on the use of the associated petroleum gas processing by the commercial technologies currently offered by domestic and foreign licensors. This will allow complete utilization of associated petroleum gas via processing into liquid and solid marketable products without formation of commercial quantities of dry lean gas.

As shown by viability studies, the investment attractiveness of the APG utilization projects discussed can be achieved with a reasonable choice of the end commercial product and the processed gas amount of no less than 300 million m^3 $year^{-1}$.

This does not eliminate the problem of viable gas-chemical processing of small (10–100 million m^3 $year^{-1}$) APG volumes. A solution to this problem can be found in the development of low-cost technologies for preparation of synthesis gas and its processing via small number of stages, e.g., to aromatic hydrocarbons.

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