

CURRENT PROBLEMS

ETHANOL AS A HIGH-OCTANE, ENVIRONMENTALLY CLEAN COMPONENT OF AUTOMOTIVE FUELS. Current Aspects of Use

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The principle of the action of antiknocks consists of preventing explosive decomposition of the products of pre-ignition oxidation of the fuel before normal combustion of the fuel blend begins. There are several theories that explain the essence of knock combustion. The most widely accepted one is the so-called peroxide theory.

At high temperatures where the ratio of the rates of formation of hydroperoxides and decomposition of peroxide radicals attains $\sim 10^{-4}$, products of decomposition of peroxide radicals and in the case of decomposition of the secondary radicals formed from *n*-paraffins, highly reactive aldehydes enter the flame front.

When ethanol and/or other oxygenates are incorporated, the antiknock value of automotive gasolines increases, since the heat of combustion of the fuel-air mixture decreases with an increase in the concentration of oxygen in the fuel, heat is removed from the combustion chamber more rapidly, and the maximum temperature of combustion decreases as a result. This makes it possible to increase the degree of compression of the fuel-air mixture and thus increase engine efficiency.

In the USA, the leading automobile companies – Ford, General Motors, and Daimler-Chrysler – recommend using oxygen-containing fuels, ethanol, for example. It does not pollute the atmosphere, has good performance characteristics, and is an excellent cleaning agent. In new cars, ethanol keeps the engine clean and in older cars, it strips pollutants deposited in the fuel feed system. The substances separated sometimes accumulate in the fuel filter and are removed by replacing the filter.

All alcohols adsorb water. The water condensate formed in the fuel feed system is absorbed by ethanol as it cannot scale off and freeze. For this reason, it is not necessary to add antifreeze to the fuel line in winter.

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Ethanol is a fuel for automobiles with engines of both old and new design. In internal combustion engines manufactured before 1969, the valve seats are unhardened, so that it can be necessary to replace the lead-containing antiknock in the fuel to prevent premature wear. Ethanol blends do not cause charring of the valve, since ethanol burns at a lower temperature than unleaded gasoline. This is also responsible for the use of pure alcohol as fuel in many high-performance racing engines.

Modern computerized autos have higher performance characteristics than those not equipped with computer systems when correctly used. Improved performance is attained by automatic correction of fuel feed when the operating conditions change or a new fuel is used.

Dehydrated ethanol containing a minimum of 99.5% basic substance has been most widely used as fuel. The positive properties of alcohol fuels are totally manifested when used in pure form. In converting a car to operating with pure alcohols, it is necessary to:

- increase the fuel tank capacity (to preserve the usual fueling run, since specific consumption of alcohol is much higher than for gasoline);
- increase the degree of engine compression ϵ to 12-14 for complete utilization of the high antiknock value of the fuel;
- readjust the carburetor for higher flow rates and a higher degree of leaning of the blend.

The advantages of alcohols are the high efficiency of operation and high antiknock value. The efficiency of the alcohol engine is higher than for the gasoline engine in the entire range of compositions of working blends. For this reason, the specific energy consumption per unit of power decreases. The amount of harmful emissions simultaneously decreases significantly.

The high antiknock qualities of alcohols are due to their predominant use in internal combustion engines with positive (spark) combustion. The low saturated vapor pressure and high evaporation heat of alcohols make it almost impossible to start carburetor engines at temperatures below 10°C.

To improve the starting qualities, 4-6% isopentane or 6-8% dimethyl ether are added to the alcohols, which ensures normal starting of the engine at an ambient temperature of -20 to -25°C . The engines are equipped with starting heaters for the same purpose. Additional heating of the fuel blend, with the exhaust gases, for example, is necessary in unstable operation of the engine at high loads due to the poor evaporation of alcohols.

Due to the difficulties listed above, use of pure alcohols is undesirable and it is better to add them to ordinary petroleum fuels in amounts of up to 30%.

Brazil, where ethanol has been used since 1939, has the greatest experience in use of fuel ethanol. Due to the high oil prices in the 1970s, the Brazilian government made a decision to manufacture autos that operate on pure ethanol to reduce the dependence on imported oil and create added value for sugar cane growers. Today more than 4.2 million vehicles in Brazil utilize ethanol as fuel. Approximately 40% of the autos operate on pure (100%) ethanol and the rest run on a blend of 24% ethanol and 76% gasoline.

Research on ethanol-containing fuel compositions has been conducted in Russia for more than 20 years. Formulas for ethanol-based additives are the result.

For example, a composition is proposed in [1] that includes low-octane gasoline and an oxygen-containing component in the form of the distillation product of a 1:0.8-1:1.3 blend of the head fraction of ethanol distilling at 78-79°C and fusel oil (95-102°C). The composition is inexpensive and has high physicochemical and performance characteristics. This additive is recommended for addition to gasoline in the amount of 10-14%.

A gasoline-based composition has been patented [2]. It is proposed for expanding the line of high-octane unleaded gasolines with improved environmental properties that reduce the amount of carbon monoxide and hydrocarbons in exhaust gases. The composition contains 5-15 wt. % ethanol additive which

includes, wt. %: 6-20% aromatic amine; 0.1-1.5% crotonaldehyde; 0.2-2% acetaldehyde; 0.5-1.5% water; 0.1-4% organometallic additive. N-methyl aniline or a mixture of toluidines is used as the aromatic amine.

Ethanol-based octane-boosting additives were created at VNII NP: VOKE with a stabilizer – fusel oils – and multifunctional LAZURIN. The specifications for these additives and for ethanol-containing unleaded automotive gasolines (TU 38.401-58-2444 – 99) [4], and technology for manufacturing gasoline – ethanol fuels and the instructions on using, storing, and shipping them were developed there.

An additive that includes high-performance antiknocks – an aromatic amine and organic derivative of manganese, and a mixture of oxygenates: ethanol, methanol, and methyl *tert*-butyl ether – is proposed in a patent [5]. In addition, a detergent whose presence is mandatory in automotive gasolines under European Union standards is contained in the additive.

A method for obtaining stable high-performance antiknock additives that allow reducing consumption of octane boosters in production of commercial gasolines has been patented [6]. The additive contains ethanol stabilized with C₃-C₅ aliphatic alcohols or ethers or the aldehyde-ether-alcohol fraction obtained from wood ethanol production wastes. It has a specific odor uncharacteristic of ethanol, which prevents mistakenly using it as drinking alcohol.

Experience in using ethanol fuels has revealed some of their drawbacks related to the difference in the physicochemical properties of gasoline and alcohol:

- high corrosiveness with respect to many construction materials;
- low heat value;
- negative effect on rubber and plastics (penetrates hoses and tight seals, which increases fuel losses to evaporation);
- separation in the presence of water;
- high saturated vapor pressure and consequently high probability of formation of vapor locks in the fuel system.

Most of these drawbacks can be easily eliminated. The corrosion rate incases with an increase in the water content, but up to a certain limit: maximally up to 0.6 g/(m²×h) at a 60 wt. % water content. The corrosion rate of copper M1 in ethanol is 0.4 g/(m²×h) at 85 wt. % water content. To improve the antiwear properties and reduce corrosiveness, it is recommended that a package of modifiers, including additives to improve self-ignition, a lubricant, and a corrosion inhibitor, be added to alcohol fuel.

AI95E gasoline containing 5-10% industrial ethanol (TU 38.302-15-02 – 94) was tested at AvtoVAZ. It was found that gasoline with a 5% ethanol content does not negatively affect industrial rubber items. In accordance with GOST R 51176, it is approved for production and use.

The ignition limits of the gasoline-ethanol blend are wider than for pure gasoline. Operation on lean blends is possible because of this. Despite the lower heat value, ethanol-containing fuel consumption increases insignificantly: by 5% on average. By selecting alcohol-resistant polymeric materials, fuel losses from evaporation can be eliminated.

Phase instability caused by the presence of small amounts of water and consequently the restricted reciprocal solubility of the components is the basic drawback of gasoline-alcohol fuels. This drawback can be overcome by adding the corresponding modifiers and stabilizers to alcohol fuels. The water content affects separation of alcohol gasolines to the greatest degree.

For ensuring the stability of these gasolines in production, storage, and use, it is necessary to: prevent water from entering them; use stabilizing additives, in other words, cosolvents that homogenize the

gasoline – water – alcohol system. It is also recommended that the alcohol be added to the gasoline immediately before delivery of the automobile.

The following have been proposed as stabilizers for gasoline – alcohol blends: C_3 - C_{12} aliphatic alcohols of normal and branched structure, phenols, alkyl acetates, ethers and esters, their organometallic derivatives, ketones, amines, surfactants, and glycols and their ethers, aldehydes, ketals, acetals, alkyl carbonates, carboxylic acids, and blends of these compounds.

Stabilizers prevent separation of alcohol-containing gasoline at temperatures from -40 to -23°C . Fusel oils that ensure homogeneity of the fuel at temperatures above -25°C are good and inexpensive stabilizers.

The ability of gasoline – ethanol blends to separate is a function of the composition of the gasoline and the alcohol and water content in the composition. The cloud point decreases with an increase in the content of aromatic compounds and alcohol in the gasoline. However, the water content is a much more important factor for these fuel blends.

At the beginning of the 1970s, the possible ethanol content in gasoline was investigated with a number of methods aimed at obtaining products. The possibilities of a suitable blend of gasoline and ethanol in the pipeline terminal are currently being carefully investigated.

ETHANOL DEHYDRATION TECHNOLOGIES

Ethanol itself, which initially contains some water, is the basic source of water in alcohol fuel. For this reason, dehydration of ethanol is the most effective method of reducing the water content in fuel. The main problem in dehydration consists of forming an azeotrope of ethanol with 4 vol. % water which cannot be removed by simple distillation.

The dehydration problem is solved by distillation methods (azeotropic, extraction, salt, and vacuum) and hybrid methods that combine distillation with separation, adsorption, and membrane separation. Pervaporation (evaporation through a membrane) – a process based on the difference in the rates of penetration of components through a polymeric material – is becoming increasingly important.

All methods of producing absolute alcohol can be divided into several types based on the use:

- low-temperature solid water-binding materials;
- liquid water-binding substances;
- azeotropism phenomena;
- solutions of salts that shift the azeotropic point (salt dehydration);
- phenomena of diffusion of vapors through porous membranes;
- vacuum.

The alcohol dehydration method with solid dehydrating substances has been used on industrial scales. Calcium oxide is the best known of the solid absorbents [7]. There are two opinions on the possibility of using it in the literature: for removal of large quantities of water and for post-dehydration for a water content of hundredths of a percent. However, this method is not widely used.

Glycerin is primarily used as a liquid water absorbent [8]. In using pure glycerin, alcohol of 99.2 vol. % strength is obtained, and with glycerin solutions of dehydrating salts (CaCl_2 , K_2CO_3), alcohol with 99.9-100 vol. % strength is obtained. However, this method, too, like the dehydration methods based on the different rate of diffusion of alcohol and water vapors through membranes and vacuum distillation, have not become widespread [9].

The azeotropic method of dehydration is of the greatest industrial importance. The dehydration method using salt distillation developed by L. L. Dobroserdov is also promising [10].

However, no optimum dehydration method that is simultaneously effective, cheap, environmentally save, and suitable for a wide range of moisture contents has yet been proposed. For this reason, the problem consists of selecting and improving an existing or creating a new optimum method.

Dehydration with zeolites in steady-state conditions. The essence of the method consists of adsorption of water by type NaX zeolites (pore size of 0.3 nm). These zeolites are used for dehydration as molecular sieves. The moisture removal mechanism consists of not only adsorption of water molecules on the active site of the zeolite but also filtration of the molecules through pores whose size permits passage of water molecules alone, separating them from the alcohol molecules.

The capacity of the zeolites for water is 18 wt. %. The problem consisted of obtaining alcohol with a different residual water content: 3.3, 3, 2.7, 2.5, and 2 vol. %. The amount of zeolites necessary for obtaining alcohol with a given water content was determined by calculation for each sample (50 ml). The samples were prepared as follows; the zeolites were added in the calculated amount to 50 ml of ethanol, and the samples were tightly sealed and left for 24 h. The alcohol was then separated from the water-saturated zeolites and the residual moisture content was determined. The losses of alcohol were 2-4 vol. %.

When zeolites were added to ethanol in the amount of 11.68, 10.29, 8.90, 7.51, and 6.12 g, the residual water content in it was 2, 2.34, 2.74, 3.22, and 3.25 wt. %. It follows from these results that dehydration of alcohol with zeolites in steady-state conditions is acceptable for obtaining alcohol of a given "purity" in a wide range of moisture contents. Subsequent regeneration of the zeolites by calcination saves on consumption of additional reagents.

This method can be considered a combined method, since it uses two processes: adsorption of water molecules on the active sites of zeolites and physical filtration through 0.3-nm micropores (the water molecule is 0.3 nm in size and the ethanol molecule is 0.4 nm). However, use of this method on the industrial scale is not expedient since dehydration is a periodic and very lengthy process (the cycle lasts for the order of one day).

This is due to the low diffusion rates of water to the outside of zeolites. In steady-state conditions, only the thermal motion of water molecules uniformly distributed in the entire volume of the alcohol, which is not large at room temperature, is the driving force of external diffusion.

We can say that continuous adsorption in the liquid phase is characterized by high rates. The kinetics of the process is limited by the internal diffusion rate, which is low due to the small pore size, comparable to the size of the molecules of the substances. For this reason, this method is not very efficient in small units. In addition, the lifetime of the zeolites in the continuous liquid-phase process is not completely utilized, since "breakthrough" begins before the water molecules reach the deep active sites in the zeolite.

Dehydration with zeolites in the vapor phase. The method consists of distilling the alcohol through a column packed with zeolites NaX with 0.4 nm pores. In contrast to the mechanism of dehydration in steady-state conditions, the mechanism of this method is based on adsorption alone. Selection of the type of zeolites is based on the ratio of their adsorption activity and selectivity.

Zeolites of the NaY type adsorb water most actively, but they also relatively actively adsorb polar ethanol, which increases losses of the target component. Zeolites NaX, which have a lower affinity for polar compounds, allow reducing competitive adsorption and increasing the selectivity of dehydration.

Dehydration is more efficiently conducted in the vapor phase. For a hydrophilic zeolite such as NaX, the active site – water bond is stronger than the active site – alcohol bond. The high vapor temperature weakens these bonds, so that primarily water is adsorbed.

The large pore size allows passing both water and alcohol molecules in them, which could cause competitive adsorption and thus reduce the life of the zeolite during dehydration and increase losses of the target alcohol. However, at the boiling point, the thermal motion of the molecules is significantly intensified, and since type NaX zeolites have a higher affinity for the polar water than for the less polar alcohol, desorption will predominate for ethanol in these conditions and only water will be adsorbed.

Several similar experiments which differed in the rate of passage of ethanol vapors through a column packed with zeolites were conducted. Each time the column was packed with new (regenerated) zeolite. The experiment was conducted with the following method: 50 ml of alcohol was placed in a flask and distilled through

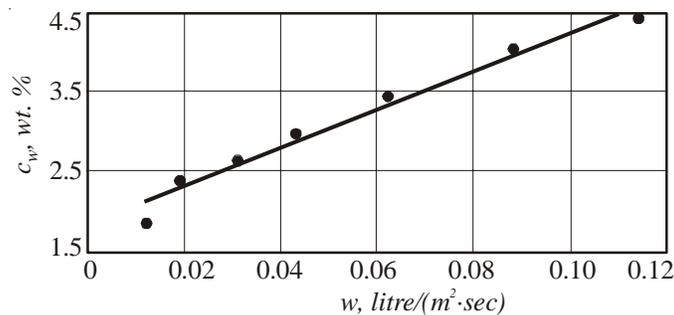


Fig. 1. Residual water content c_w as a function of the rate w of distillation of ethanol through zeolites NaX with 0.4 nm pores.

a column 3 cm in diameter at different rates (0.012-0.11 liter/sec×m²). The distillate obtained was analyzed for the residual water content. The zeolites were regenerated by calcining at 350°C for 4 h.

The results of the experiments are shown in Fig. 1. The dependence of the residual water content on the rate of distillation of ethanol through the zeolites is almost linear. In practice, it is necessary to consider another factor – the capacity of the zeolites, which determines the size of the equipment – the adsorbers and time between regenerations.

As a consequence, after selecting the distillation rate and volume of the zeolites (adsorber size), an efficient and flexible process for dehydration of ethanol by zeolites in the vapor phase, which can easily be implemented in industry can be obtained.

Dependence of phase stability on the concentration of ethanol in gasoline. Despite the fact that the proposed process for dehydration of ethanol is efficient, environmentally clean, and comparatively inexpensive, using it complicates production of ethanol-containing fuels. In world practice, dehydrated ethanol containing a minimum of 99.5% basic substance is the most common octane booster. However, dehydration of ethanol to this degree is not always required.

For this reason, it is important to determine the optimum residual moisture content in ethanol at which the phase stability of the composition, corresponding to the requirements of GOST R 52201 – 2004, is not perturbed. It will be different as a function of the quantitative ratio of alcohol and gasoline.

The cloud point with different volume contents of ethanol was determined to assess the mutual solubility of the components of the alcohol – gasoline composition [7]. A winter gasohol cloud point, equal to – 30°C at the production site, was accepted as satisfying the GOST.

The results of the evaluation are shown in Fig. 2. The stability of the compositions increase with an increase in the alcohol content, which is in agreement with the published data.

Ethanol actually does not require such a deep degree of dehydration even in the traditionally low concentrations. At a 10 vol. % ethanol content, the maximum acceptable with the active GOST, the residual water content can attain 2.5 vol. %, while dehydration is totally unnecessary for a composition containing 50 vol. % (and hardly greater than 40 vol. %) alcohol.

The level of ethanol consumption and production has increased significantly over the past 20 years due to the high performance characteristics and competitive price of this fuel. When ethanol obtained from renewable biomass is used, the global warming effect is partially compensated for as a result of gasoline consumption. Many countries are either engaged in large-scale production and consumption of ethanol or are instituting measures to stimulate expansion of its production and areas of application.

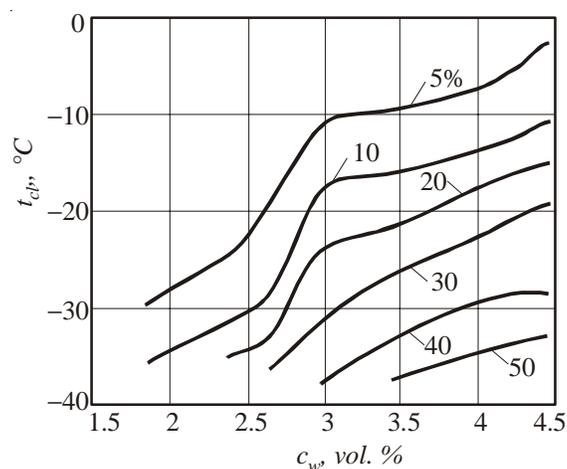


Fig. 2. Cloud point t_c of alcohol – gasoline blend as a function of water content c_w in alcohol for compositions with different alcohol contents (see figures on curves).

The introduction of new technologies will assist in reducing the environmental and monetary costs of ethanol production. Harmful emissions with auto exhaust gases decrease when it is used. Ethanol is a renewable type of fuel and for this reason has advantages that gasoline does not.

In many countries, the petroleum industry has had tax breaks and subsidies for many years. We can hypothesize that the costs related to pollution of the air and water can be totally applied to the total cost of gasoline in the very near future.

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TECHNOLOGY

CHARACTERISTICS OF CATALYTIC REFORMING WITH CONTINUOUS REGENERATION OF THE CATALYST

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The results of a pilot run of the LF-35/21-1000 reforming unit with continuous regeneration of the catalyst at LUKOIL – Nizhegorodnefteorgsintez Co. are reported. It was found that all of the blocks and units operate in accordance with the project requirements. Dependences that correlate the quality of reforming naphtha with its yield and the yield of hydrogen-containing gas and power consumption with the output of the unit were obtained.

Catalytic reforming naphtha occupies a leading position (52.8 vol. %) in Russia's gasoline stock (more than 30 million tons/year) [1]. This is due to catalytic reforming units with periodic catalyst regeneration, the base for production of high-octane components of unleaded automotive gasolines, as well as catalytic cracking naphthas, in all large oil refineries [2, 3]. The proportion of catalytic reforming and cracking naphthas is decreasing significantly in high-quality gasolines due to stiffening of the requirements for the content of benzene (less than 1 vol. %), aromatics (less than 35 vol. %), and olefins (less than 5 vol. %) [4].

The universal introduction of catalytic reforming in oil refinery (OR) manufacturing schemes is also due to the fact that hydrogen-containing gas (HCG) is the second target product of this process. The concentration of hydrogen in HCG is 75-93% as a function of modification of the process. Production of environmentally clean jet and diesel fuels is directly correlated with the presence of industrial hydrogen in the refineries, i.e., catalytic reforming units [5].

The basic trends in improving catalytic reforming are:

- increasing the efficiency of the catalysts;

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Table 1

Hydrotreating block operating indexes	By design	By regime	
		1 – 3	4 – 6
Output in feedstock, m ³ /day	–	2819–2900	3104–3709
Feedstock space velocity, h ⁻¹	4.8–8.1	5.3–5.42	4.24–7.03
HCG circulation ratio, nm ³ /m ³	60–150	87.6–113.75	80.33–146.3
Excess pressure, MPa			
at compressor outlet	–	3–3.16	3–3.16
circulating HCG (CHCG) in product separator	2.3–2.4	2.44–2.45	2.44–2.45
Temperature at reactor inlet, °C	285–343	320	320
Temperature drop over reactors, deg	–	From 0 to +1	From 0 to +11
Concentration of hydrogen in CHCG, vol. %	≥75	98–99.3	98–99.6
Content in feedstock, ppm			
sulfur	≤500	150–440	190–460
nitrogen	≤1	0.6–0.8	0.6–0.8

- revamping and retooling the units with a stationary bed of catalyst with a step with continuous regeneration of the catalyst;

- introducing units with continuous regeneration of the catalyst;

- improving process and heat- and mass-exchange equipment [6].

In 2004, LUKOIL – Nizhegorodnefteorgsintez Co. completed construction of the LF-35/21-1000 unit based on Platforming CCR UOP technology at a pressure of 0.35 MPa under a medium-term program for re-equipping and developing production.

After completion of construction and starting the unit up, studies were conducted to determine the optimum composition of the feedstock and target product, power consumption and real consumption of material and technical resources, to establish the correspondence of the real operating parameters with the rated parameters, to optimize operation of control systems, and to determine the cycle between repairs based on the results of operating compressor equipment in the different operating conditions of the unit.

The studies of the feedstock hydrotreating block were conducted for 138 days, the reforming block was investigated for 132 days, and the catalyst regeneration block was studied for 95 days. The feedstock load varied from 67 to 120 tons/h, and the catalyst circulation rate varied from 400 to 715 kg/h. The unit operated in six regimes.

The basic indexes of operation of the hydrotreating block are reported in Table 1. In all regimes, the operating conditions for the block corresponded to the rated conditions. The quality of the hydrogenation product satisfied the established requirements: maximum of 0.2 ppm residual sulfur content in hydrogenation product, 0.4 ppm nitrogen content. These data were obtained at a feedstock space velocity of 5.5–6 h⁻¹, hydrogen to feedstock circulation ratio of 120–140 nm³/m³, pressure at the compressor outlet of 3.1 MPa, and pressure in the 200 V₄ separator of 2.45 MPa.

The temperature at the bottom of the 200 V₆ stripping tower was 221–223°C, the pressure at the top of this tower was 0.92 MPa, and the reflux ratio was 30–40% (40–50 m³/h). The moisture content in the hydrogenation product was 7–8 ppm. Hydrogen sulfide was totally absent.

Table 2

Reforming block operating indexes	By design	By regime	
		1 – 3	4 – 6
Output in hydrogenation product, tons/day	–	2077–2200	2269–2700
Feedstock space velocity, h ⁻¹	0.97–1.95	1.29–1.47	1.33–1.64
HCG circulation ratio, nm ³ /m ³	1.95–7.65	1.84–5.4	1.84–5.4
Excess pressure, MPa			
at outlet from CHCG compressor	–	0.394–0.457	0.394–0.457
in 300 R4 reactor	–	0.312–0.35	0.312–0.35
in product separator	–	0.249–0.25	0.249–0.25
Temperature at reactor inlet, °C	≤548	494–518	494–526
Temperature drop over reactors, deg	–	224–282	224–282
Concentration of hydrogen, vol. %			
in CHCG	≥75	88.4–93.2	88.4–93.2
in HCG from unit	≥90	91.3–96.7	91.3–96.7
Content in feedstock, ppm			
sulfur	≤0.5	0.2–0.4	0.2–0.4
nitrogen	0.30–0.45	–	0.3–0.45
Weighted mean temperature in catalyst bed, °C	–	468–491	468–493
Coke content, wt. %			
on catalyst	3–7	3.47–5.72	3.47–5.72
same going from air consumption for regeneration	–	2.28–6.97	2.28–6.97
Coke formation rate, kg/h			
going from air consumption for regeneration	–	10–50	10–40
going from feedstock quality and process parameters	–	19–133	19–110
Amount of dust from catalyst, kg/day	–	2–15.5	2.2–12
Catalyst consumption, kg/day	21.768	0.2–13.34	1.59–12
Total amount of catalyst dust after startup, kg	–	2251.1	2323.8
Amount of added catalyst, kg	–	2200	2200
Octane number (research) of target product	90–103	94.7–101.1	96.1–100.8

The concentration of hydrogen in CHCG varied in a narrow range – from 98 to 99 vol. %, and the concentration of hydrogen sulfide varied from 500 to 600 ppm. Fresh HCG entered the hydrotreating block in the amount of 0.1 wt. % in feedstock. The dry gas (0.2 wt. %) was sent to the fuel system. The naphtha cuts distilling below the initial boiling point of the feedstock were removed from the unit in the amount of 14–20 tons/day at the beginning of the studies and 3 tons/day at the end.

The basic operating parameters of the reforming block over the entire duration of the studies are reported in Table 2. Feedstock was fed into the block in the amount of 85–120 tons/h and the ratio of hydrogen to feedstock was 3.1–6.9 mole/mole. In production of gasoline with an octane number of 96 and 101 by the research method (RON), the temperature in the catalyst bed was maintained at 503 and 523°C, and the total temperature difference between reactors was 243 and 270°C.

Table 3

Component	Content in HCG, vol. %			
	at beginning of cycle		at end of cycle	
	in 300V ₁	in 300V ₅	in 300V ₁	in 300V ₅
Hydrogen	92.6	92.6	92.8	94.6
Hydrogen sulphide	Absent			
Methane	1.6	2.72	0.87	1.92
Ethane	1.87	2.31	1.07	1.92
Propane	1.67	2.06	1.02	1.4
Isobutane	0.64	0.42	0.41	0.13
<i>n</i> -Butan	0.53	0.12	0.4	0.03
1-Butene	Traces	–	0.01	0.01
1-Isobutene	0.01	–	Traces	–
2- <i>trans</i> -butene	Traces	–	–	–
Isopentane	0.47	0.05	0.38	–
<i>n</i> -Pentane	0.21	0.02	0.19	–
ΣC_5	0.4	–	2.85	–

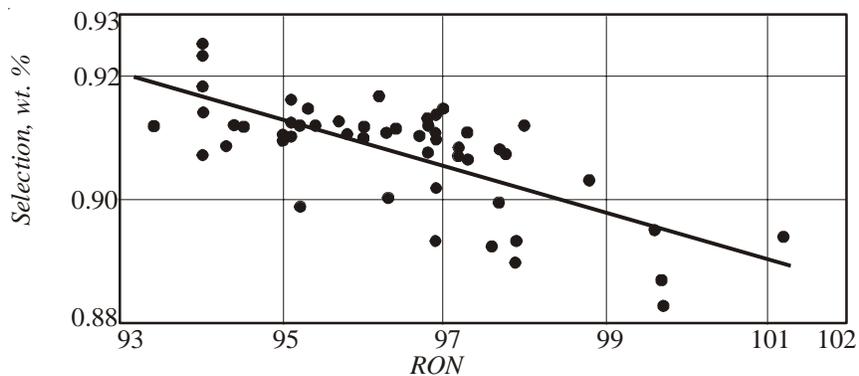


Fig. 1. Effect of the octane number (RON) of reforming naphtha on selection of catalyst.

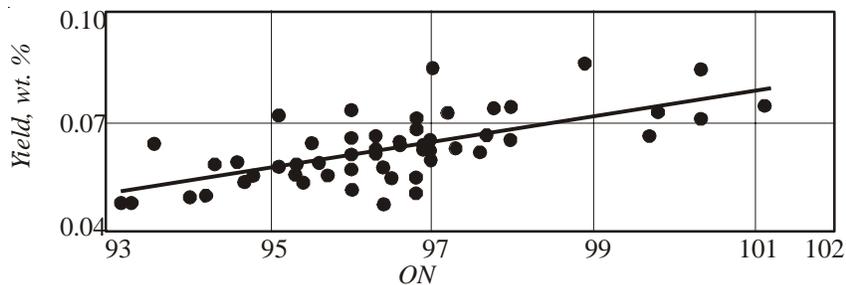


Fig. 2. Effect of the octane number (RON) of reforming naphtha on yield of HCG.

The real temperature at the reactor inlet was 3.5-8° lower than the calculated temperature. The moisture content of the CHCG entering the reactors varied within the limits of 10-15 ppm. The moisture content in the CHCG

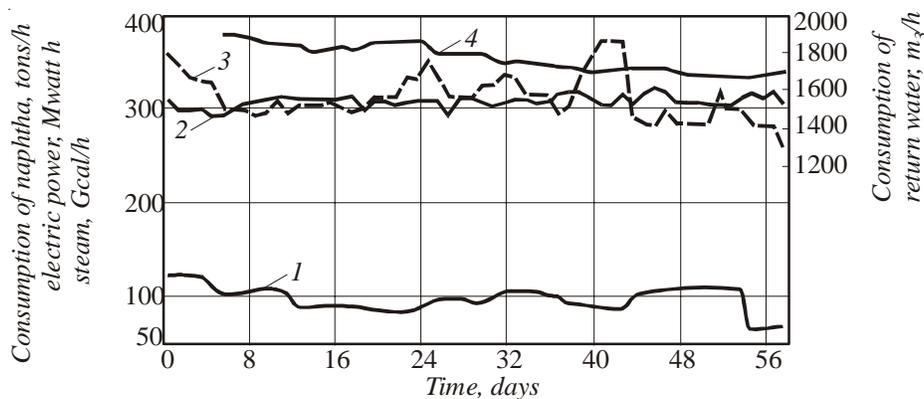


Fig. 4. Change in consumption of energy resources for reforming in time: 1) naphtha; 2) electric power; 3) steam; 4) return water.

$$y_3 = -0.000076x^3 + 0.010619x^2 - 0.338037x + 3.990720$$

where y_3 is the concentration of benzene in the target product; x is the initial boiling point of the reforming feedstock.

The consumption of energy resources and production of steam in the unit as a whole were constantly monitored during the studies (Table 4, Fig. 4). During the entire time, 0.09-0.27 Gcal/h of steam was taken from the LF-35/21-1000 for the needs of the enterprise.

Mathematical processing of the statistical data allowed establishing the dependences of the specific power consumption on the consumption of feedstock over the unit as a whole:

$$y_4 = 0.0003x^3 - 0.835x^2 + 6.37972x + 0.0053$$

$$y_5 = 0.0019x - 0.0023$$

$$y_6 = 0.001022x - 0.00023$$

$$y_7 = -0.0001x^3 + 0.0091x^2 + 1.0054x - 0.0056$$

$$y_8 = 0.1558x + 2.2055$$

where y_4 is the electric power consumption, kWh/ton; y_5 , y_6 are the production and consumption of steam, Gcal/(h·ton); y_7 is the reference fuel consumption, tons r.f./ton; y_8 is the return water consumption, m³/ton; x is the feedstock consumption, tons/h.

In addition, the real consumption of reagents and catalysts in comparison to the design data and licensor's recommendations were determined during the research. The requirements of the design plans and specifications and the real data on consumption for agents and catalysts, as well as the consumption standards established with generalized data on the real consumption of reagents and catalysts in consideration of the licensor's requirements are reported in Table 5.

The design indexes of operation of the waste-heat boiler, steam turbine, heat circuit, and heat-supply systems were confirmed during the run. To improve operation of the waste-heat boiler, a filter was installed in front of the deaerator for chemically treated water.

Comprehensive testing of the working capacity and safety of the electrical equipment was conducted. All systems and protective devices, automatics, alarms and controls, and control-measuring instruments for electrical units operating at voltage up to 1000 V and higher were tested. The operation of all equipment corresponded to the design parameters.

The dynamic equipment operated normally. The loads on the electric motors and the vibration indexes of the dynamic equipment did not exceed the values in the standards.

During the fixed run, 68 valve rings were replaced in the 300S2A-300S2S compressors. The analysis of the operation of these compressors showed that most of the breakdowns of the discharge valves took place in severe conditions of operation of the unit: at high loads (up to 155 m³/h) for feedstock and a high concentration of hydrogen in the HCG.

Prolonged operation of the compressors without shutting down for valve repairs was observed at a 91 vol. % and lower concentration of hydrogen in the HCG. This suggested that the discharge valves were not

Table 5

Reagent, catalyst	Consumption			
	by design	real		based on developed standard
		in October	in November	
Dichloroethane, kg/ton	0.0195	0.031743	0.023510	0.0254
Mixed natural mercaptans, kg/ton	0.0012	0.000363	0.000380	0.0005
Caustic soda (100%), kg/ton	0.0685	0.026021	0.020891	0.04
Dodigen 481 corrosion inhibitor, kg/ton	0.0011	–	–	0.0011
Grade A propane fraction, kg/ton	0.00297	0.034959*	0.0297*	0.00594
Hydrazine hydrate, g/ton of steam	0.0993	0.0920	0.0134113	0.0993
S-120 catalyst, kg/ton	0.002748	0.002748	0.002748	0.002748
Active aluminum oxide, kg/ton	0.02816	–	0.028160	0.02816
R-274 catalyst				
from dust collectors (dust + crumb), kg/day	21.7	2.7	3.385	10
support, g/ton	–	–	–	Standards reviewed
platinum + irreversible losses, g/ton	–	–	–	Same
Trisodium phosphate, g/ton steam	0.0462	0.00881	0.00762	0.0231
Molecular sieves, ton/day	0.0244	0.0244	0.0244	0.0244
Takeoff (wt. %) of catalyzate with RON of				
95	–	–	–	91.8
101	–	–	–	89
Energy resources for unit				
fuel, kg ref. Fuel/ton feedstock	–	–	–	90
electrical power, kwh/ton feedstock	–	–	–	135
steam, Mcal/ton	–	–	–	180
return water, m ³ /ton	–	–	–	24
Notes.	*Based on real feed time.			
	** After each load of catalyst			

designed for use in conditions of a high concentration of hydrogen: 91 vol. % and higher versus 76 vol. % according to the design.

The temperature at the compressor stage outlet increased significantly with an increase in the concentration of hydrogen, which caused rapid ring wear. Rings designed for severe operating conditions were selected to increase the operating time between repairs.

It was found during the tests that the technical state of the towers, capacitor equipment, pipelines and fittings, relief valves, dynamic equipment, and ventilation equipment was satisfactory and satisfied the design parameters of the manufacturing process.

The high working capacity of the breakdown protection system (BPS), pressure, flow, temperature, and level sensors in the process equipment was noted during the run.

All parts of the LF-35/21-1000 unit thus operate efficiently according to the design requirements. The mathematical dependences obtained allow predicting the quality and yield of the target product and determining power consumption for production of 1 ton of target product of a given quality. The standards for consumption of reagents and catalysts were refined and operation of CS, control-measuring devices and automatics, SS, and BPS was corrected as a result of the studies.

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**PETROLEUM COKE CALCINING UNIT. STARTUP AT
LUKOIL—VOLGOGRADNEFTEPERERABOTKA LLC**

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In 2003, LUKOIL Oil Co. made a decision to complete a two-furnace calcining unit on which construction had stopped in 1990 at LUKOIL – Volgogradneftepererabotka Ltd. (LUKOIL – VNP Ltd.). Until 1990, the unit was being constructed with Kennedy Van Saun technology (US) using imported equipment. Then two calcining furnaces (77.7×3.2 m), two afterburner furnaces (23×5 m), two coke coolers (12.5×2.3 m), and one waste-heat boiler were installed.

The unit was designed for calcining petroleum coke of isotropic structure and had a total output of 100,000 tons/year in raw coke for two furnaces when appropriately equipped with basic and auxiliary equipment.

In consideration of the change in LUKOIL Oil Co. priorities, it was decided to finish building and revamp the unit to increase the output to 280,000 tons/year in raw coke. The feedstock was changed: instead of coke of isotropic structure, it was decided to calcine “ordinary” coke from the operating delayed coking units at LUKOIL – VNP Ltd to obtain calcined coke for production of anode products in the aluminum sector.

The bid for developing the technology and equipment for implementing the project for completion of construction and revamping was won by the State Unitary Company RB Petrochemical Processing Institute (RB PPI SUC) and the general project engineer was LUKOIL – Rostovneftekhmproekt Co.

The project was to be executed in three stages. The first stage consisted of completing construction and revamping one line to attain output of 100,000 tons/year with respect to raw coke in accordance with the output of the waste-heat boiler constructed according to the initial project. The second stage would include completion of construction and revamping of the second line and construction of a new waste-heat boiler to attain output of 140,000 tons/year with respect to raw coke. In the third stage, the output of the first line would be brought to 140,000 tons/year in raw coke and the output of the active waste-heat boiler would be increased or another one would be built.

RB Institute of Petrochemical Processing State Unitary Enterprise. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 5, pp. 13 – 16, September – October, 2007.

To ensure the assigned (by 2.8 times) increase in output, RB PPI SUC developed the corresponding calcining technology and detail designs for a series of basic and auxiliary equipment.

The experience from many years of successful operation of the petroleum coke calcining unit at Sibneft' – Omsk OR Co., , designed with RB PPI SUC technology, was taken into account in developing the process technology [1]. The experience of foreign firms and experience in operating calcining units with Kennedy Van Saun Co. technology at Fergansk, Krasnovodsk, and Gur'evsk OR were also taken into consideration. RB PPI SUC accumulated great experience on updating the individual parts and equipment in startup and operation of these units [2-6].

The basic aspects of the petroleum coke calcining technology at LUKOIL – VNP Ltd. satisfy the basic requirements and in comparison to the technologies used in the RF, CIS, and at many foreign companies, is sufficiently complete. A diagram of the process is shown in Fig. 1.

The following problems remained unsolved in the first stage of revamping the first line due to the undefined possibilities of efficiently utilizing the individual types of equipment:

- transporting the raw coke to the calcining furnace; the initial design solutions do not ensure feeding coke of uniform quality due to segregation in “bunkers;”
- adapting the calcining furnace parameters to the conditions for calcining regular coke;
- treating stack gases to remove dust and sulfur dioxide.

The design of the *calcining furnace* was left unchanged in the first stage.

The length of the *afterburner furnace* was increased to increase the residence time of the coke dust for more complete combustion. The units for feeding in air for burning coke dust and combustible volatiles were updated. New technical solutions were aimed at intensifying mass exchange between stack gases and air. Feed of

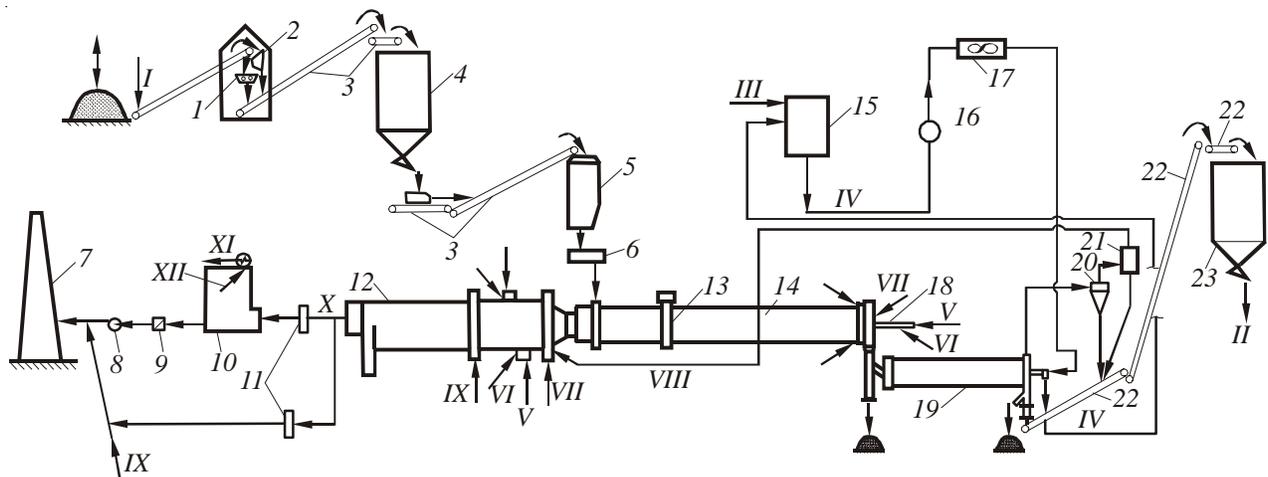


Fig. 1. Diagram of the first line of the petroleum coke calcining unit: 1) crusher; 2) sieve; 3) raw coke conveyor; 4) crushed coke storage bunker; 5) loading bunker; 6) weighing batcher; 7) smoke stack; 8) exhaust-gas fan; 9) damper; 10) waste-heat boiler; 11) guillotine gate; 12) afterburner furnace; 13) drive; 14) calcining furnace; 15) cooling water tank; 16) cooling water circulation pumps; 17) air cooler; 18) burner; 19) calcined coke cooler; 20) cyclone; 21) filter; 22) calcined coke conveyor; 23) calcined coke storage bunker; I) raw coke; II) calcined coke; III) chemically treated water; IV) circulating chemically treated water; V) fuel; VI) primary air; VII) secondary air; VIII) aspirated air; IX) diluted air; X) stack gases; XI) steam; XII) boiler water.

aspirated air from the calcined coke cooler to the afterburner furnace through the air inlet was organized. This solution eliminates discharge of coke dust that “gets through” the dust removal system with the aspirated air.

The *coke cooler* was replaced by a new cooler made at Uralkhimmash Co. Its design was developed by RB PPI SUC and is protected by RF patents. In many characteristics, the new cooler has advantages over the domestic and foreign analogs. The main advantage is the longer warranty – a minimum of ten years, versus a minimum of two years for the analogs. In addition, the cooler is distinguished by high efficiency of heat removal, compactness, low water consumption, and accessibility for repairs of the basic design elements.

The unit was equipped with a new *part for oiling the calcined coke* to eliminate dust. The oiling technology and mixer with helical contact devices were developed by RB PPI SUC and have been patented. The mixer eliminates grinding of the calcined coke, in contrast to the screw mixers usually used in world practice. The dust suppression efficiency attains 95-98%.

RB PPI SUC developed *dual valves – air locks* for the raw coke input devices and calcined coke discharge devices. They ensure operation of the unit at high output with minimal inflow of air.

All parts and equipment not ensuring high output were replaced by new Russian equipment.

The unit was equipped with modern process monitoring and control equipment. The working design and design of the *control system for automation and monitoring of the operation* of the calcining unit were developed by Kvantor Engineering Co. This system included two automatic control blocks.

One of them controls operation of the calcining and afterburner furnaces, calcined coke cooler, stack gas utilization system, auxiliary fuel preparation and intraplatform communications systems, and the other controls operation of the conveyer lines, raw and calcined coke bunkers, systems for loading raw coke into the calcining furnace and loading calcined coke into railway cars.

Each block is separated as a subsystem which allows synchronizing control and regulating processes of different intensity such as: loading coke into silos, loading coke into the calcining furnace, utilization of stack gas heat in the waste-heat boiler, control of the furnace burners, etc.

The original design solutions were used for monitoring operation of the calcining furnace, calcined coke cooler, oiling device mixer, and conveyor speed. Contactless inductive proximity sensors eliminated use of complicated mechanical devices. Due to the high degree of protection of their jackets, the system was sufficiently reliable, especially in conditions of dust on the conveyors.

To measure the coke level in the bunkers, *radar level gauges* with special high-strength cable wave guides were used and radio-isotope devices were used as level alarms.

High-temperature optical pyrometers are installed where the calcined coke comes out of the furnace to monitor the temperature of the furnace lining and the temperature in the fuel combustion zone by a contactless method. To prevent formation of a coke dust coating on the lenses of the optical pyrometers and optical flame alarms, a system for blowing compressed air through is provided.

The temperature, vacuum, content of oxygen and carbon monoxide in the stack gases are monitored along the entire process line (calcining furnace, afterburner furnace, including the pipe for taking off stack gases). This allows regulating coke calcining, and utilization of the heat liberated with the stack gases by increasing-decreasing feed of fuel to the burners, feed of air to the furnaces, the rotation rate of the body of the calcining furnace, feed of raw coke into the calcining furnace, and other parameters. The quality of the calcined coke and the savings of fuel and electricity, respect of environmental standards, etc., are ensured as a result.

The number of instruments and cable lines was reduced and processing of the results of measurements was simplified as a result of using multiparameter devices in the liquid fuel, gas, steam, air, nitrogen, and water lines.

A weighing batcher with a separate control block installed in the operator's premises was used for feeding the raw coke into the calcining furnace. The process of loading the coke into railway cars and then weighing them was automated.

With respect to the degree of automation, the LUKOIL – VNP Ltd. calcining unit is *one of the most up-to-date. The operator of the unit controls all of the basic operations and process parameters. Video observation* of the movement and granulometric composition of the raw coke on the weighing batcher belt is provided.

Protections and blocking for emergency situations are implemented in the design: presence of gas, failure of the basic calcining furnace and calcined coke cooler drives, pumps, sudden shutdown of one or more conveyors, etc.

The automated control system for manufacturing processes (ACSMP) and accident prevention (AP) are implemented with Invensys equipment. *Algorithms for controlling and locking the unit were developed with RB PPI SUC specifications.* Screen molds, FID-regulation blocks, etc., were executed in special SCADA editor routines – the I/A Series system.

The unit went on line in August 2005 – two months after work to put it into operation began. The output attained: 12.5-13.5 tons/h in raw coke, corresponds to the annual output of the first line of 94-101,000 tons/year, i.e., the rated output planned for the first stage of revamping.

Despite the long time (more than 15 years) the assembled basic and auxiliary equipment had stayed on open platforms and the unassembled equipment had been stored in warehouses, there were no serious problems with startup and operation. The inspections performed by the plant's technical service, reconditioning, and screening of broken auxiliary equipment allowed avoiding serious problems with equipment "failures." The problems that arose were quickly solved by plant management, specialists from RB PPI SUC, LUKOIL – Rostovneftekhimproekt Co., unit personnel, and the plant's technical service.

In April 2007, after 20 months of operating the unit, concrete results were obtained. On the whole, it operated satisfactorily.

The typical coke calcining regime satisfied the standards of RB PPI SUC specifications:

Output in raw coke, tons/h	12.5-13.5
Calcining furnace body rotation rate, min ⁻¹	1.045-1.25
Temperature, °C	
calcining furnace lining in combustion zone	1222-1237
stack gases	
coming out of calcining furnace	781-839
coming out of afterburner furnace	1021-1085
entering waste-heat boiler	813-897
coming out of waste-heat boiler	271-278
cooling water in circulation cooling system	
entering calcined coke cooler	38-46
coming out of calcined coke cooler	56-74
Oxygen content in stack gases coming out of afterburner furnace, vol. %	5.5-6.5
Output of steam in unit (flow from unit), tons/h	12-13.4
Parameters of steam	
temperature, °C	257-262
excess pressure, MPa	0.085-0.093

The quality of the calcined coke (see Table 1) satisfies the requirements of the aluminum sector for coke used in production of calcined anodes. The slightly high content of dust particles in the calcined coke is due to the high content of fine and powder (less than 1 mm) particles in the raw coke.

The problems that arose in getting the unit up and running were basically due to adapting the individual kinds of equipment to the conditions of operating at the new output, 100,000 tons/year, and in some cases, to use of equipment designed for the high output of 140,000 tons/year (after the third stage of revamping): the fans for feeding air into the afterburner and calcining furnaces, exhaust-gas fan, etc.

Let us analyze the efficiency of operation of the individual types of equipment in the unit operating period examined.

Calcining furnace. At output of 9-12 tons/h in raw coke through the compacting unit gap on the butt joint between the calcining furnace and the afterburner furnace, it operates satisfactorily, while at higher output (12.5-13.5 tons/h) the coke pours out through the compacting box. The cause is formation of a “hill” of coke in the loading zone into the furnace by the hopper feeder.

The hill is converted into a “springboard” for the coke to slide down, especially large particles to the side of the compacting gap. Narrowing of the furnace’s smoke-flue space above the “hill” increases the velocity of the stack gases and entrainment of coke dust particles. The small slope (1°11’) of the furnace and low rotation rate (0.522-1.045 min⁻¹) of its body cause the coke to be “held” in the loading zone and move slowly to unloading.

These furnace characteristics are defined by the initial design, based on the conditions of calcining coke of isotropic structure – low heating rate and long residence time (5 h) of the coke in the furnace. The existing calcining furnace is not adapted to the conditions of calcining ordinary coke for the aluminum sector at an optimal furnace residence time of 1.5-2 h. This problem must be solved. Due to spilling of the coke through the gap in the butt joint between the calcining furnace and the afterburner furnace, the losses are increased as a result of entrainment of coke dust and even large particles of coke into the afterburner furnace and problems are created with transport of the spilled coke.

RB PPI SUC and Uralkhimmash Co. performed calculations and issued recommendations on increasing the maximum rotation rate of the furnace body from 1.045 to 1.25 min⁻¹. As a result of implementing this recommendation, spilling of coke at output of 12.5-13.5 tons/h decreased significantly. Nevertheless, the problem persisted. To accelerate removal of coke from the loading zone, RB PPI SUC proposed a technical solution with screw thresholds which will be tested in the very near future. A more efficient technical solution is possible in the future – increasing the slope of the calcining furnace’s body, which will ensure output of 140,000 tons/year in raw coke.

Table 1

Indexes	Coke	
	raw	calcined
Content, wt. %		
total moisture	7–10.5	–
volatiles	8–10.9	–
total sulfur	1.4–1.6	1.4–1.6
Ash content, wt. %	0.05–0.44	0.3–0.6
Real density, g/cm ³	–	2.06–2.09