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CATALYSIS IN PETROLEUM  
REFINING INDUSTRY

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## Prospects for Conversion of Refinery Gas to High-Octane Oxygen-Containing Components of Motor Fuels

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**Abstract**—Prospects for conversion of refinery gas to high-octane components of motor fuel were discussed. The feedstock of the Russian petrochemical complex can be expanded by introducing light hydrocarbons—nonmarketable refinery waste products—in the production of ecologically safe high-octane components of gasoline based on *tert*-butanol and isopropanol. A series of articles in the field of related applied research and experimental developments were announced.

**Keywords:** refinery gas, high-octane components, isomerization, selective oxidation, dimerization, metathesis of olefins, hydration of olefins

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### INTRODUCTION

Today Russia faces the task of increasing the petroleum refining efficiency from 72% to 92% by the year 2030. This problem will be mainly solved by scaling up the use of catalytic cracking processes. These processes account for 36% of the total primary oil refining in the United States and only 6 or 7% in Russia. The planned scaling up of catalytic cracking in Russia's refining will inevitably be accompanied by an increase in the production of hydrocarbon gases (HGs). In general, 5–20 wt % of petroleum transforms into HGs, and their rational use remains an open question. Reducing the resources of light oil and the transition to the use of its heavy grades as a feedstock will also lead to an increase in the yield of HGs. In the nearest future, the startup of new cracking and hydrocracking units is expected to lead to a two- or threefold increase in the production of HGs.

The main problem in converting the refinery HGs into more valuable products is the necessity of their preliminary separation into fractions, which increases the cost of the final product. But even after fractionation, not all the components of HGs can find effective application. Unlike olefins, light alkanes, which constitute a significant part of refinery gases, are usually burned to produce heat.

Table 1 shows the typical annual balance of waste gases of Gazpromneft–Moscow Oil Refinery over the last five years as an example. The ethane–ethylene fraction is unsalable, and the *n*-butane fraction

can be sold only partially, after mixing with propane as a propane–butane fuel. The total annual volume of the fractions is ≈63.5 thousand tons for ethane–ethylene and ≈76 thousand tons for *n*-butane including waste butane and butane sold as a low-margin product (propane–butane mixture). By the end of 2018, it is planned to increase the production of hydrocarbon gases from 174 to 259 thousand tons per year due to modernization of production.

According to the Climate Doctrine of the Russian Federation, by the year 2020 it is planned to reduce greenhouse gas emissions to no more than 75% of the 1990 level. The reduction will be mainly achieved due to the improvement of the quality of car fuel and fuel efficiency. According to the estimates of the International Energy Agency (IEA), World Business Council for Sustainable Development (WBCSD), and International Automobile Federation (FIA), the average consumption of motor gasoline per 100 km of run will decrease to 5.5–6.0 L by 2020 and 4.5–5.0 L by 2025–2030. It is impossible to achieve this result without increasing the degree of fuel compression in the engine, which requires the use of automobile gasolines with an octane number of at least 95 RON units<sup>1</sup>. The use of efficient ecologically safe octane-raising additives, as well as high-octane gasoline components corresponding to Euro-5 and Euro-6, will improve the environmental situation in the cities of Russia and

<sup>1</sup> RON is the octane number measured by the research method.

**Table 1.** Waste hydrocarbon gases at Gazpromneft–Moscow Oil Refinery

Name	Amount, t/year
Ethane	50199
Ethylene	13364
Propane	61485
<i>n</i> -Butane	23665
Isobutane	22863
Propylene	2792
<b>Total:</b>	<b>174368</b>

allow the product of higher level of processing to enter the foreign motor fuel markets.

A comprehensive solution of the above two problems (effective use of HGs and production of high-octane gasoline) may be the creation of a technology for processing the refinery HGs into environmentally friendly components of motor fuel with high RON. Taking into account the composition of the refinery HGs (Table 1), emphasis should be laid on the processing of the ethane–ethylene, *n*-butane, and isobutane fractions. These fractions have not found an equivalent market and are used today mostly as fuel gases, which are sold on the market at prices comparable to those of the crude oil and natural gas.

#### POSSIBLE TECHNOLOGICAL SOLUTIONS

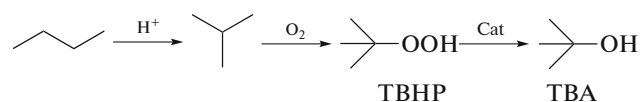
A promising final product of the processing of butane fractions is *tert*-butyl alcohol (TBA); the product of the processing of the ethane–ethylene fraction is isopropyl alcohol (IPA). These alcohols are well miscible with other components of gasoline and are environmentally safe. Importantly, their use as a component of motor fuel in amounts from 7% (TBA) to 10% (IPA) is allowed by the Technological Regulations of the Customs Union TC 013/2011 and does not require additional certification. Alcohol additives are used for more complete combustion of fuel and reduction of hazardous emissions of cars [1]. The antiknock properties of TBA (RON 113) are close to those of methyl *tert*-butyl ether (MTBE, RON 116), but TBA and IPA have higher boiling points, which increases the stability of fuels based on them [2]. Compared to ethanol used in the United States and Europe, IPA and TBA have higher calorific efficiency, which is important for more complete utilization of engine power.

It should also be taken into account that in advanced countries, the use of MTBE as a high-

octane additive is gradually rejected because of its adverse effects on the man and environment. In the United States, the use of MTBE in gasoline was banned at the federal level in 2006. In the EU countries, despite the absence of legislative restrictions, the consumption of MTBE is gradually declining in favor of ethanol and ETBE. In view of these world trends, prospects for further wide use of MTBE in Russia are highly questionable.

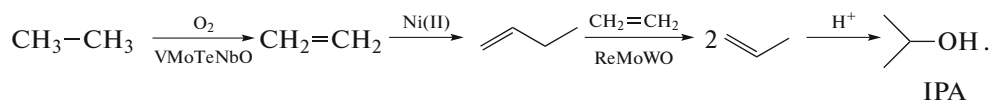
The overall production of high-octane gasoline in Russia reached  $\approx 15$  million tons in 2016. According to the technological regulations of the Customs Union, the oxygen content in high-octane gasoline should not exceed 2.4 wt %, which corresponds to 1.67 million tons of TBA and is comparable to the volume of modern production MTBE in Russia (1.38 million tons in 2015). If we consider the possibility of replacing MTBE by TBA and IPA, then we can assume that the annual demand for TBA and IPA will be  $\sim 1.7$  million tons in the coming years taking into account the renewal of the car fleet and prospects of growing of demand for high-octane gasoline. Therewith, the maximum volume of the product will be limited by the resources of the butane and ethane–ethylene fractions, which are quite sufficient,  $\sim 1.8$ – $2.0$  million tons per year.

**The conversion of butanes into TBA** can be performed in two stages:



At the first stage, the *n*-butane fraction is isomerized into isobutane. A preliminary study showed that the acid-catalyzed isomerization of *n*-butane into isobutane can be performed in a low-temperature mode (150–160°C) at a pressure of 2.3–2.5 MPa using a highly effective heterogeneous catalyst—palladium-promoted sulfated zirconia [3]. At the second stage, TBA may be obtained by direct oxidation of isobutane. *tert*-Butyl hydroperoxide (TBHP) formed in the oxidation of isobutane at a temperature of 120–140°C and a pressure of up to 3 MPa decomposes into TBA in the presence of a catalyst [4]. As is known, TBA that is suitable for use as a high-octane component forms as a byproduct in Lyondell and Huntsman processes for the production of propylene oxide, which are based on the oxidation of isobutane with oxygen [5]. Note that when TBA is prepared by hydration of isobutylene, it is obtained as an azeotrope containing 12% water, which makes it impossible to directly use it as a component of motor fuel.

**The conversion of ethane and ethylene into IPA** can be performed in four stages:



At the first stage, the ethane–ethylene fraction undergoes highly selective oxidative dehydrogenation on multicomponent oxide catalysts at 400–450°C and 0.1–0.2 MPa [6–8]. The resulting ethylene is further subjected to catalytic dimerization to form a mixture of butenes, in which 2-butene is dominant [9, 10]. Then cross-metathesis of ethylene and 2-butene on heterogeneous catalysts (Re, Mo, and W oxides) is performed, resulting in the formation of propylene. Propylene produced in this way does not contain a propane impurity, and the propylene selectivity is close to quantitative [11, 12]. At the final stage, propylene undergoes hydration at temperatures of 140–160°C and a pressure of up to 10 MPa to give IPA, which can be used, along with TBA, as an octane-raising component of gasoline.

Importantly, all of the above-presented technological solutions are based on environmentally safe catalytic processes. The proposed approaches are quite universal and can be used to solve the problems of qualitative conversion of saturated refinery gases not only into octane-raising oxygen-containing additives, but also into other valuable petrochemical products. In the above processes for conversion of the ethane–ethylene and *n*-butane fractions, the intermediate products are 2-butene, propylene, and isobutane, which have a wide range of applications and can be forwarded to the production of methyl ethyl ketone, polypropylene, alkylate, and other valuable derivatives. The final product of conversion of the *n*-butane fraction—TBA—can be used to prepare isobutene, methyl and ethyl *tert*-butyl ethers, isoprene, and isoprene rubbers. In addition, IPA and TBA of higher degree of purification can be used as individual commercial products. All these products are in demand on the market, which increases the competitiveness of the proposed solutions and production flexibility and creates opportunities for its further development.

The proposed technological solutions for processing refinery gases into corresponding oxygenates are based on energy-efficient transformations, which is their important competitive advantage.

It should be noted that oxidation has not been used for the production of fuel components. There were only a few publications on the oxidation of individual components preliminarily isolated from refinery gases to obtain individual petrochemical products. The new approach opens up wide opportunities for scientific and technical research and patenting the results for legal protection.

## CONCLUSIONS

The development of new environmentally safe methods for conversion of refinery gases into high-

octane components of gasoline will help to increase the flexibility and profitability of oil refineries in Russia. The new competitive technological solutions will lead to reduction of combustion of refinery gases due to the production of high-margin products from these gases, the creation of new ecologically safe high-octane motor fuel components (RON > 100), and expansion of the feedstocks and component base for the production of gasolines and petrochemical products.

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