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Development of new catalytic processes for processing petroleum feedstock

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Abstract: Currently such factors as the use of heavier feedstocks, permanent strengthening of requirements to oil and gas product quality, introduction of technical regulations for oil products, which, in turn, necessitate the development of new technologies and catalysts, have a great influence on the global oil-refining and petrochemical industry development. Recently, a special attention is given to the development of new catalysts and processes for producing middle distillate fuels suitable for cold and arctic climatic conditions. Catalytic hydrodewaxing and isodewaxing processes are the most efficient in this field. Research into controlling a functional structure of catalysts and creation of catalytic systems based on zirconium dioxide modified by tungstate anions are of outstanding interest. The trend of the use of heavier petroleum feedstocks and the need to improve the oil conversion level demand will be based on destruction of high-molecular-weight compound structures with producing light and middle cuts. So, the most important processes for heavy oil residue conversion are those enabling to control transformations of resinous-asphaltenic materials by using nanoscale catalytic systems. One of the examples of the industrial implementation of technologies using suspended catalysts is the hydroconversion process implemented currently at AO TANECO (lisencer: TIPS RAS; general designer: OAO VNIPIneft).

Keywords: catalysis; chemistry; Mendeleev XX.

Alteration in the global economic situation for recent two years resulted in major modification of the global energy complex structure. We observe a growth of the consumer number in Asia which induces the demand for petroleum products. A slight growth of liquid hydrocarbon consumption will be concentrated in the transport sector of developing countries. In these circumstances some excess capacities are observed; also, new capacities put into operation in the Middle East and Asia lead to a global excess of petroleum products in the market. Global problems of the oil industry associated with hydrocarbon price drop are getting worse for Russia due to financial sanctions, weakening of the rouble and changes in fiscal policy.

At the same time, the development of oil-refining and petrochemicals industries worldwide is currently affected by above-mentioned factors, use of heavier feedstock, its worsening quality, composition changing, and permanent toughening of the requirements to products of oil refining and gas processing. The above-listed factors lead to the necessity of developing new technologies and catalysts, on the one hand, and to the modernization and the improvement of operational efficiency of existing process units and plants, on the other hand.

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It should be noted that there is a limited number of revolutionary innovation technologies implemented in the industry plants. The main modernization elements are developments connected with the improvement of the existing technologies and catalytic systems, optimization of heat transfer, improvement of control systems and energy performance of individual process units and a plant as a whole. A special attention is taken to the development of new catalysts since at the current stage of oil-refining technology development catalytic processes permit to obtain products satisfying environmental and operational requirements and to implement processes of deep conversion of petroleum feedstock.

According to [1], catalytic processes can be divided into thermal catalytic processes including isomerization, catalytic reforming and catalytic cracking, and thermal hydrocatalytic processes including hydrotreating, hydrogenation and hydrocracking. Special mention should go to the group of catalytic processes for processing gaseous feedstock; currently, among these processes the most interest is attracted to alkylation, oligomerization and isomerization.

The switchover to production of gasolines to meet the requirements of Class 5 set a number of tasks aimed at creation of a gasoline combination of a given composition and properties.

Injection of a catalytic isomerization product into gasoline compositions as a component allows for significant improvement of the environmental and operational fuel performance, namely, increasing the octane numbers of the light portion of the gasoline, reducing benzene content and total aromatics content, and equalizing the gasoline octane numbers throughout the whole mass of evaporated fuel. There are several types of isomerization technologies in the global oil-refining industry using various catalytic systems: zeolite systems, chlorinated alumoplatinum systems and oxide systems based on the sulfated zirconium oxide. Recently, the most common are the last two catalyst types operable at low temperatures. This is due to the fact that these catalysts permit to obtain the isomerization product having a high octane number (RON 88–93). Among Russian technologies, it worth to mention Isomalk-2 technology developed by PAO NPP Neftekhim. The Isomalk-2 technology is the advanced technology for isomerization of light gasoline fractions. A distinguishing feature of this technology is the use of oxide sulfated catalyst SI-2 which, firstly, assures running of the process in a low-temperature area from 120 to 180 °C being thermodynamically favorable for the isomerization of paraffins, and secondly, has high stability to catalytic poisons (water, sulfur and nitrogen). The characteristics of the isomerization catalysts in comparison with foreign analogues are given in Table 1 [2].

PAO NPP Neftekhim is successfully developing n-butane isomerization technologies (Isomalk-3); a process unit based on this technology was built and put into operation in China in 2015. In the same country, it is planned to build another two process units using Isomalk-3 technology in 2017. At present, PAO NPP Neftekhim is launching on the market a new technology Isomalk-4 that allows for isomerization of C_7 and has no industrial analogues in the world. Recovery of the 70–105 °C cut from the reforming feedstock and producing an iso-component with the octane number over 80 enable to improve the efficiency of the production of high-octane Euro-5 motor gasolines.

Table 1: Performance comparison of the Isomalk-2 isomerization catalyst SI-2 and its foreign-produced analogues.

Property	**Low-temperature isomerization**			
Process	**Penex**	**Axens**	**Par-Isom**	**Isomalk-2**
Company	UOP (USA)	Axens (France)	UOP (USA)	NPP Neftekhim
Catalyst	I-82, I-84	IS 614A	PI-241	SI-2
Temperature, °C	120–180	120–180	140–190	120–180
Pressure, MPa	3.0–4.0	2.0	3.2	2.5–2.8
Space velocity, h^{-1}	1.5	2.0	2.5	2.5–3.5
Catalyst	Pt on chlorinated Al_2O_3		$Pt/ZrO_2\text{-}SO_4^{-2}$	
Mole ratio $H_2:CH_4$	0.5:1.0	0.5:1.0	2.0:1.0	2.0:1.0
Isomerization product yield, % (vol.)	99	–	97	98
RON per pass	83–86	84–85	81–83	82–84

Using high-strength acids in the alkylation process causes technological and ecological problems. The process is mainly developing in two directions: development of new process equipment and development of new catalytic systems. The first direction is represented in Russia by a technology developed by the RAS group using a jet reactor. The main distinguishing feature of this technology against the existing analogues is the significant increase in a stable catalyst service life at the expense of arranging a special state in the reaction zone of vapor and liquid mixture of feedstock and reaction products in a film mode, i.e. so-called “structured” alkylation. The second direction is development of the technology of solid acid alkylation. The domestic technology of sulfuric acid alkylation using solid catalysts is ready to pilot tests. This technology was developed by RAS A.V. Topchiev Institute of Petrochemical Synthesis (TIPS) and is economically competitive against the existing liquid-acid alkylation technologies. The proposed structured-mode reactor design in combination with zeolite-containing catalysts provides for obtaining products that surpass conditional alkylation products in terms of quality. The key element of the process is a special system for supply of vapor and liquid mixture of feedstock in a film mode. As a result, a three-phase mode of streams participating in the reaction. A size of the film phase of the feedstock that contacts with the heterogeneous catalyst surface does not exceed 50–1000 nm. The obtained product is characterized by a low sensitivity (i.e. a difference between RON and MON), does not contain olefins, aromatics and benzene, and has low sulfur content [3].

In Russia, reformate, i.e. a catalytic reforming product, is one of the main high-octane components of finished gasoline products. The main directions of the catalytic reforming process development are using semi-regenerative reformers with high-stability polymetallic catalysts capable to operate under severe conditions for the purpose of reducing pressure and using CCR technology.

State-of-the-art reforming catalysts contain maximum 0.3 % w. of platinum and maximum 0.4 % w. of rhenium. To modify the catalysts additional promoters are used for optimization of a porous structure and reduction of sodium and iron impurities to provide for higher thermal stability, improved selectivity and resistance to coke formation of the reforming catalysts. Theoretical studies and specific systemic approach enabled specialists from RAS SB Institute of Hydrocarbons Processing Problems to develop trimetallic PR-81 catalysts (Table 2) based on the evidence of various active platinum states available in reforming catalysts – high-dispersion metal platinum and ionic platinum. These catalysts provide for higher stability with maintaining activity and selectivity throughout the whole catalyst service life. It is availability of ionic complexes presented on the catalyst surface that assures high activity and selectivity of paraffin aromatization. As a result, a high yield of aromatic hydrocarbons is achieved due to more favorable ratio of the rates of targeted aromatization reactions and undesirable paraffin hydrocracking reactions. It was established that monolayer deposition of coke precursors only occurs on ionic platinum centers with subsequent migration to a carrier and self-regeneration by hydrogen and a stage of graphitization does not present actually; so, the coke amount on these centers is extremely low and active centers of the ionic platinum-based reforming catalysts are characterized by a higher resistance to sulfur, moisture and presence of hydrocarbons with a boiling temperature over 180 °C [4].

Table 2: Performance comparison of PR-81 reforming catalyst and its analogues.

European average value	PR-51, 71 (Russia)	PR-81 (Russia)	REF-23 (Russia)
Reforming product yield, % w.			
82–85	86–88	90	84–85
Hydrogen yield, % w.			
1.6–2.0	2.4–2.6	2.8	2.0
Hydrogen content in hydrogen-rich gasses, % vol.			
73–80	83–86	86	–
Mean integral temperature, °C			
480	470	465	–
Octane number, RON			
95–98	95–98	98–100	95–98

Among catalytic reforming units, the most efficient are those with a dynamic catalyst bed and its continuous regeneration, which permit to run the process under the most thermodynamically favorable conditions and to achieve a high octane number and a product yield. As of today, no continuous catalyst regeneration technologies were developed in Russia. All the operating units based on this technology were built by foreign design. PAO NPP Neftekhim and OOO Lengiproneftekhim propose a process developed in Russia for catalytic reforming of gasoline fractions with continuous catalyst regeneration (CCR) based on catalyst RC-12 that successfully pass pilot long-run tests. The catalyst RC-12 is characterized by a high selectivity, low coke formation under severe operating conditions, versatility of process running, high density and minimum reduction of a specific surface area throughout the catalyst service life, and a high mechanical strength ensuring minimum abrasive wear and dust generation. The catalyst service life is at least 8 years; the reformate octane number is 98–104 RON.

A special interest is attracted to developments in the area of catalytic cracking being a key deep-conversion process both in Russia and abroad. Current trends in the catalytic cracking process development are connected with processing of heavier petroleum feedstock and residues, combination of fuel and petrochemical patterns (producing gasoline, diesel fuel and propylene) and shortening of contacting the feedstock and catalysts. Promising studies are performed by KBR (Maxofin process) and UOP (Millisecond process).

Russia is one of the countries that developed its own competitive state-of-the-art process of catalytic cracking in a once-through reactor using a zeolite-containing microspheric catalyst (G-43-107, KT-1). The proprietary domestic catalytic cracking technology allows for processing sour (sulfur content from 1.8 up to 2.5 % w.), poor-cracking feedstock (cuts having IBP of 315–330 °C and EBP of 530–550 °C) and is on a par with best international analogues. Competitiveness of this technology was currently confirmed by implementation of the 880-kTA unit project for OAO TAIF-NK with participation of research and design organizations (OAO VNIINP, RAS A.V. Topchiev Institute of Petrochemical Synthesis (TIPS), and OAO VNIPIneft. The technology was implemented using the existing equipment of OAO TAIF-NK by means of revamping an idle isopentane dehydrogenation unit. The unit is operating without preliminary hydrotreatment of feedstock and produces a gasoline component for the plant not having a catalytic reformer. Similar units were not built in Russia for 25 years. Nevertheless, a development level turned out to be very high: the unit used a new once-through reactor providing for a short time of contacting hydrocarbon vapors with the catalyst under conditions approaching to plug flow; the reactor is equipped with improved feed and recycle injection units with radial slot-type nozzles. The proposed feed injection system provides for almost single exposure of feed drops to the catalyst. To avoid overcracking of the feed at reactor outlet a separation device is provided, which allows for fast and efficient separation of the main portion of the catalyst from hydrocarbon vapors; a new coked catalyst injection unit is provided in the regenerator. The unit design provides for uniform catalyst distribution across the regenerator cross-section. Due to counterflow of the catalyst and the air in a lower portion of the bed the regeneration efficiency is improved. The gasoline yield (less than 210 °C) is 51.8 % w. [5].

Of significant interest are the developments of some Russian research teams in the field of technologies for producing competitive microspheric cracking catalysts, including those having a minimum content of rare-earth metals and additives, including rare-earth element oxides, to increase the olefin yield and the octane number, fixing of sulfur and nitrogen oxides being promoters of carbon oxide burning. In 2007, the Ishimbay catalyst plant completed the modernization of a main production unit using Japanese equipment and the installation of a train for producing microspheric cracking catalyst (FCC). KNT Group is working to improve a structure and a formula of the catalysts under development and those currently produced. They have a state-of-the-art laboratory being in close touch with RF and CIS research institutes, including RAS SB Institute of Catalysis. Currently, due to developments of its scientific center, KNT Group is producing granulated thermoform catalytic cracking (TCC) catalysts being on par with granulated TCC catalysts produced by its competitors. KNT Group produces two brands of the granulated TCC catalysts: Adamant Super designed for processing vacuum gas oils to maximize gasoline and light product yields and Adamant Extra designed for obtaining a maximum yield of light olefins.

OAO VNIPIneft has completed the design for modernization of Omsk Catalyst Plant which allows for producing new cracking catalysts (Avangard series) with low sodium oxide content (less than 0.25 % w.) and improved thermal stability developed by RAS SB Institute of Hydrocarbons Processing Problems after start-up of Stage 2 of zeolite ultra-stabilization and 4^{th} ion exchange on the zeolite. The Avangard series catalysts are designed for cracking of hydrotreated vacuum gas oil (sulfur content from 0.02 to 0.2 % w.) with gasoline cut recovery of at least 60 % w. and RON not less than 93.0. Since 2012 a bi-zeolite cracking catalyst of A, B, M and H makes has been produced in Omsk by the formula developed in the RAS SB Institute of Hydrocarbons Processing Problems. The microspheric bi-zeolite cracking catalyst was developed using the ultrastable zeolite Y (USY) and the ZSM-5 type zeolite. A semisynthetic low-erosive matrix is used in the catalyst. Comparative characteristics of the catalysts are given in Table 3. The catalyst is designed for heavy oil feedstock cracking to produce a high-octane motor gasoline component with controlled draw-out of petrochemicals feedstock (light olefins) and can be used at all types of cracking units with microspheric catalysts.

The motor gasoline component produced using the bi-zeolite catalysts has a high octane number. The catalyst allows for a 20 %-increase in the light olefin recovery compared to mono-zeolite catalysts. Commercial operation showed that technical and economic advantages of this new catalyst brand lie in the high gasoline cut recovery (up to 55 % w.). Commercial production of the catalyst was set at the AO Gazpromneft – Omsk Refinery Catalyst Plant. The bi-zeolite catalysts of two brands are used at commercial cracking units: Unit 200 of the KT-1 Complex and Unit 43–103 with a total throughput up to 4.0 MTA.

It is worth to mention also the AO TANECO 850-kTA coker HGO hydrotreating unit project based on the Axens's licensed technology. This technology never was implemented in Russia earlier. The hydrotreating unit is designed for producing the hydrotreated coker HGO with sour content of max. 300 ppm (w.) and a yield of at least 76 % w. The detail engineering documentation for this project has been developed by OAO VNIPIneft.

Recently, special attention is focused on the development of new catalysts and processes for producing middle-distillate fuels for cold and Arctic climate conditions. Here, the most efficient processes are catalytic hydrodewaxing and isodewaxing. The most interest is attracted to researches in the field of functional composition control of the catalyst and creation of catalytic systems based on zirconium dioxide modified by tungstate anions. At present, OAO VNIPIneft is performing engineering activities for the 4.0-MTA diesel hydrotreating and isodewaxing unit project for AO ANKhK. This project is truly at the cutting edge in terms of using high-technology equipment, energy-efficient design solutions, and application of unique high-efficient catalytic technologies. The technology proposed by EMRE combines deep hydrogenation of heteroatomic compounds, saturation of aromatic hydrocarbons and isomerization of paraffins. Diesel fuel produced at this unit and having a sulfur content <10 mg/kg will meet advanced standards after injection of a necessary additive set. This unit is able to produce simultaneously summer and winter diesel fuels due to the two-train process flow chart (Fig. 1: Train a and Train b). Every train includes two concurrent reactors using layered main and auxiliary catalysts. The use of hydrotreating (HDT) and MIDW catalysts in Train B reactors allows for producing winter fuels with given low-temperature properties and a high yield (more than 95 %) when processing straight-run summer diesel fuel [6].

A large-scale and important project is the construction of a state-of-the-art, high-technology complex for producing catalysts of catalytic cracking and hydroprocesses based on Russian technologies in Omsk (15-kTA unit producing catalysts for catalytic cracking, 4-kTA unit producing catalysts for diesel hydrotreating and 2-kTA unit for regeneration/reactivation of hydrogenation catalysts). The implementation of this project will

Table 3: Performance comparison of catalytic cracking catalysts developed by RAS SB Institute of Hydrocarbons Processing Problems.

Index, %	Competitive catalyst	ONPZ catalyst make M	Advanced catalyst avangard series
Conversion	79.7	80.2	82
Gasoline yield	54.4	56.6	58.0
Coke yield	2.9	3.2	4.0
Light cracker gas oil	12.7	12.9	9.5
Liquefied gas yield	20.5	18.7	18

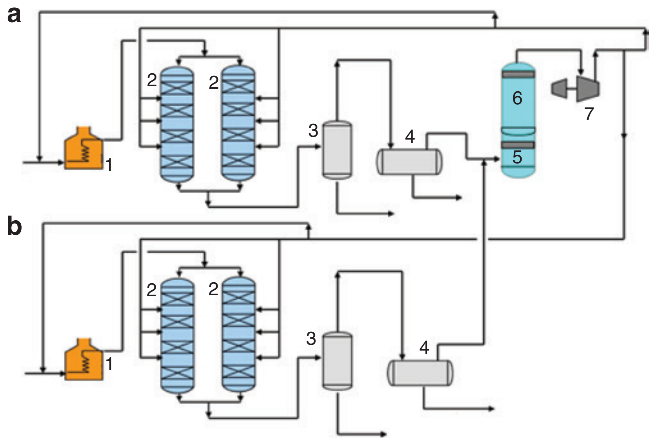

Fig. 1: Process flow chart of the diesel hydrotreating/hydroisodewaxing unit at AO ANKhK.
1 – Reactor feed heater, 2 – Reactor, 3 – High-pressure hot separator, 4 – High-pressure hot separator, 5 – High-pressure separator of amine absorber, 6 – High-pressure amine absorber, 7 – Cycled gas compressor.

enable to meet the demand of Russian oil-refining industry for catalysts of key petroleum feedstock conversion processes. These catalyst production technologies were developed by leading Russian research and development institutes: RAS SB Institute of Catalysis and RAS SB Institute of Hydrocarbons Processing Problems. At present, OAO VNIPIneft is developing design documentation for this complex. This project has been assigned a National Project status.

A trend to using heavier petroleum feedstock and the necessity to achieve a higher oil conversion level require developing additional processes based on destruction of high-molecular compounds with formation of light and medium fractions. In addition, resins and asphaltenes being abundant in heavy petroleum feedstock are responsible for coke formation and catalyst deactivation during their processing. Therefore, the most important technologies for processing heavy oil residues are technologies which permit to control transformation of resinous-asphaltenic materials by means of using nano-scale catalytic systems. The process of hydroconversion implemented now at AO TANECO (Originator: RAS A.V. Topchiev Institute of Petrochemical Synthesis (TIPS); General Designer: OAO VNIPIneft) can serve as an example of commercial implementation of technologies using slurried catalysts in Russia. The hydroconversion technologies is characterized by a high process flexibility which allows for running the residue stock hydroconversion within a wide range of process variables using efficient technological and engineering solutions. A distinguished feature of the hydroconversion process is using a slurry-reactor being a hollow vessel that creates a large reaction volume and operates practically in a mode of plug flow reactor, and mixers that are developed based on a unique technology and permit to control a size and dispersion of the slurry obtained after catalyst injection into feedstock. Specific features of using the catalyst are as follows: it is used in a form of nano-particles formed directly in the reaction area in the initial material to obtain an active form of the catalyst under reaction conditions; no carriers for catalytically active components are available contrary to conditional heterogeneous catalysis. The main advantages of the proposed technology are as follows: a low yield of residue (fractions 520 °C +) in the hydroconversion process (less than 5–10 %) against 26–31 % in such processes as H-oil and LC-fining and 45–66 % in other processes. The key advantage of this technology is almost no-residue processing of heavy petroleum feedstock since vacuum residue is sent to oxidative regeneration of a catalytic component with simultaneous development of heat. The pressure of the proposed process is 7.0 MPa which is significantly less than for foreign analogues (15.0 MPa). It should be noted that spent catalyst does not present in the process [7].

For the purpose of residue processing AO TANECO is creating a delayed coking unit producing the furnace coke planned to be utilized as fuel at the Nizhnekamsk cogeneration plant.

Based on the delayed coking units, the Ufa State Petroleum Technological University (UGNTU) has developed a technology that enable producers to obtain not only standard coke but also a coking additive being in demand in the metallurgical industry and used as an additive to coal charge for furnace-size coke (instead of metallurgical coke).

The coking additive contains 15–25 % of volatile substances which results in a number of features impossible when using the coke containing 11 % of volatiles. Using the coking additive allows for producing high-quality pellets without a binder and high-quality furnace coke without mixing with other cokes which permits to perform non-ferrous metal smelting.

UGNTU, jointly with GUP Bashgiproneftekhim and PAO ANK Bashneft Bashneft-Ufaneftekhim, have designed and built a delayed coking unit based on the new proprietary technology. The unit was built using Russian-made equipment and entirely automated. At present, a coking additive production is also provided at Bashneft-NOVOIL, a branch of PAO ANK Bashneft [8].

Advance from an original concept and fundamental research to the implementation is a complicated multistage process which sometimes is getting protracted for several years. Nevertheless, in recent years some new high-efficient catalysts and technologies being aligned in the times and in demand not only in the Russian market were created and commercially implemented. It could be stated that at present the Russian market is being shaped for catalysts and catalytic technologies of a high scientific and technological level.

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