Scientific Foundations and Technological Arrangement of the Process of Obtaining Synthetic Oligodecene Oil for Automobile Transport

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Abstract

A new catalytic system for obtaining synthetic oligodecene oil for motor transport is developed. The system includes metal aluminium with particle size 4–40 μm, alkyl aluminium halide (in particular, $(C_2H_5)_{1.5}AlCl_{1.5}$), organic halogenated compound (in particular, *tert*-butyl chloride $(CH_3)_3CCl$). It was shown that the application of this system in combination with a tubular-slit reactor of oligomerization allows one to solve a set of the main problems connected with obtaining oligodecene oil. Thus obtained results were confirmed using pilot installations and were implemented in the project of the Nizhnekamsk plant of synthetic oil.

URGENCY OF THE PROBLEM

Intense development of technology, creation of new types of high-powered engines, complicated machines, devices and instruments is accompanied by elevation of requirements to lubricants. Various kinds of oil are used in modern technology to lubricate slider or roller elements and as a medium to transmit force or heat; this helps one to decrease the rate of metal corrosion, to increase lifetime and reliability of machinery performance, to decrease specific fuel consumption and toxicity of emissions of vehicles, and to increase performance lifetimes of machinery to a substantial extent. At present, about 1 % of the whole amount of petroleum produced is processed into lubricants. Conventional petroleum (mineral) oil in many cases fail to meet the modern performance requirements. As a result of investigations carried out by some foreign companies in order to improve the quality of lubricants, processes of obtaining synthetic lubricants are developed and realized on the industrial scale. These lubricants can be used successfully within temperature range from −70 to +290 °C (the best lubricants based on mineral oil can be used at a temperature from −20 to +240 °C). Performance lifetime of the synthetic lubricants can reach 8000 h (for mineral oil, this parameter is only 500–2000 h). Wide application has been won by the synthetic oil based on polyalphaolefins (PAO). Replacement of petroleum lubricants by synthetic ones provides fuel saving, a decrease in expenses for oil, repair works, destruction or utilization of wastes. Replacement of mineral oil by synthetic one improves the ecological characteristics of mechanisms, so the rate of production of synthetic oil is growing. At present, the world production of PAO oil (PAOO) exceeds 400 000 t per year. Further increase in PAOO production rate is limited by the production of the initial olefin raw material (in particular, decene-1). Synthetic oil based on PAO had not been manufactured in Russia before 2004. At the same time, vehicles running today in Russia include about 22 million cars (among them, more than 5 million cars manufactured abroad), 5 million lorries, 600 000 buses, a large number of various special vehicles: ambulances, fire-engines, militia cars, collector cars, vehicles of the Russian Emergency Ministry. Each vehicle consumes about 10 l of motor oil per year as a mean; therefore, consumption of synthetic motor PAOO only in automobile industry can be 150-200 thousand tons per year. Synthetic motor oil is also used in civil and military aviation, sea transport, other kinds of transport, in rocket and space systems, *etc.* Along with motor oil, PAOO may be used as the basis for transmission, reducer, vacuum, compressor, refrigeration, transformer, cable, spindle, medical, perfume oil, as well as heat carriers, components of lubricating-cooling and hydraulic liquids and plasticizers for polymers and caoutchouc [1]. In view of the absence of industrial production of synthetic PAOO in Russia, the home market of synthetic motor and other kinds of oil represents the products of foreign manufacturers (Chevron, Mobil, Shell, Mesta, Esso, Amoco and other companies). Realization of this technology in Russia is especially urgent because of the northern position of the country with extremally low temperatures characteristic of many months; this determines the necessity to use synthetic PAOO with low pour points (down to −95 °C) in automobiles and other kinds of modern machinery.

It follows from the above-considerations that development and industrial implementation of original Russian production of synthetic PAOO is an important scientific and technological problem. It should be noted that large-scale realization of this technology in industry is also required by the need to improve defensive capacities of Russia.

EXISTING SOLUTIONS

In foreign technologies implemented on an industrial scale, oligomerization of decene-1 is carried out under the action of multicomponent catalysts including boron trifluoride. These catalysts are characterized by extremely high corrosion activity and are very dangerous for human health, so they are to be handled with extreme security measures (shift mean MPC of the air of working area is 0.1 mg/m^3 of the air). The use of these catalysts in oligomerization of decene-1 causes the necessity of particular orientation of production toward manufacture of PAO-4 and requires special materials for equipment. In these technologies, oligomerizate, liquid and gaseous wastes are purified from boron trifluoride and hydrogen fluoride with the help of aqueous solutions of NaOH or KOH.

SCIENTIFIC FOUNDATIONS AND TECHNOLOGICAL ARRANGEMENT OF THE NEW TECHNOLOGY

Three groups of cation catalysts of olefin oligomerization were developed and patented: $(C_2H_5)_{1.5}AlCl_{1.5}$ (EASKh)−NiX_2−$(CH_3)_3CCl$(TBKh) (I), EASKh−$C_2H_5OCH_2CH_2OH$−TBKh (II) and Al(0)−EASKh (HCl)−TBKh (III) [2−4]. The effect of different factors on the kinetic features of oligomeriation of decene-1 and other olefins, the structure, fraction composition and physicochemical properties of the resulting oligomerized olefins was investigated. The features and optimal conditions of realization of the stage mechanism of cation oligomerization of various olefins were revealed.

In particular, it was shown [5, 6] that the following processes take place during cation oligomerization:

– before entering the oligomeric product, decene-1 gets isomerized under the action of the developed catalysts (I−III) into a mixture of positional and geometric isomers of decene with intramolecular positions of double bonds;

– under the action of the developed catalysts (I−III), decenes with intramolecular position of double bonds (including decene-5) get oligomerized as easily as decene-1;

– oligomerization of decenes with intramolecular position of double bonds results in the formation of more branched oligodecenes (solidifing at lower temperatures) than in the case of decene-1.

Institute of the Problems of Chemical Physics (IPCP), RAS, together with the Serbian company "Neftyanaya Industriya Serbii" (NIS) and Tatneft-Nizhnekamskneftekhim-Oil JSC (Tatneft-NKNKh-Oil) developed scientific foundations and original technological (instrumentation) arrangement of the process of obtaining unsaturated, hydrogenated and aromatized polyolefin bases for synthetic lubricants. The technological arrangement of this process includes the units of preparation of the initial raw material and solutions of the components of catalyst, decene oligomerization, isolation of the worked-out catalyst, purification of the oligomerizate, its separation into narrow fractions, hydrogenation of the isolated PAO fractions followed by compounding of the hydrogenated fractions with the help of a set of packings [7].

The proposed technology may additionally include the stages of conversion (metathesis) of hexene-1 into decene-5, carried out preliminarily or simultaneously with oligomerization of decene-1 isomerization into a mixture of decenes with different intramolecular position of the double bond in olefin molecule [1, 6], dechlorination of chlorine-containing oligodecenes and the stage of depolymerization of high-molecular oligodecenes into the target products. These stages help improving the technological and economical indices of the technology, solving specific chemical problems, and they also increase the flexibility of the developed technology with respect to the products.

Decene-1 was shown to be the best raw material for PAOO production [1, 5, 7]. However, its resources are limited, and its price exceeds $1000 US per one ton. Conversion of restrictedly used hexene-1 into decene-5 allows one to double decene resources and decrease its cost substantially [2] because hexene-1 is almost twice as cheap as decene-1.

It should also be mentioned that the metathesis stage allows obtaining not only decene-5 from hexene-1 but also tetradecene-7 from octane-1, and a mixture of decene-5, dodecene-6 and tetradecene-7 from a mixture of hexene-1 with octane-1. The indicated olefins with intramolecular position of double bonds, similarly to the corresponding alphaolefins, are an excellent raw material for obtaining linear mono- and polyalkyl benzenes (MAB and PAB, respectively), which serve as the raw material to obtain rapidly and completely biodegradable alkyl benzenesulphonate domestic detergents, oil dopes, oil for different purposes, plasticizers and other petrochemical products. It should also be noted that the stage of hexene-1 conversion into decene-1 is optional (that is, not functionally necessary).

Oligomerization of decenes according to the considered technology under the action of cation catalysts (I, II) is carried out in a high-productive turbulent tubular-slit reactor of the original design (heat transfer surface is 40–400 m^2/m^3 of the reaction volume) under isothermal and isobaric conditions with residence time less than 10 min [7, 8]. The reactor was designed, manufactured and runs without reclamation at the Nizhnekamsk Plant of Synthetic Oil. It may also be used to carry out other fast physical and chemical processes in the liquid and gas phases under isothermal regime.

The stage of dechlorination of monochlorooligocenes formed during oligomerization and present in the oligomerizate promotes the transformation of organic chlorine into the ionic one, which is then removed from the oligomerizate by means of aqueous-alkaline washing. Six original methods were developed to solve this problem. Each of them is multi-purpose and can be used separately to solve similar problems in other chemical processes, in oil processing, and in dechlorination of various liquid and solid chlorine-containing organic wastes.

The stage of thermal depolymerization of high-molecular oligodecenes obtained at the stage of oligomerization and isolated during the separation of the oligomerizate into fraction is intended for correction of the molecular mass distribution and fraction composition of oligodecenes. The importance and reasonableness of this stage in industry have sharply decreased after the development of a two-component readily available cation catalytic system (III) which is safe for transportation, storage and use, and stable when stored in the air [4]. Its use in oligomerization solves the problem of governing the fraction composition and branching extent of the products of decene oligomerization. The consumption of this catalyst, either expressed in mass units or, especially, in price, does not exceed the corresponding characteristics for the best catalysts including boron fluoride ones.

The worked out cation catalyst and ionic chlorine obtained from chlorine-containing oligodecenes, similarly to other technologies of cation oligomerization of olefins or alkylation, is removed from the oligomerizate by aqueous-alkaine washing [9].

Separation of the oligomerizate into narrow fractions according to the proposed technology is carried out similarly to other technologies, except for the fact that high vacuum in separation columns is provided by an original vapour-ejecting vacuum system.

Hydrogenation of the isolated oligodecene fractions according to the technology of IPCP RAS–NIS–Tatneft-NKNKh-Oil is performed under the action of an original highly efficient catalyst under mild technologically favourable conditions. Temperature and pressure at the stage of hydrogenation according to this technology are much lower in comparison with other technologies [10].

The technology was mastered at the continuous experimental set-up in IPCP with the productivity of 250 kg of oligodecenes per day and at the demonstration continuous automated (computer-controlled) set-up of IPCP and Rafineriya Nefti Novi Sad company (Serbia) with the productivity of 100 kg of oligodecenes per day.

As a result of experimental mastering of the technology, bases of synthetic oil were obtained and certified (VNIINP, NAMI-KhIM, AVIATEKhMAS); compositions of commerial oil for various purposes were developed; the initial data were prepared for the "Process of obtaining oligodecene bases of synthetic oil", technical and economic feasibility of the process was carried out; the basic and working projects of the production of oligodecene bases of synthetic oil were developed.

On the basis of these documents, the Nizhnekamskiy Plant of Synthetic Oil was built and put into operation in 2003. Its productivity is 10000 t of oligodecene bases of synthetic oil per year [7].

The main feature of the new automated plant is flexibility of technology and a completed technological cycle: from the production of raw material to the production of ready synthetic and semisynthetic oil [7].

CONCLUSIONS

The existing processes of obtaining lubricant oil are based on oligomerization of linear alpha-olefins (mainly decene-1) under the action of multicomponent catalysts containing boron trifluoride. These catalysts are characterized by extremely high corrosion activity and physiological harmfulness and require special materials for technological instrumentation and strict safety measures.

We developed a new catalytic system allowing one, in combination with the specially developed tubular-slit oligomerization reactor, to solve a set of problems connected with obtaining oligodecene oil. In particular, it allows one to carry out oligomerization of decene-1 in decene as a medium, which excludes the necessity to use solvents, helps one to save energy resources and simplifies the technological flowchart of the process. The new catalytic system allows one to control the fraction composition and structure of oligomerization products and to broaden the raw material basis of the production of synthetic oil by involving not only individual olefins from propylene to tetradecene but also various olefin fractions, as well as olefin-containing wastes of petrochemical and oil-processing industry without any substantial changes in the technological scheme.

The obtained results were the grounds for the construction of a plant of synthetic oil, which was built and launched into operation in 2003 in Nizhnekamsk. This plant, which was built according to the home development and operating with the home raw material basis, not only brings the home industry to the level of advanced technology in petrochemistry but also ensures the possibility for Russian automobile, armoured vehicles and aviation to get free from foreign industry.

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