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PRODUCTION OF UNSATURATED, HYDROGENATED AND AROMATIZED OLIGOOLEFIN BASES OF SYNTHETIC LUBRICANTS

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Abstract. *A new technology of obtaining the unsaturated, hydrogenated and aromatized poly-alpha-olefin (PAO) bases of synthetic oils has been developed. Decene-1 is an ideal raw material which provides whole complex of physico-chemical and commercial properties of PAO bases of synthetic oils. Oligomerization of decene-1 is performed in decene-1 own medium in isothermic regime using the original highly efficient turbulent split-tube flow reactor. This process leads to the formation of highly branched hydrocarbons with moderate molecular weights (MW) and narrow molecular weight distribution. Separated in narrow MW range fractions of PAO-2, PAO-4 and PAO-6 are characterized by low solidifying point, low volatility, high viscosity index, and their characteristics are practically identical to the commercial analogues ones.*

Key words: *poly-alpha-olefin bases of synthetic oils*

Introduction

Intensive technical development and design of powerful engines, new types of complicated machines, mechanisms and devices impose increasing requirements to the lubricants. Modern technologies use oil of different types to lubricate some rolling and sliding units, and as a media for heat and strain transferring. The oil application reduces metal corrosion rates, increases life-time and reliability of mechanisms. It allows diminishing specific fuel consumption and harmfulness of exhaust gases in transport, as well, highly enhances the terms of machine life. At present, more than 1 weight % of all produced petroleum is converted to the different lubricants. In some cases, traditionally used petroleum (mineral) oils are not satisfied to the modern requirements for exploiting new types of techniques. A number of leading companies (Mobil, Chevron, Nesta, Shell, Esso, and Amoco) were carrying out investigations and engineering developments of the technologies to increase the lubricant quality. As a result, it has been elaborated the design and industrial realization of the technology of the production of synthetic lubricants which can successfully work at temperature from -70 to +290°C (the best synthetic lubricants on the mineral base are exploited at temperature from -20 to +240°C). The term of working life for the synthetic lubricants can achieve 8000 hours, and for petroleum oils – from 500 to 2000 hours. The synthetic oils on the poly-alpla-olephine (PAO) base are widely used now. The replacement petroleum oils by synthetic ones leads to the real economy of fuel, decreasing cost of the oil and the equipment maintenance, and expenses of the wastes recovery or liquidation. The use of synthetic oils instead of petroleum ones highly improves ecological characteristics of the mechanisms. Thus, the production of the synthetic oils grows rapidly. At present, the world production of the synthetic oils on the PAO base amounts to above 400 000 tons in a year. The following growth of the PAO production is limited by the raw materials (particularly, by decene-1) production. The main user of the synthetic PAO oils is automotive transport. There are about 20 millions cars in Russia including more than 5 millions foreign ones. Each car uses about 10 liters of engine oils in a year (on the average). Therefore, only automotive industry can use from 150 to 200 thousand tons of the synthetic PAO-oils in a year. Besides, civil and war aircraft, marine and other modes of transport, rocket and space systems and other special equipment also use synthetic engine oils. Poly-alpha-olephines can be used as a basis for transmission, reducing gear, vacuum, compression, refrigerating, transforming, cable, spindle, medical, cosmetic and other oils. They also can be used as heat-carriers, components of cooling lubricants and hydraulic fluids, plasticizers for polymers and rubbers. The prime cost of the poly-alpha-olefine bases of the synthetic oils (PAO-2, PAO-4, PAO-6) at the European factories with capacity of 10 to 30 thousand tons per year is varied from 1400 to 1800 US $ per ton, respectively. Because of the European companies are specialized only on the PAO-4 production, the most valuable high-viscous kinds of PAO (in particular, PAO-10 and PAO-10+) are not produced in Europe. More expensive PAO-10 and PAO-10+ are produced in the USA by "Shevron". A number of companies including Chinese "Jilin Chemical Group Corporation" and South-Korean "Gamro Fine Chemical" are interested in production of these and more viscous PAO bases of synthetic oils (up to PAO-100).

Realization of the synthetic PAO oils production in Russia will allow highly diminishing cost of these products, organizing a lot of new working places, and providing automotive, aircraft and other branches of the industry with the synthetic lubricants of high quality. This technology is very important and necessary for Russia, because Russia belongs to the northern countries, and extremely low temperature is typical for a lot of its regions for many months.

So, the industrial production of the PAO oils in Russia is a very important, broad and still free niche. That is why, the engineering design and commercial realization of the original synthetic PAO oils production is a very significant scientific, technical and industrial task.

Existing Engineering Solutions

In the present-day technologies, oligomerization of decene-1 is performed using multi-component catalysts including BF_3. These catalysts are characterized by extremely high corrosion activity, and they are very dangerous physiologically, so they need to keep exact safety measures when they are working with them (the average-shift maximum allowable concentration in the air of the working zone is 0.1 mg/cubic meter of air). The use of such catalysts for the decene-1 oligomerization leads to a very restrained specialization (the PAO-4 production only) and requires special materials to produce a lot of the equipment units. These technologies use NaOH and KOH water solutions for washing both oligomerizate, and liquid and gaseous wastes from BF_3 and HF.

Technological Fulfillment of the Process

IPCP RAS jointly with Yugoslavian company «NIS» and Russian company OOO «Tatneft'-Nizhnekamskneftechim-oil» have elaborated scientific backgrounds and original technological design of the production of unsaturated, hydrogenated and aromatized poly-olephine bases of synthetic lubricants [1-13].

Elaborated by IPCP RAS and the above-named partners technological design of this process, as well as design of other similar processes, includes units for the preparation of raw materials and solutions of the catalyst components, units for the oligomerization of decenes, units for evolving dead catalyst, for cleaning oligomerizate, for separating oligomerizate to narrow fractions, as well for the hydrogenation of the evolved narrow PAO fractions and then for compounding the hydrogenated fractions with additives. If it is commercially necessarily, this process could involve some additional stages, for example, metathesis of hexene-1 to decene-5 and depolymerization of high-molecular oligodecenes. The new technology provides apparatus facilities for involving these additional stages in the basic process.

Scientific and Technological Backgrounds of the New Process

The following engineering solutions are set in the base of the new process:

- it has been developed four variations of original, high efficient, respectively safe and accessible catalysts. They allow achieving high extents of the conversion of decene-1 to oligodecenes (more than 95 weight %) at temperature from 20 to 150°C and atmospheric pressure in 3-5 minutes (under optimal conditions) (see Table 1);
- it has been shown (both theoretically, and experimentally) that changing the catalyst nature and composition, as well the oligomerization conditions allow to vary the fraction composition of obtaining oligodecenes in wide range. In particularly, it has been shown that the composition of the most usable trimer fraction of decene-1 (PAO-4) can be regulated in the range from 20 to 60 weight % (calculated on the decene-1 converted);
- the oligomerization of decene-1 is performed in the decene-1 own medium. It excludes the use of any solvents, leads to the economy of energy, and simplifies the technological solution of the process;

Table 1. Conditions and results of decene-1 oligomerization under action of model catalytic systems $(C_2H_5)_nAlCl_{3-n}$ (AOC) – $(CH_3)_3CCl$ (TBCl). AOC – 0.04 mol/l; S - conversion.

Nature AOC	TBCl, mol/l	T, °C	τ, min	S, weight %	Dimer, weight %	Trimer, weight %	Tetramer, weight %	R/1000CH$_2$ *	
								CH_3-	trans-CH=CH
$Al(C_2H_5)_3$	0.20	20	3	98.5	11.8	27.6	16.3	443.3	8.6
			6	98.1	9.9	22.0	12.6	230.4	7.6
			10	99.8	9.8	22.6	13.5	299.2	5.6
			15	99.9	9.7	21.8	13,4	269.4	9.1
			30	99.8	11.4	24.5	15.3	375.0	10.5
			60	99.9	11.7	27.6	17.4	293.5	7.9
$C_2H_5AlCl_2$	0.16	20	10	100	13.8	29.8	16.7	333.9	18.5
			60	99.0	14.2	29.8	18.9	287.0	12.0
$(C_2H_5)_{1.5}AlCl_{1.5}$	0.12	75	10	100	8.6	32.6		594.0	9.2
$AlCl_3$	0.17	95	60	100	27.8	47.5	14.6	341.0	14.2

*iso-olephines in the reaction products are not detected

– the oligomerization of decene-1 is performed in isothermic regime using the original highly-efficient compact (up to 100 tons of the product per 1 cubic meter of the reaction volume per hour) turbulent split-tube flow reactor with residence times from 3 to 10 minutes. Because of the high surface of the heat exchange (40-400 m^2/m^3 of the split-tube reaction space), such construction allows performing the process in isothermic or autothermic regime;
– it has been developed the original fulfillment of the deactivation and dead catalyst evolution stages using the water-alkaline washing method;
– decene-1 is an ideal raw material which provides whole complex of physico-chemical and commercial properties of PAO bases of synthetic oils. But its resources are highly limited. Probably, it is the reason why "Shevron" has become to produce PAO-2.5, PAO-5 and PAO-7 by oligomerization of dodecene-1. At present, decene-1 is produced in Russia at OAS "Nizhnekamsknephtechim" oligomer plant (Tatarstan) only. It has been shown in IPCP RAS that some other decenes (from decene-2 to decene-5 including) can be used as raw materials instead of decene-1. Now they are not produced anywhere in the world. IPCP RAS joint with TOO "Chimokam" (Tatarstan, Nizhnekamsk) has developed the technology of the individual decene-5 obtaining by the disproportionation (metathesis) of hexene-1 under atmospheric pressure and temperature of 60 – 80°C in hexene-1 own medium. Decene-5 is produced by suspension techniques with the available catalyst. The conversion of hexene-1 (which is produced at OAS "Nizhnekamsknephtechim") to decene-5 would allow increasing almost twice production of the decene PAO bases of synthetic oils and essentially decreasing their prime cost;
– this process is universal. The investigation shows that not only individual olefins but different olefin-containing unusable wastes of petrochemical and petroleum-refining industry can be used as raw materials in the PAO production. Low cost of such raw materials allows essentially decreasing the prime cost of the obtaining synthetic oil bases;
– the elaborated process of the decene-1 oligomerization gives colorless oligomers which are the highly branched hydrocarbons with the moderate molecular weight, narrow molecular weight distribution, and containing one double bond per each oligomer molecule. Separated in narrow MW range fractions of PAO-2, PAO-4 and PAO-6 are characterized by low solidifying point, high viscosity index, low volatility, and their characteristics are practically identical to the properties of their commercial analogues;
– it has been elaborated a catalyst of the express-positional isomerization of decene-1 to the mixture of cis- and trans-decene isomers with intramolecular position of the double bonds. The use of such raw materials in the oligomerization allows essentially increasing these products branching and diminishing their solidifying point;
– it has been elaborated an original technology of hydrogenation of olefin unsaturated oligomers on highly active low-percentage palladium catalyst (0.2 weight % Pd/Al_2O_3) at temperature from 200 to 250°C and hydrogen pressure up to 2 MPa in the alternation cyclic suspension regime in the capacitive batch reactor. The hydrogenated di-, tri-, tetra-, and oligodecenes are colorless clear liquids. They consist of highly branched hydrocarbons with moderate molecular weights. The examination of the hydrogenization products by means of ozonolyse and IR-, PMR-, ^{13}C-NMR- spectroscopy showed that the double bond content decreased by two orders and the branching was remained the same during the hydrogenization. The characteristics of the hydrogenated decene-1 trimers (for example, PAO-4) (kinematic viscosity at 40°C and 100°C, viscosity index, solidifying point, flash point in open crucible, density, etc.) are practically identical to the corresponding properties of the commercial products and to the typical characteristics of PAO-4 used as a basis for motor synthetic and semisynthetic oils (see Table 2). It has been shown that the hydrogenation of olefins provides essential increasing their thermooxidation stability;
– it has been elaborated a new method of blocking oligomer double bonds by aromatic fragment during the decene-1 oligomerization. This leads to the high rise of the thermooxidation stability. This technology allows obtaining one more kind of products, namely "aromatized" oligodecenes synthetic oils stable to the thermooxidative destruction.

Table 2. Physical characteristics of hydrogenated fractions of oligodecenes obtained by decene-1 oligomerization with the $(C_2H_5)_{1.5}AlCl_{1.5} – Al – (CH_3)_3CCl$ cationic catalytic system.

Characteristics	PAO-2	PAO-4	PAO-6
Kinematic viscosity at 100°C, cSt	1.84	3.90	5.96
Viscosity index	-	129	138
Solidifying point, °C	-72	-70	-68
Flash point, °C	>155	215	235

Advantages of the Elaborated Technology

– soft conditions of all processes fulfillment;
– original and simple technical equipment;
– high specific productivity of the equipment;
– high selectivity and versatility of the technology which provides obtaining a wide variety of PAO;
– ecological safety;
– low capital costs and low investment outlay.

Perspectives of the Use and Development of the Elaborated Technology

The technology of the production of the hydrogenated bases of synthetic oligodecene oils elaborated by IPCP RAS jointly with "NIS" and OOO "Tatneft'Nizhnekamskneftechim-oil" (Technology I) is the basic (all-sufficient) technology, the owner of which will be able to produce hydrogenated bases of the synthetic oligodecene PAO-2, PAO-4, PAO-6, and PAO-10+ oils.

Some individual technical solutions on the base of the technology I (for example, the aperture split-tube reactor, the catalyst, and the hydrogenation technology), as well some secondary (additional and independent) technologies elaborated by ICPP RAS jointly with different organizations can be used as self-dependent.

They include the following:

II. The technology of metathesis of individual hexene-1, octene-1 and their mixtures to decene-5, tetradecene-7, and dodecene-6, respectively. Realization of the "Metathesis technology" will highly (by two or three times) increase variety of raw materials for the basic technology, reduce the prime cost of the oligoolefin synthetic oils, and increase the total technical and economic indices of the basic technology.

III. The technology of monoalkyl-benzenes production by benzene alkylation with decenes, dodecenes, and tetradecenes;

IV. The technology of di- and polyalkyl aromatic synthetic oils and heat carrier agents production.
When it is commercial necessarily, the use of the technologies II and III will allow the owner of the technology I (without any reconstruction, catalyst replacement, and practically without changing the basic process regime) to produce linear monoalkyl-benzenes (LAB) (a raw material for the household and technical surface active agents), as well di- and polyalkyl aromatic synthetic oils and heat carrier agents.

V. The technology of ethyl- and methyl- aluminumsesquichlorides $R_{1.5}AlCl_{1.5}$ (EASCh and MASCh) (components of cationic, metallocomplex, and metallocene catalysts) production;

VI. The technology of tret-butyl chloride $(CH_3)_3CCl$ (components of cationic catalysts) production;

VII. The technology of biphenyl sodium (a reagent for the qualitative express-analysis of organically bonded chlorine) production;

VIII. The technology of thermo, chemical, and catalytic dechlorination of organochloric compounds;

IX. The technology of hydrogenation;

X. The technology of PAO-2, PAO-4, PAO-6, and PAO-10+ compounding to the ready to use commercial oils.

Thus, the presented technology is universal in respect to the olefin raw materials, and it is versatile in the view of wide variety of the products. The technology allows using different catalysts, methods and regimes of the oligomerization what provides obtaining wide variety of PAO, LAB and PAB. The use of the complex metalloorganic catalysts (like $TiCl_4$ + EASCh) in this process allows converting decene-1 and other alpha-olefins to high-viscous PAO (like PAO-40 and PAO-100) which are not produced by anybody. Full or particular replacement decene to cycloolefins (cyclopentene, cyclohexene or cyclooctene) in the concerned process provides obtaining synthetic polynaphtene oils (which are not produced by anybody now).

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