

C₆ α -Olefins' Oligomers and Co-Oligomers as Synthetic Components for Petroleum Oils

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Abstract

This study investigated the results of double co-oligomerization of C₆ α -olefins with dicyclopentadiene and indene. Obtained oligomeric compounds of various molecular mass and composition, which were used as synthetic component of petroleum oils to improve their viscosity-temperature and anti-corrosive properties. The researches were carried out to substantiate that the possibilities of co-oligomerization in a directed synthesis are broad and that they could be used in the production of new oligomeric compounds with required properties in petrol chemistry.

Keywords

Co-Oligomers of α -Olefins, Co-Oligomerization, Viscosity-Temperature Properties, Anti-Corrosive Properties, Petroleum Oils

1. Introduction

Operating characteristics of oils, such as viscosity and viscosity-temperature properties specify possible temperature scope of their application since viscosity level defines viscosity grade of lubricating oils. The production of oils with improved viscosity-temperature characteristics is therefore one of the important problems in petrol chemistry.

The production of oils with better viscosity-temperature properties is usually carried out by adding polymeric compounds, namely viscosity-index improvers into their composition. However, during the operation cycle, viscosity-index improvers are being destructed under thermal and mechanical influence. The molecular mass of initial polymer decreases and viscosity of the thickened oil drops below acceptable level [1] [2].

The simplest and faithful way among the different ways of gaining the oil with

the good viscosity-temperature property is considered the usage of the viscosity admixtures—from the polymer combinations. Some polymers, such as polyisobutylenes, polyalkylmethacrylates, polyvinyl butyl ethers are used as the viscosity additives [3]-[9]. But the additives shown today are considered “classics” and they aren’t used, because they don’t meet the requirements of the modern technique.

Oligomerization products of C_8 - C_{12} α -olefins actually are used as synthetic oil [10] [11] [12].

In order to improve viscosity-temperature properties of petroleum oils and to avoid the shortcomings mentioned above, it was proposed to include into composition different synthetic components—relatively low-molecular polymers, e.g. oligomers and cooligomers of α -olefins that are not subjected to destruction during operations [13] [14] [15] [16].

Synthetic components, relatively low molecular weight oligomers of α -olefins ($M = 2000 - 5000$) are used at a concentration of 20% - 30%. Their price of the viscosity index is increased to 93 - 100 (according to the modern requirements, viscosity index price of the oils with kinematic viscosity at 100°C $8 \text{ mm}^2/\text{s}$ should not be less than 93). But, these components are not very resistant to thermal destructive influences.

However, the way to improve the viscosity-temperature properties of petroleum oils is not economically profitable, because it can improve only one property of the oils.

Copolymerization, a method of chemical modification, is used to impart the necessary properties (two or more) to polymer compounds. It is considered to be the simplest method of targeted synthesis. For this purpose, α -olefins (in particular hexene-1) are oligomerized with carbocyclic or vinylaromatic monomers.

Studies show that the involvement of aromatic fragments in the oligomeric chain increases their resistance to thermal influences, and the carbocyclic moiety imparts anticorrosive and depressant properties to petroleum oils.

The study of the thermo destructive properties of industrial oil I-12A with the addition of modified oligomers of α -olefins and industrial polyisobutylene (for example, KP-10) showed that the decrease of the viscosity for the first is in the range of 3.0% - 5.0%, and for the second it is in the range of -12.0% - 13%.

This article is also devoted to the preparation and the investigation of chemically modified α -olefins with carboxylic and aromatic monomers. Hexene-1 and 4-methylpentene-1 were used as α -olefins, and dicyclopentadiene as the carbocyclic monomer and indene as the aromatic monomer.

2. Experiments

2.1. Metodoljy of Co-Oligomerization of C_6 -Olefins with Dicyclopentadiene and Indene

For the synthesis of double co-oligomerization, hexene-1 and 4-methylpentene were used as initial C_6 -olefins. Their double cooligomers with dicyclopentadiene

[13] and indene [14] had been synthesized.

The process was methodically carried out as follows. In a three-necked flask equipped with a mechanical stirrer, thermometer and dropping funnel, the calculated amount of solvent (hexane or heptane) and catalyst were loaded. The reaction mixture was stirred while being cooled to the desired temperature. Then a mixture of the C₆-olefins with dicyclopentadiene (or indene) was fed through a dropping funnel in a certain ratio.

The feed rate of the mixture is adjusted so that the temperature rise does not exceed 1 - 2 °C. The reaction mixture is stirred until the temperature rises. The catalyst is then decomposed by the 1% - 3% solution of NaOH. The reaction mass is washed with a mixture of water-isopropyl alcohol to neutral medium, filtered, the solvent and light fractions are distilled off under vacuum. After that, the yield of the co-oligomers, their kinematic viscosity and molecular weight are determined.

2.2. Some Aspects of Co-Oligomerization of C₆-Olefins with Dicyclopentadiene and Indene

Co-oligomerization were carried out in the presence of catalyst AlCl₃ at -10 °C - 40 °C with dicyclopentadiene and at 20 - 40 °C with indene. At the catalyst concentration 0.1% - 0.3%, the yield of co-oligomer was insignificant. Increase of catalyst consumption to 0.5% - 0.8% resulted in the increase of the yield of the reaction product up to 80% - 93%. In this case, molecular mass value was not considerably changed; as ionic polymerization molecular mass value didn't depend on catalyst concentration. Further increase of catalyst consumption to 1% - 2% did not change the yield and molecular mass of oligomer. It was therefore decided to keep consumption of aluminum chloride within the range of 0.8% - 1.0% for α -olefin used in oligomerization (Figure 1).

Oligomerization of 4-methylpentene-1 resulted in the obtaining of higher molecular products than oligomerization of its unbranched analogue—hexene-1

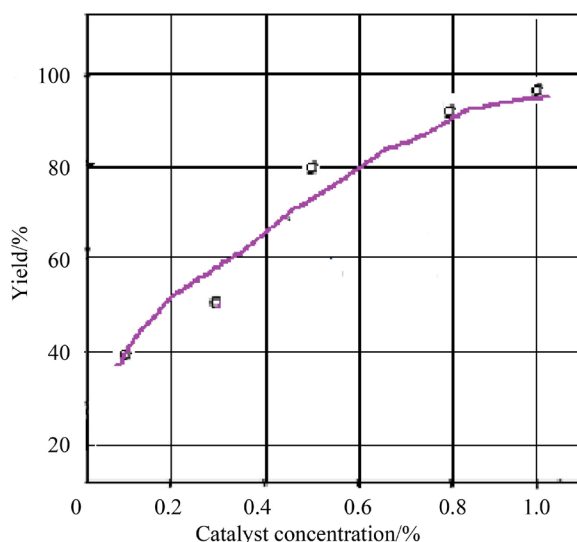


Figure 1. Dependence of co-oligomer's yield on catalyst concentration.

within similar conditions. It is explained by structural peculiarities of compounds. As a matter of fact, the activity towards cationic polymerization was raised by methyl groups, the strong electron-donors.

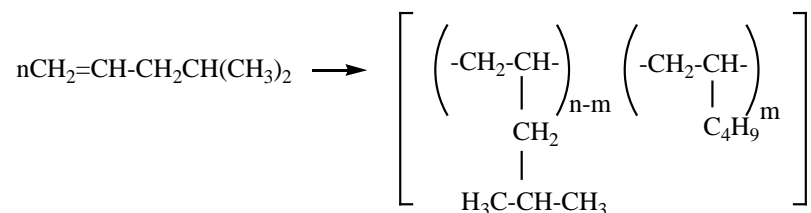
In case of hexene-1 methyl group was joined by third carbon atom with relation to double bond, while in 4-methyl-pentene-1 two methyl groups were joined by second carbon atom with relation to double bond that determines different behavior of indicated monomers during the reaction of oligomerization.

To enhance thermal stability of synthesized oligomers and to create an additional reaction centre for conducting chemical modification, parent α -olefins—hexene-1 or 4-methylpentene-1 were subjected to co-oligomerization with dicyclopentadiene and indene.

It was found that the insertion of the co-monomers into co-oligomerization with C_6 -olefins led to the reduction of molecular mass value. And it means the involvement of cyclic co monomers in restricting the length of oligomeric chain at the expense of alkylation.

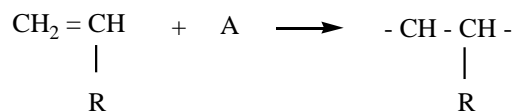
It should be pointed that both co-monomers of α -olefins are industrial products within reach that proves the reasonability of carried out investigations, since the interest to chemical product is strictly determined by the availability of raw material resources.

The obtained structures of the products were studied by IR- and PMR-spectroscopic methods. It was found out that links of 4-methylpentene-1 entered into oligomeric chain in rather isomerized form, like creating formation of co oligomer with hexene-1 and 4-methylpentene-1 links [3]:



Chemical bond between co-monomers' links is absent, *i.e.* as a result, we have obtained a pure co-oligomer with alternated monomer links that determined physicochemical properties of synthesized compounds included into lubricant oils.

In general, the reaction co-oligomerization may be represented as follows:



where $\text{R} = -\text{C}_4\text{H}_9$ or $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$



3. Results and Discussion

3.1. The Effect of the Co-Oligomers on Viscosity-Temperature Properties of Oils

The carried-out investigations have resulted in obtaining of co-oligomeric compounds with molecular mass about 700 - 2000 and outcome 87% - 93% depending on conditions of reaction and on the ratio of initial monomers.

Synthesized oligomers and cooligomers were examined as synthetic components of petroleum oils to improve their viscosity-temperature and anti-corrosive characteristics.

The effect of co-oligomers hexene-1 with dicyclopentadiene and 4-methylpentene-1 with and indene on viscosity-temperature characteristics of petroleum oil (M-6) is given (Table 1 and Figure 2). Viscosity-temperature properties of copolymers are determined in the thermostat of VIS-T-09-3 brand (Figure 3). This thermostat is designed to maintain the set temperature during measurements using glass viscometers in accordance with GOST 33, ASTM D445, IP 71, ISO 3104 and DIN 51366.

As indicated, co-oligomers at concentration 20% - 30% help to obtain basic oil (viscosity about 8 ± 0.5 mm²/sec at 100°C) with high viscosity index.

Table 1. Effect of cooligomers (molecular mass 1000) on viscosity-temperature characteristics of M-6 oil.

Cooligomer amount/%	Viscosity at temperature (°C)/(mm ² ·sec ⁻¹)		Viscosity index/I	Corrosion/(g·m ⁻²)
	40	100		
Cooligomer of hexene-1 with dicyclopentadiene				
0	39.14	5.8	80	180
5	44.80	6.2	82	160
20	67.10	7.9	90	90
30	70.00	8.5	94	42
40	74.70	9.0	96	5.0
50	79.10	9.9	101	4.6
Cooligomer of 4-methylpentene-1 with indene				
0			80	180
5			81	162
20			89	92
30			93	43
40			95	5.3
50			100	4.7

3.2. The Effect of the Co-Oligomers on Anti-Corrosive Properties of Oils

Note that co-oligomers with both dicyclopentadiene and indene links have anti-corrosive properties as well; at concentration 40% - 50%, corrosiveness of M-6 oil were completely eliminated (table and Figure 4). The anticorrosive properties of M-6 oil with added co-oligomers are determined in the DK-NAMI type device in accordance with GOST 13371-67 (Figure 5). The device is designed for testing according to GOST 20502-75 of lubricating oils (method for determination of anti oxidation and anti corrosive properties).

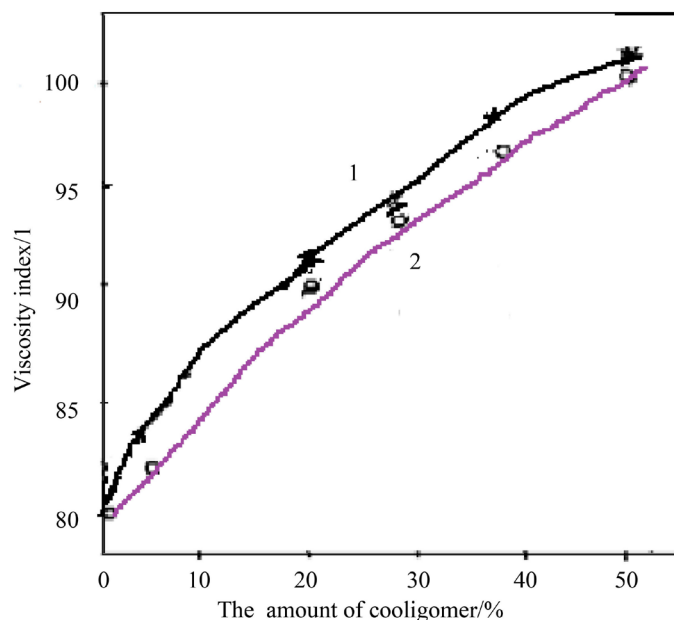


Figure 2. The effect of co-oligomer hexene-1 with dicyclopentadiene (1) and of co-oligomer 4-methylpentene-1 with indene (2) to Viscosity Index of the oil M-6.

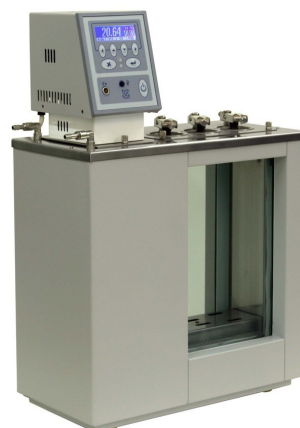


Figure 3. Thermostat VIS-T-09-3.

As proved [1], corrosiveness is the consequence of oxidation and is caused by oxidation products. Including carboxylic (dicyclopentadiene) and aromatic (indene) links into oligomeric chain causes chemical modification of the structure, and co-monomeric fragments impart anti-oxidative properties to the synthetic component. As a result of the above, the compound also acquires anti-corrosive properties.

4. Conclusions

In conclusion, the base oils with a high viscosity index were obtained by adding oligomers of hexene-1 and 4-methylpentene-1 and their co-oligomers with dicyclopentadiene and indene. The optimal percentage of oligomers and co-oligomers is 20% - 30%. In addition to viscosity-temperature properties, the

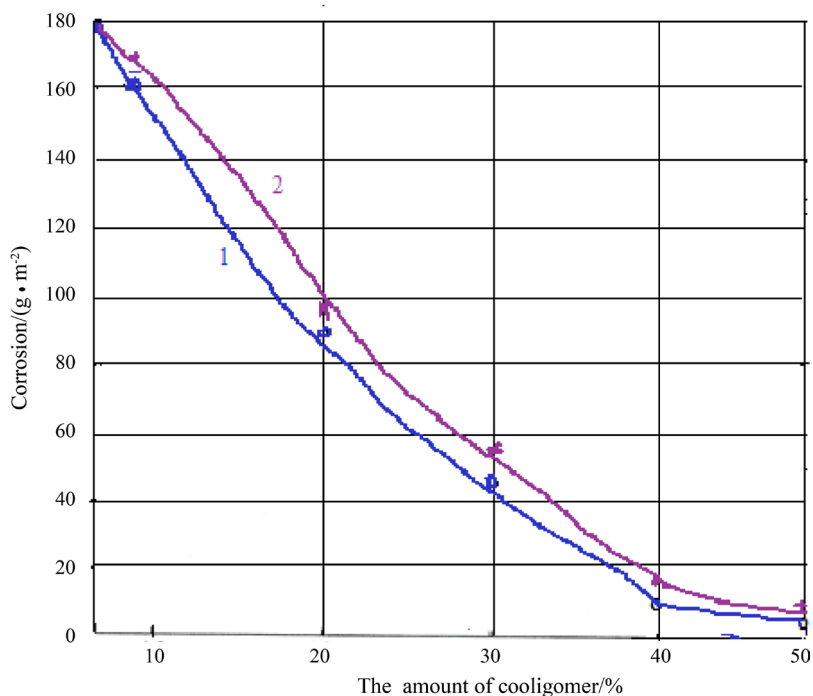


Figure 4. The effect of cooligomer hexene-1 with dicyclopentadiene (1) and of cooligomer 4-methylpentene-1 with indene (2) to Anti-corrosive properties of the oil M-6.



Figure 5. Apparatus for determination of anticorrosive properties.

anticorrosion characteristics of base oils are also improved. The investigation carried out indicates that synthesized oligomeric compounds slightly differ from each other in improving viscosity-temperature properties of distillate oils.

Synthesized oligomers and co-oligomers are also raw materials for the preparation of polyfunctional additives for lubricating oils [5].

Thus, by performing co-oligomerization of properly selected monomer pairs, a synthetic component having the action of a multifunctional additive without a functional group can be obtained. That is, the joint oligomerization is a method of chemical modification of the structure, which allows the directed synthesis of compounds with their functional characteristics.

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