

THE OBTAINING OF HIGH THERMOSTABLE SYNTHETIC OILS FROM OLIGOMERIZATION OF HEXENE-1

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Abstract

In the article thermal and thermo-oxidative stability of oil fractions (b.b. $\geq 350^{\circ}\text{C}$) obtained by oligomerization of hexene-1 in the presence of aluminium, dichloroethane based catalytic complex and bimetallic catalytic complex obtained from the modification of chrome salt has been studied. The differential scanning calorimetry curves of the synthesized oil fraction have been recorded in atmospheric medium. It has been established that in spite of the change at 174.49°C in thermal properties of oil obtained during the using of aluminium, dichloroethane based catalytic complex. And obtained oil fraction when the oligomerization of hexene-1 in the presence of the catalytic system modified with chrome salt up to 193.93°C is thermally stable. Study of thermal properties of investigated oligomer products shows that thermogravimetric curves in terms of character are similar, but the shift in thermal durability of oils obtained in presence of catalytic system modified with chrome salt is seen. In the case of taking aluminium based catalytic complex as a catalyst for oligomerization of hexene-1 maximum at 285°C in termogravimetric curve is recorded, the maximum at 330°C of decomposition velocity of oil obtained in presence of bimetallic catalytic complex have changed. It has been established by the conducted researches that oil fractions obtained by oligomerization of hexene-1 in the presence of bimetallic catalytic complex modified by chrome salt shows high thermostable property and are of special importance as qualified motor oils

Keywords: *lubricating oils, oligomerization, hexen-1, oligomeric products, thermostability*

Introduction

The replacing of machinery and engines with new ones, applying high qualified fuels to them for operating in effective and less harmful condition for environment are important factors. One of the important requirements in this field is the development of lubricant materials able to maintain the complex properties during changing of exploitation condition. The lubricant oils of future must meet the requirements of energy conservation and environmental protection, besides

low freezing point and volatility, must have high thermostability, viscosity index and flash point [1-5]. It should be noted that synthetic oils in comparison with mineral oils have a number of advantages. Polyalphaolefin (PAO) oils obtained by oligomerization of α -olefins have special place among synthetic oils. It is known that one of the most important issues in these synthesis is creating of catalytic systems with high activity and selectivity for increasing effectiveness of the process [6-9]. In this purpose the effective bimetallic catalytic complex (NCC/CrCl₃), have been formed from the modification of highly stable active new catalytic complex (NCC) with chrome salt, the composition and structure of catalytic complex have been investigated by modern physical methods [10]. Regularities of the oligomerization process of hexene-1 in the presence of bimetallic catalytic complex have been studied and established that it is possible to obtain oligomers characterizing with high yield and physical indicators, narrow molecule-mass distribution as a result of oligomerization. Oligomer products composition, physical and chemical properties have been investigated by using modern analysis methods [11]. The presented article is devoted to the results of the investigation of the heat and physical properties of oil fractions obtained from oligomerization of hexene-1 in the presence of bimetallic catalytic complexes obtained through modified NCC and CrCl₃.

Experimental Part

It should be noted that study of thermal-physical properties of oligomerization products obtained on the bases of α -olefins are of great importance. These properties has a great impact on the exploitation properties, especially thermooxidation properties of the synthesized oils in the result of the oligomerization process [12]. Thermostability property to oxidation of PAO oils obtained during the applying of aluminium based new bimetallic catalytic systems to oligomerization process of α -olefins have been investigated. For this, thermal and thermooxidation stability has been studied by differential scanning calorimetry (DSC) analysis of oil fraction (b.b. $\geq 350^\circ\text{C}$) obtained by oligomerization in the presence of NCC and NCC/CrCl₃ of hexene-1. Differential scanning analysis of synthesized oil fractions was carried out at Q-20 Thermoelectron Corporation (USA) at temperature range 100-500 °C, fever rate 10 d/min. in presence of air. The NCC and DSC curves of oligohexene fraction obtained with the presence of its modification are given in Fig. 1 (a) and 1(b). It is seen from Fig. 1(a) that in spite of the change at 174.49°C in thermal properties of oil obtained during the using NCC, maximum of broad halo effect have been registered at 323.98°C and it can be associated with the thermooxidation of the exo effect oil. We see absolutely different scene when the oligomerization of hexene-1 in the presence of the catalytic system modified with chrome salt is conducted (Fig. 1(b)). Oil up to 193.93°C is thermally stable and exo effetics in the values of further increase of temperature of 296.95; 332.69; 347.92 and 350°C attract the attention. The oxidation processes characterized with 5- exo effects in the place of halo curve in NCC shows that oils are not homogeneous for molecule masses and besides they have generally narrow molecular mass distribution.

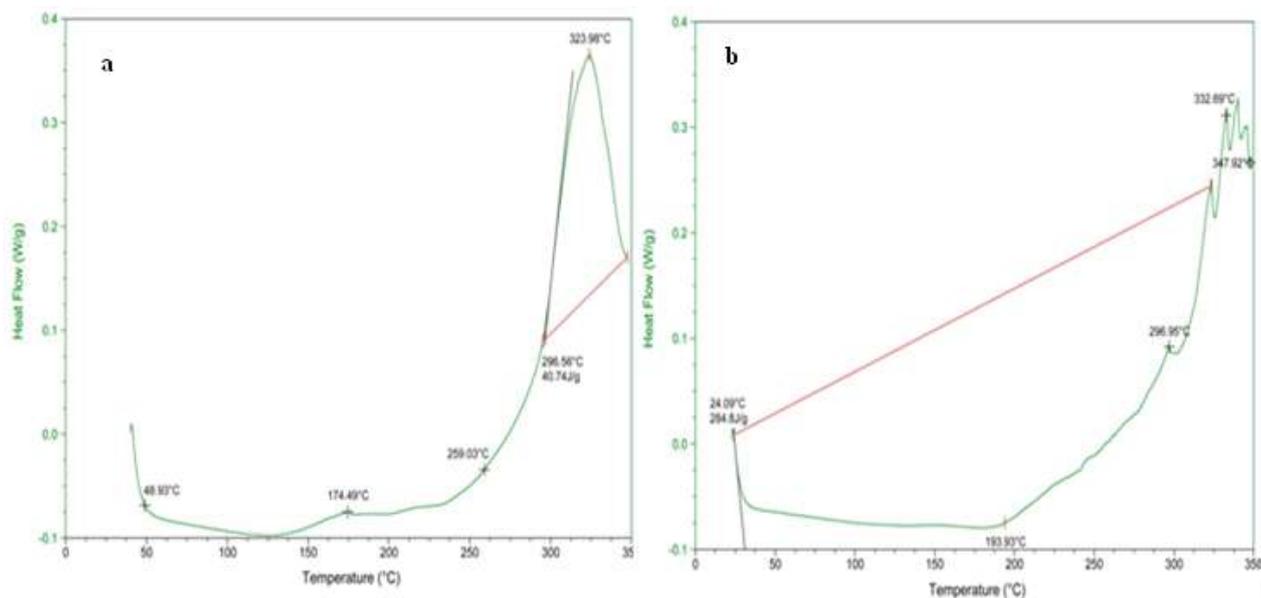


Fig. 1. DSC curves of the oil fractions obtained by the NCC (a) and NCC/CrCl₃ (b)

In order to study thermal properties of investigated oligomer products thermogravimetric (TG) and differential thermal analysis (DTA) methods have been used. Researches carried out in the air atmosphere at 10 °C / min speed of heating in the "STA Platinum Series" derivatograph; also at the diapasons of temperature 20-1000 °C in the dynamic and isothermal mode. Al₂O₃ used as a standart. The duration of the experiment is 200-400 minutes. As seen (Fig. 2(a,b)) thermogravimetric curves in terms of character are similar, but the shift in thermal durability of oils obtained in presence of catalytic system modified with chrome salt is seen. At the oil fraction b.s $\geq 350^{\circ}\text{C}$ which obtained in the presence of CTC through hexene-1 oligomerization, it observed endoeffect at the range of temperature 200-300 °C and 325-500 °C. The maximum of disintegration rate was observed at 285 °C. The decomposition of oil fraction which obtained in the presence of NCC/CrCl₃ through hexane-1 oligomerization, observed at the temperature range 210-370°C and 370-580°C by endoeffect. If to take NCC as catalyst for oligomerization of hexene-1 maximum at 285°C in DTG curve is recorded, the maximum at 330°C of decomposition velocity of oil obtained in presence of NCC/CrCl₃ have changed, in the result the different was 45°C (Fig. 2 (a,b)).

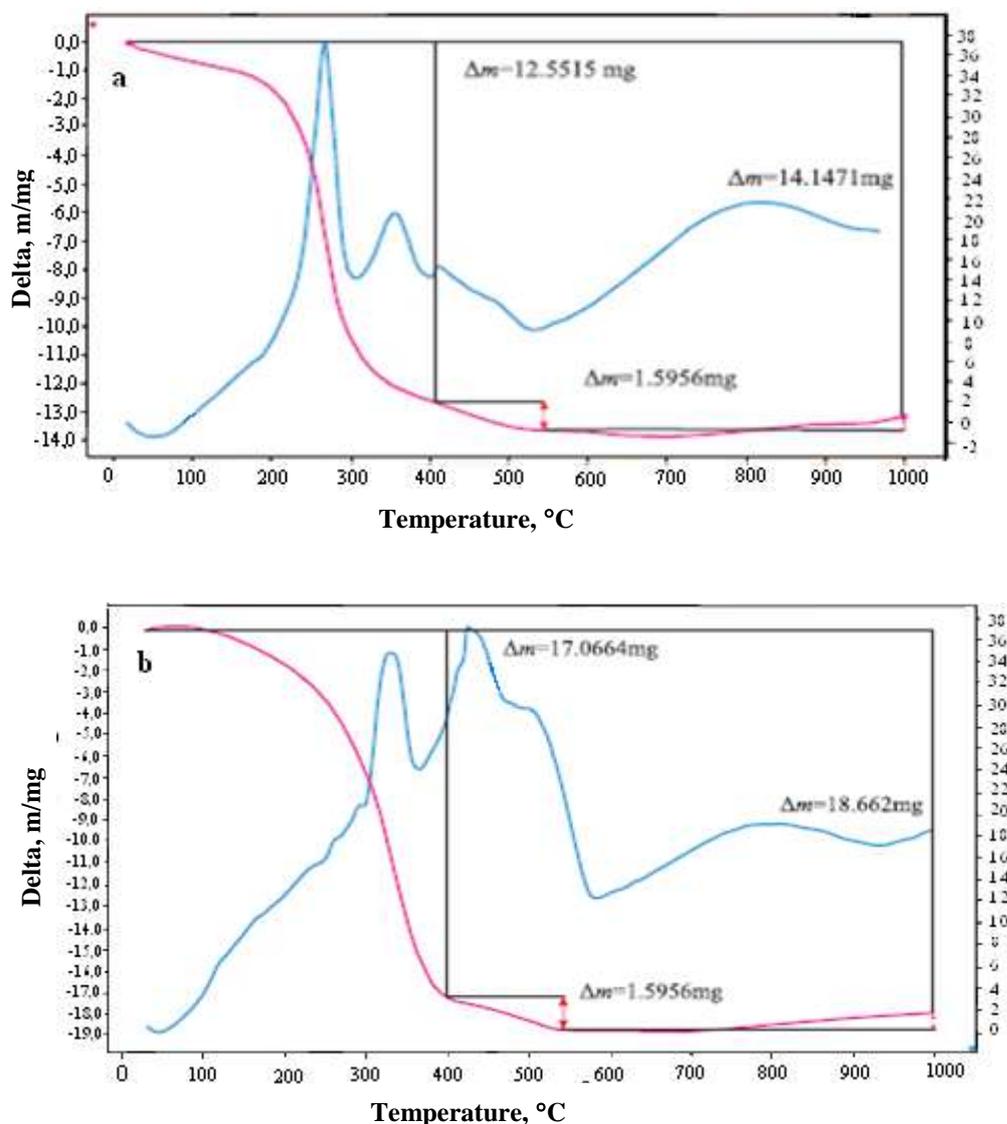


Fig. 2. Thermogravimetric curves of the oil fractions obtained by the a –NCC, b –NCC/CrCl₃

Results and Discussions

Tests on GOST 11063-77 have been conducted in order to study thermooxidation stability with amount of 300-450°C oil fractions precipitation synthesized at temperatures of 40°C, 50°C, 60°C in the presence of NCC/CrCl₃ catalytic complex and the the results were compare to T-46 mineral base oils shown below.

Table 1. Dependence on time of precipitation formation at 200°C in oil fractions of 300-450°C obtained at various temperatures (1-40°C; 2-50°C; 60°C)

Time, hours	Amount of sediment, % wt.			
	T-46 mineral base oil	Oil fractions obtained at different temperatures		
		1	2	3
10	0.8	0.033	0.03	0.022
20	1.5	0.04	0.037	0.034
30	2	0.053	0.049	0.045
40	2.25	0.067	0.055	0.061

As it is evident from the table, the precipitation amount in oil fractions is changed slightly depending on the time. The precipitation formed in 300-450°C oil fractions synthesized at 40°C, 50°C, 60°C during 40 hours amounts to 0.067%, 0.055%, 0.061% correspondingly. As a result of the studies carried out for comparison, it has been determined that the precipitation in the content of T-46 mineral base oil amounts to 0.8% - during 10 h, 1.5% - during 20 h, 2% - during 30 h and 2.25% - during 40 hours correspondingly.

Conclusion

Thermal and thermo-oxidative stability of oil fractions obtained by oligomerization of hexene-1 in the presence of aluminium, dichloroethane based catalytic complex and bimetallic catalytic complex obtained from the modification of chrome salt has been studied. According to the carried out studies, conclusion can be made that the oil fractions obtained by hexene-1 oligomerization has high thermostability in the presence of the bimetallic catalytic complex modified by chrome salt and they are of special importance as qualified motor oils.

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