



INVESTIGATION THE OLIGOMERIZATION PROCESS OF HEXENE-1

Ibragimov Hikmet Jamal Alizade Shahla Allahverdi., Amirov Fariz Ali., Aliyev Fariz Ramik
Institute of Petrochemical Processes named after Academician
Yu.H.Mamedaliyev, Baku, Azerbaijan.

Abstract

In article for oligomerization and alkylation processes, to obtain a useful and highly stable active catalyst, New Catalytic Complex (NCC) synthesized which is based on aluminum metal using $C_2H_4Cl_2$ and this complex has shown high stability in alkylation, oligomerization processes compared to other aluminum-containing catalysts. It is difficult to regulate the molecular mass distribution of received products during oligomerization, either Intensificate the oligomerization process of olefins that is why this process take place in presence of obtaining of bimetal catalytic complex with a highly stable activity from the modification of the New Catalytic Complex(NCC) with transition metal chloride. Comparatively studied oligomerization of Hexen-1 in present of new bimetallic catalytic complex which was modified by NCC and chromium salt ($NCC/CrCl_3$), effect of temperature, reaction time, concentration of the catalyst and the proportion of catalyst components (Al:Cr) in the process was investigated. It was determined that at the initial time (10 min) conversion hexene-1 and the yield of purposeful oil fraction were low. Increasing time, conversion rate of Hexen-1 increases and the optimal time for the process is considered as 60 minutes. In low concentrations of catalyst (0,1-0,3) oligomerization of hexene-1 is low but in high concentrations (>1%) reaction goes with high rate, at optimal concentration 0,5% mass both the yield of oil fraction and its chemical-physical properties were high. In oligomerization process investigated ratio effect of catalyst components Al: Cr that was used Al: Cr=(4-32):1 mol. It has been revealed that oligomerization of Hexen-1, at low mol ratio of components (4:1), received yield of oligomer fraction decreases while mol ratio increases (16:1, 32:1). Studies determined that bimetallic complex at 8:1 mole has shown the maximal activity in oligomerization process of Hexen-1. The effect of the temperature on the oligomerization process was studied in the range of 30-60°C, increasing the temperature up to 50 °C has a positive effect on the course of the process and despite providing complete oligomerization of hexene-1 its also providing increasing the amount of oil fractions with high viscosity. According to the researches, the optimal conditions for the oligomerization process of hexene-1 with the participation of the bimetallic catalytic complex: reaction time – 60 min., concentration of catalyst – 0,5 % by wt., mol ration of components Al:Cr = 8:1, temperature – 50 °C. In known optimal condition its possible to obtain oligomers with physical indications, characterized by narrow molecular mass distribution, by new catalytic complex that was modified by chromium salt. Such products have special importance, as low-freezing, high viscosity index qualitative engine oils. Synthesis of bimetallic catalytic complexes, with their presence in oligomerization of olefins and fractions, opens wide range perspectives in synthesis of different high-molecular compounds in industry.

Keywords: new catalytic complex; oligomerization; hexene-1, oligomers, synthetic oils

INTRODUCTION

Technical progress prevents the friction of different mechanisms, increasing the role of lubricants, as the most important elements of the technique, that's why different requirements for their quality are emerged and increased. Petrol oils (mineral oils) do not obey to modern technical requirements of exploitation.

In this regard, synthesis of multifunctional lubricants which must obey modern requirements is one of the main problems facing scientists. It is known that synthetic oils can be obtained by oligomerization and cooligomerization of α -olefins.

Nowadays widely used polyalphaolefin oils play a special and more important role in the production of new lubricants with high performance properties. Chemical composition of polyalphaolefin oil (PAOO) shows itself as wide molecular weight distribution characterized by branched long chain aliphatic hydrocarbons. These lubricants are distinguished by their high viscosity index, low freezing temperature, can be used in a wide range of temperatures ranging from -65°C to 230°, differing from mineral oils with high thermal stability. PAOO can be completely mixed with petrol oils; it is easily adaptable with additives, ecologically safe. This oils used as engine, aviation, transmission, white oils, refrigerators, vacuum-based oils, or oil lubricants such as base components.

It should be noted that processing of raw materials by modern methods allow to regulate physical and chemical properties of products at a wide range and improving new methods for the quality of oils.

EXPERIMENTAL

For oligomerization and alkylation processes, to obtain a useful and highly stable active catalyst, New Catalytic Complex (NCC) synthesized which is based on aluminum metal using $C_2H_4Cl_2$ and this complex has shown high stability in alkylation, oligomerization processes compared to other aluminum-containing catalysts. In this article presented intensification of the oligomerization process of olefins, regulation of molecular mass distribution of received products during oligomerization in presence of NCC, which is based on obtaining of bimetal catalytic complex with a highly stable activity from the modification of the NCC with transition metal chloride. For this purpose, a new bimetallic catalytic complex was synthesized by modifying NCC catalyst by Cr(III) chloride. The synthesis of bimetal complexes was carried out in situ with the introduction of metal compounds into the system at the time of the emerging radicals as a result of the interaction of Al+DCE. Influence of transition metals on catalytic centers in bimetallic complexes, their nature and structure were studied by physical methods.



RESULTS AND DISCUSSION

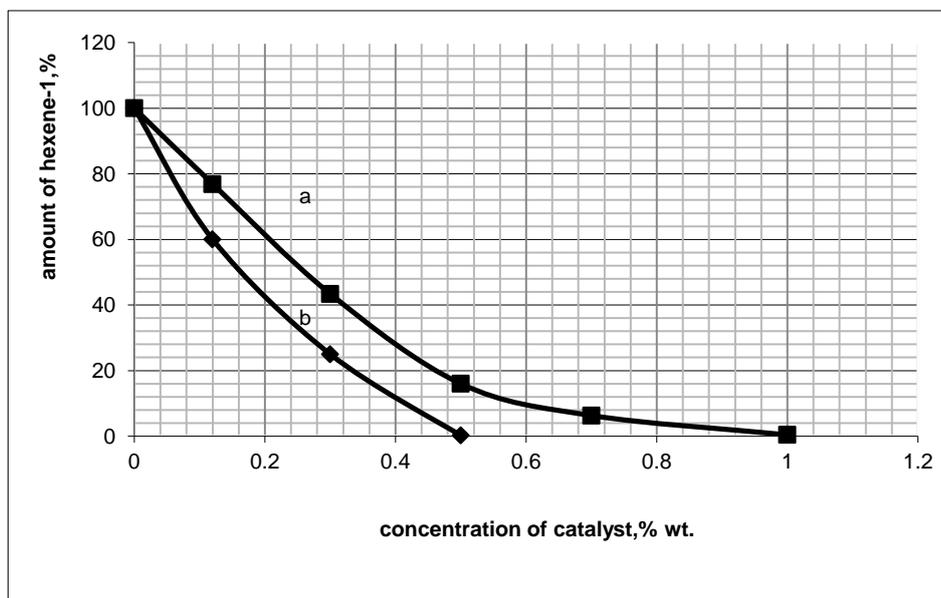
The synthesized bimetallic catalytic complex was studied in the oligomerization process of hexene-1. The oligomerization of hexene-1 with the presence of NCC and NCC/CrCl₃ was comparatively studied; effect of temperature, reaction time, concentration of the catalyst and the proportion of catalyst components (Al:Cr) in the process was investigated.

Table 1. The effect of reaction time in oligomerization process of hexene-1 with the presence of NCC/CrCl₃ (concentration of catalyst – 0.5% wt., temperature - 50°C)

Reaction time min.	Yield of oligomerization product, %				Loss, %
	Fr.300°C	Fr.300-350°C	Fr.350-450°C	Fr.450°C	
10	58	22,5	16	2	1,5
20	49,7	19,7	22,8	5	2,8
30	38	17,8	36	7	1,2
40	25,5	20	46,6	5,8	2,1
50	11,6	29,5	52	4,1	2,8
60	7	34	54,4	3,4	1,2
70	6,8	33	55,3	3,6	1,3

As seen from Table 1, at first 10 min. transformation of hexene-1 is low and therefore, the T_{≤300°C} fraction predominates at the oligomerization product. Increasing the reaction time increases the yield of high molecular weight oligomers and fraction of 300-450°C in 60 min. has maximum yield of the oil fraction. Increasing time does not practically affect the process and the optimal time for the process is 60 min. may be considered.

During the experiments, it is identified that the rate of oligomerization hexene-1 directly depends on the catalyst's concentration (picture 1).



**Figure 1. The effect of catalyst concentration in oligomerization of hexene-1:
a- NCC; b- NCC/ CrCl₃**

As shown in the figure, at low concentrations of catalysts NCC and NCC/ CrCl₃ (0.1%) the oligomerization of hexene-1 has proceeded weak and the yield of oligomerization products is between 40-60%, depending on the nature of the catalytic system. As a result of increasing the amount of catalysts in the system, the oligomerization process is



accelerating and the complete conversion of olefins is achieved at 0.5-1.0% by wt. concentration. Should be noted that the bimetallic catalytic complex is more active in this process compared with NCC and provides quite high activity in low concentration (0.4-0.5%), providing hexene-1 practically full oligomerization. Giving more than 1.0% of the catalyst concentration to the system causes oligomerization of hexene-1 and the process can not be controlled.

Influence of Al : Cr ratio on oligomerization process included in various bimetallic complex studied in 1 mol ratio Al:Cr $r = (4-32): 1$ (Picture 2).

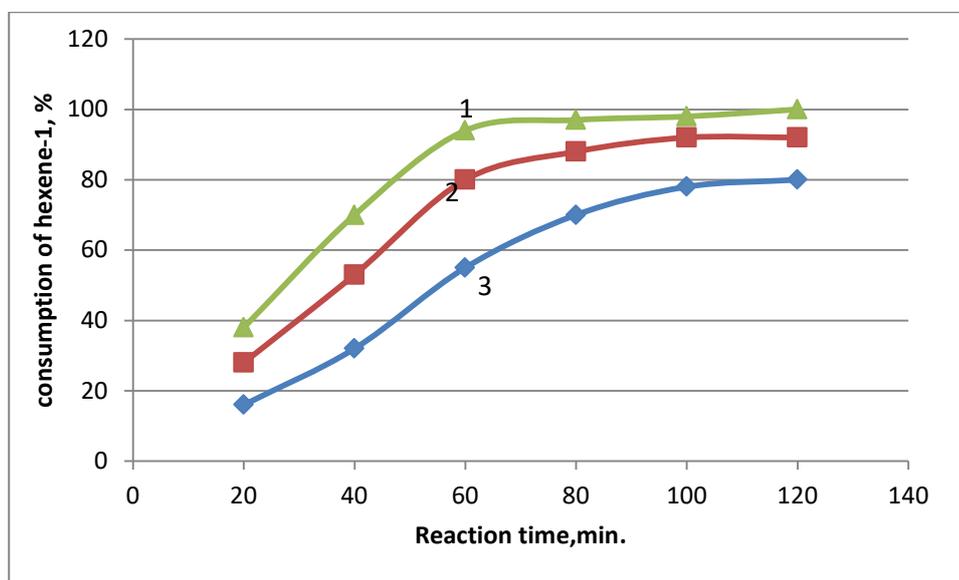


Figure 2. The dependency of different mole ratios (1 – Al:Cr = 8:1; 2 – 16:1; 3 – 32:1) on the oligomerization time of hexene-1 with the presence of NCC/CrCl₃

In low mole ratio of components (4:1) metal salt, which forms the complex, provides complete formation of bimetal centers, but the remaining CrCl₃ precipitate from the system as a mechanical mixture. The catalytic complex obtained at this ratio also shows itself in the process of oligomerization of hexene-1, the yield of the received oligomer fraction decreases sharply. It has been determined that bimetallic complex with 8:1 mol is the most active in oligomerization process of hexene-1 (Pic. 1) and oligomerization product of hexene-1 decreases as this ratio increases from (8:1) to (32:1). Note that, based on experiments; it was found that the conversion of 32:1 mole was slightly different from the transformation of hexene-1 by the presence of NCC.

In oligomerization process, the effect of the temperature was investigated in 30-60°C interval. Experimental results show that increasing temperature to 50°C has a positive effect to the process and not only guarantees complete oligomerization of hexene-1, it also provide increasing amount of oil fraction which has high viscosity (table 2).

Table 2. Effect of temperature to oligomerization of hexene-1 in presence of NCC/CrCl₃ (concentration of catalyst – 0.5% wt., reaction time – 60 min.)

Temperature, °C	Conversion, % wt..	Yield of oligorimation product, % wt.				Loss, % wt.
		<300°C	300-350°C	350-450°C	>450°C	
30	60	5,1	30,7	48,4	12,6	3,2
40	72	6,2	32,1	50,3	8,3	3,1
50	100	7	34	54,4	3,4	1,2
60	100	8,3	31,2	57	2,1	1,4

At its seen from table 2, the maximum yield of 300-450°C and >450°C oil fractions in the presence of NCC/CrCl₃ oligomerization process is observed at 50°C and the result is 91.8%.

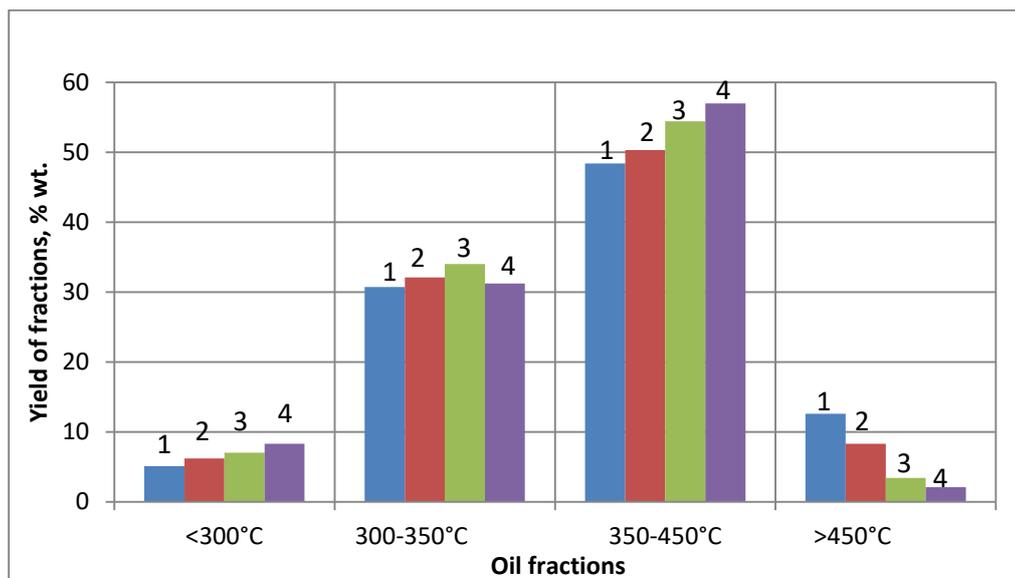


Figure 3. Yield of oil fractions from oligomerization of hexene-1 at different temperatures (1 - 30°C, 2 - 40°C, 3 - 50°C, 4 - 60°C)

CONCLUSION

According to the researches, the optimal conditions for the oligomerization process of hexene-1 with the participation of the bimetallic catalytic complex: reaction time – 60 min., concentration of catalyst – 0.5 % by wt., mol ration of components Al: Cr = 8:1, temperature – 50°C.

As it is shown in the table below (Table 3) detected that, it is possible to obtain oligomers with physical indications, characterized by narrow molecular mass distribution which obtains at optimum conditions by new catalytic complex that was modified by chromium salt.

Table 3. Data of products that results from oligomerization of hexene-1 in present of NCC and NCC/CrCl₃ (concentration of catalyst – 0.5% mass., reaction time – 60 min., temperature – 50°C)

Indicators of T>350 °C oil fraction	Catalysts	
	NCC	NCC/CrCl ₃
Yield, % (depending on total amount of oligomerization product)	84	92
Density	0,8334	0,8366
Viscosity, mm ² /sec., 100 °C	4,3172	6,488
Viscosity index	120	122
Refraction index	1,4625	1,4632
Iodine unit, grY/100gr	5,14	4,55
Flash point, °C	220	234
Freezing point, °C	-48	-43

Thus, with the presence of aluminum based bimetallic catalytic system, during the oligomerization process allows to get more superior physical-chemical properties of oil fraction, which can use as quality engine oils.



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