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INCREASING THE YIELD OF POLY-α-OLEFIN OIL

R. Sh. Kuliev

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Synthetic lubricants are increasingly widely used in technology, especially in automotive transport, where poly-α-olefin (PAO) oils are preferred [1 – 4]. The highest quality lubricants of the SHPD class are manufactured with these oils for diesel engines [5]. With lower consumption of PAO oil, the cleanness of carburetor engines is better, consumption of additives is slowed, and they combine better with elastomers [4].

Feedstock cannot be totally converted into oil when they are manufactured by polymerization of α-olefins in the presence of aluminum chloride as catalyst. The yield of oil as a function of the feedstock is 74.5 – 83 wt. % (Table 1) and does not exceed 83% even in polymerization of individual α-olefins [6].

We investigated the possibility of increasing the yield of PAO oil in polymerization of α-olefins on $AlCl_3$ catalyst. $C_8 - C_{14}$ α-olefins distilling within the limits of 140 – 240°C obtained by cracking of waxes were used as the feedstock.

The α-olefin and olefin-containing hydrocarbons were polymerized in previously determined optimum conditions [7]: amount of catalyst: 4 wt. % in α-olefins; temperature: 30°C; contact time: 3 h.

The possibility of polymerization of α-olefins contained in <350°C cuts and these cuts together with α-olefins was verified. It was found (Table 2) that as a result of three-stage polymerization of α-olefins, the

TABLE 1

Polymerization feedstock — α-olefins			PAO oils				
Method of production	cutpoints, °C	composition	yield of <350°C target cut, wt. %	viscosity at 100°C, mm^2/sec	viscosity index	solid point, °C	molecular weight
Cracking of waxes	140–240	$C_8–C_{14}$*	74.5	32.5	120.0	–28	889
Oligomerization of ethylene	65 – 240	$C_6–C_{14}$**	81.5	33.0	122.0	–18	893
Accurate fractionation	–	C_9H_{18}	74.5	32.8	120.7	–28	890
Same	–	$C_{10}H_{20}$	77.8	35.6	121.3	–28	890
Same	–	$C_{11}H_{22}$	80.1	37.7	120.3	–28	890
Same	–	$C_{12}H_{24}$	82.5	37.7	120.5	–28	890
Same	–	$C_{13}H_{26}$	83.0	40.9	120.8	–36	910

Notes. * Contains hydrocarbons, wt. %: α-olefinic, 81.7; olefinic, 11.2; paraffinic, 7.1.
** Contains hydrocarbons, wt. %: α-olefinic, 95; olefinic, 3.7; paraffinic, 1.3.

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TABLE 2

Indexes	Degree of polymerization		
	first	second	third
Group hydrocarbon composition of <350°C fraction, wt. %			
paraffins	44.6	74.3	99.5
olefins	47.3	19.4	0.4
dienes and cycloolefins	4.1	3.8	0.1
trienes	0.9	0.7	None
alkylbenzenes	2.8	1.7	None
alkenylbenzenes	0.3	0.1	None
Yield of cut, wt. %			
<350°C in initial olefins	–	28.9	20
target > 350°C			
in <350°C cut	–	71.7	30.3
in initial olefins	74.5	16	6
Physicochemical properties of PAO oil			
viscosity at 100°C, mm^2/sec	32.50	22.16	20.14
viscosity index	120	120	118
solid point	–28	–34	–36
molecular weight	889	879	868
color, STC units	4	3	3

TABLE 3

Degree of polymerization	Taken, wt. %		Obtained, wt. %		Physicochemical properties of PAO oil			
	<350°C cut from preceding polymerization	α -olefins	<350°C cut	>350°C target cut in olefins	viscosity at 100°C, mm2/sec	viscosity index	solid point, °C	color, STC units
First	22.5	77.5	24.5	93.5	32.61	120	–28	4
Second	24.5	77.5	23.5	96.2	32.60	120	–28	4
Third	23.5	76.5	21.5	97.3	32.59	120	–28	4
Fourth	21.5	78.5	20.7	97.4	32.58	120	–28	4
Fifth	20.7	79.3	20.3	97.5	32.75	120	–28	4
Sixth	20.3	79.7	20.3	97.5	32.75	120	–28	4

concentration of olefin hydrocarbons in the <350°C cut decreased from 47.3 to 0.4 wt. % and the concentration of paraffinic hydrocarbons attained 99.5 wt. %.

The yield of the >350°C cut of PAO oil increased from 74.5 wt. % after one-stage polymerization to 96.5 wt. % after three-stage polymerization. The oils obtained after the second and third stages differed from

TABLE 4

Degree of polymerization	Group hydrocarbon composition of <350°C cut, wt. %					
	paraffins	olefins	dienes and cycloolefins	trienes	alkylbenzenes	alkenylbenzenes
First	44.6	47.3	4.1	0.9	2.8	0.3
Second	73.8	19.4	3.8	0.6	2.2	0.1
Third	79.17	15.8	2.8	0.4	1.8	0.03
Fourth	84.47	11.3	2.4	0.4	1.4	0.03
Fifth	90.17	6.4	2.0	0.3	1.1	0.03
Sixth	98.30	None	1.2	0.1	0.4	None

TABLE 5

Initiator content in feedstock, wt. %	Physicochemical properties of initiator		Yield of PAO oil, wt. % in olefins	Physicochemical properties of PAO oil		
	molecular weight	*n*-paraffin content		viscosity at 100°C, mm^2/sec	viscosity index	solid point, °C
			Polymerization feedstock			
15	160	99.7	95.8	63.8	133	–28
20	160	99.7	97	47	125	–28
25	160	99.7	97	38.6	122	–28
20	150	89	97	37.5	122	–28
			C_8-C_{14} olefins			
20	160	99.7	97.5	38.6	123	–28
20	150	89	97.1	38	120	–28
20	100	100	80	59.8	130	–28
			C_6-C_{14} olefins			
20	160	99.7	97.1	38.7	123	–28
20	150	89	97.1	38.3	121	–28

the oil obtained after the first stage due to the lower viscosity and molecular weight, lower solid point, and slightly better color, while the viscosity index was on the same level.

The results of polymerization of the <350°C cut mixed with α-olefins in catalyst consumption of 4 wt. % in α-olefins are reported in Table 3. To obtain 97.5 wt. % PAO oil, it was necessary to conduct five polymerization cycles. The oils obtained after each cycle had almost the same physicochemical properties.

As Table 4 suggests, after the fifth polymerization cycle, the concentration of unsaturated hydrocarbons in the <350°C cut decreased from 55.4 to 9.83 wt. % and was a total of 1.7 wt. % after the sixth cycle. Paraffinic hydrocarbons accumulated in the light cuts in polymerization of the <350°C cut with recirculation. After the sixth cycle, it reached 98.3 wt. % or approximately 20 wt. % in polymerization feedstock.

It also follows from Tables 3 and 4 that the paraffinic hydrocarbons contained in α-olefins in the amount of 18 – 20 wt. % intensify the polymerization process. For this reason, we investigated the possibility of increasing the yield of PAO oil by adding paraffinic and naphtheno-paraffinic hydrocarbons to the system. Individual $C_{13}H_{26}$ α -olefin and mixtures of $C_8 - C_{14}$ and $C_6 - C_{14}$ α -olefins were used as feedstock.

Polymerization was conducted in the optimum conditions indicated above with addition of a mixture of paraffinic hydrocarbons with a mol. wt. of 160 containing 99.7% *n*-paraffinic, or naphtheno-paraffinic hydrocarbons with mol. wt. of 150 obtained in alkylation of the 140 – 200°C crude oil cut. The results of polymerization in the presence of initiator additives are reported in Table 5.

Addition of an initiator increased the yield of PAO oil to 97 – 97.5 wt. %. The optimum initiator content is 20% in olefins. Initiators of the paraffinic and naphtheno-paraffinic base should have a minimum mol. wt. of 150. In their presence, the viscosity of the oil increases while the other quality indexes remain high.

The yield of PAO oil can thus be increased to 97.5 wt. % with the following methods:

- three-stage polymerization of the <350°C cut separated by atmospheric-vacuum distillation from the polymerizate;
- polymerization with six-fold recirculation of the <350°C cut;
- polymerization of α -olefins mixed with paraffinic or naphtheno-paraffinic hydrocarbons with a minimum mol. wt. of 150.

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