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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Preparation of Synthetic White Oils Based on C_3 Olefin

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Abstract—The preparation is reported of synthetic white oil based on propene and propane–propene fraction of catalytic cracking gases. The influence of temperature and composition of the catalytic complex in oligomerization of C_3 olefin on the principal properties of oligomers (kinematic viscosity, molecular weight, iodine number), their fractional and structural composition, and propene conversion was examined. The main parameters of hydrogenation of propene oligomers were determined. The hydrogenated propene oligomers prepared were tested as a base of white hydraulic, brightening, compressor, cable, and other oils meeting the requirements of world standards.

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Growth of the aviation fleet, increase in production of polyethylene, polypropylene, polystyrene, and chemical fibers, and development of electrotechnical industry require growing amounts of high-quality white aviation, hydraulic, compressor, cable, and brightening oils. The common requirements to such oils are the absence of taste, color, and odor, of sulfur-containing and aromatic compounds, and of organic and inorganic impurities. There are also specific requirements determined by operation conditions.

It is rather difficult to prepare white oils on the petroleum base because of shortage of naphthene-based crudes like Balakhan crude. Special distillate of this crude was used previously as a base of AMG-10, RM, and RMTs oils. The use of crudes of other compositions requires involvement of additional processing steps to obtain dearomatized oils. Along with these problems, production of white oils by the traditional route involves environmental problems associated with the use of acid–base contacting. The use of hydrogenation methods in several steps does not ensure the required quality of white oils and requires afterpurification with refining earths.

For example, performing three-step hydrogenation of raffinate of improved purification from the vacuum distillate of Balakhan heavy crude allowed the content of aromatic hydrocarbons to be decreased to only 7.83% [1]. Further treatment of the hydrogenizate with oleum and afterpurification with an adsorbent allowed preparation of white oil meeting the requirements of the standard.

It is known that processing of olefins yields oligomers which, after hydrogenation, can be used as a base of white oils [2]. Homogeneous and heterogeneous catalytic systems are used for oligomerization of propene. The processes differ in the yield of oligomers, selectivity with respect to target fractions, fraction composition, molecular-weight distribution, and raw material conversion.

Along with the above requirements, the catalyst should effect oligomerization without side reactions such as isomerization, metathesis, alkylation, and aromatization. Aromatization is particularly undesirable, because the base of white oils should not contain aromatic hydrocarbons.

Taking into account these facts, we chose $AlCl_3$ as oligomerization catalyst. It is known that $AlCl_3$ is used in the form of complexes, as a powder, as aluminum chloride dispersions, and also as a heterogeneous catalyst. The complex of $AlCl_3$ with chlorinated hydrocarbons (or water) and aromatic hydrocarbons, known as Gustavson complex, was studied in oligomerization of butenes and their fractions [3, 4].

EXPERIMENTAL

The $AlCl_3$ complex and its various modifications were examined in oligomerization of propene and propane–propene fraction (PPF).

Experiments on oligomerization of propene and PPF were performed on batch and continuous laboratory installations differing in the volume of reactors (from 1.5 to 3.5 l) and in the mode of oligomerizate take-off [5]. Pilot batches of olefin oligomers were prepared on a semicommercial installation with a reactor volume of 280 l.

Hydrogenation of oligomers was performed on an experimental installation with reactor volumes of 0.1 and 1 l. Pilot batches of hydrogenated oligomers were prepared on an installation with reactors of volume 0.025 and 0.075 m^3, operating in series. Fractional distillation of the oligomers and hydrogenated oligomers was performed on a laboratory vacuum installation at a residual pressure of 4–10 mm Hg. Fractional distillation of the pilot batches was performed on an installation consisting of a 50-l still and a 1.9-m packed column, at a residual pressure of 10–53 mm Hg.

As a raw material we used propene C_3H_6 from an EP-300 installation (main substance content 99.8 vol %) and PPF from a catalytic cracking installation with a propene content no less than 65 vol %.

The structure of propene oligomer (PO) and hydrogenated propene oligomer (HPO) samples was studied by IR spectroscopy with UR-20 (Carl Zeiss, Jena), Specord 75-IR, and IKS-29 spectrophotometers and by ^1H NMR spectroscopy with a Tesla BS-497 spectrometer at room temperature [6].

Studies showed that the oligomerization process and the properties of oligomers of a definite molecular-weight distribution are influenced not only by the composition of the catalytic complex (CC), but also by the component ratio and process conditions, especially temperature [7].

We examined the influence of temperature and CC composition on the main properties of oligomers (kinematic viscosity, molecular weight, iodine number), their fractional composition, and propene conversion. We found that the CC consisting of $AlCl_3$, toluene, and water in a 1 : 3: 0.3 ratio ensures the maximal conversion of propene (96–98%) at a concentration of 2.5×10^{-3} mol of $AlCl_3$ per mole of C_3H_6 (Fig. 1). The conversion of propene in oligomerization of PPF containing 65–75% propene was 90–95%. At a lower concentration of propene in PPF, the conversion drastically decreased. With an increase in the oligomerization temperature from 60 to 100°C, the viscosity and molecular weight decreased, and the iodine number increased.

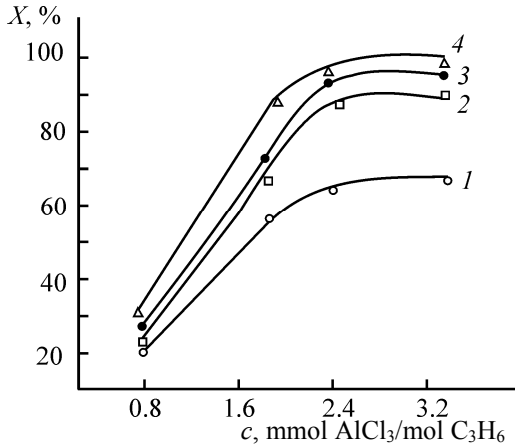

Fig. 1. Dependence of the C_3H_6 conversion X on the concentration of $AlCl_3$ incorporated in various catalytic complexes: (*1*) $AlCl_3 + C_2H_5Cl$, (*2*) $AlCl_3 + C_2H_4Cl_2 + C_7H_8$, (*3*) $AlCl_3 + C_2H_5Cl + C_7H_8$, and (*4*) $AlCl_3 + H_2O + C_7H_8$.

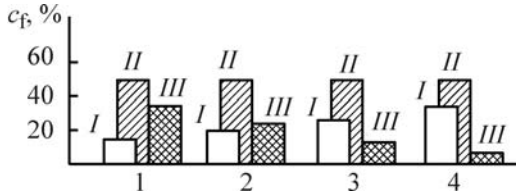

Fig. 2. Fractional composition of POs (c_f) prepared with the complex $AlCl_3 + H_2O + C_7H_8$ at different temperatures. T, °C: (1) 60, (2) 80, (3) 100, and (4) 120. Fraction, °C: (*I*) onset of boiling to 320, (*II*) 320–420, and (*III*) >420.

An increase in the temperature leads to an increase in the relative amount of low-boiling fractions boiling at temperatures of up to 320°C, whereas the amount of fractions boiling at 320–420°C varies insignificantly and the amount of the fraction boiling above 420°C appreciably decreases (Fig. 2).

The POs prepared on all the CCs at 120°C contain tars formed by PO oxidation. Therefore, performing oligomerization at this temperature is not appropriate, taking into consideration the next step of the process, hydrogenation. Tarry impurities in the oligomer may poison the hydrogenation catalyst. In view of this fact, and also taking into account the necessity for preparing target oil fractions of definite fractional composition

Table 1. Influence of the Mg content in CC on the fractional composition and properties of POs

Mg content, wt %	Oligomerization temperature, °C	Fractional composition, %			ν_{50}	MW	IN
		onset of boiling –320	320–420	>420			
2	60	32	47	21	21,4	390	44
2	80	39	48	13	16,8	350	58
2	100	41	52	9	12,2	330	66
3	60	31	49	20	20,6	380	43
3	80	36	52	12	16,2	350	60
3	100	38	54	8	12,0	330	68
5	60	32	49	19	20,4	380	44
5	80	36	53	11	16,0	350	60
5	100	38	54	8	12,0	330	66

Table 2. Composition of POs and their fractions taking into account the type of olefin groups

POs and their fractions	Content of olefin groups				
	Tetrasubstituted	Trisubstituted	Disubstituted	Vinylidene	Vinyl
Initial. prepared on CC $AlCl_3$+ C_7H_8+ H_20	0.38	0.27	0.12	0.17	0.06
220–320ºC	0.20	0.30	0.12	0.26	0.12
320–370ºC	0.54	0.14	0.10	0.14	0.04
>370ºC	0.42	0.32	0.18	0.11	0.07
Initial. prepared on CC $AlCl_3$+C_7H_8+ H_20+Mg	0.16	0.24	0.26	0.26	0.08
220–320ºC	0.08	0.26	0.26	0.26	0.14
320–370ºC	0.28	0.26	0.20	0.18	0.08
>370ºC	0.30	0.28	0.18	0.16	0.08
Initial. prepared on CC $AlCl_3$+C_7H_8+H_20+ $MgCl_2$	0.58	0.18	0.10	0.08	0.06
220–320ºC	0.26	0.28	0.18	0.16	0.12
320–370ºC	0.58	0.18	0.08	0.12	0.14
>370ºC	0.52	0.14	0.08	0.18	0.08

and molecular-weight distribution, the oligomerization temperature of 80–100°C was taken as optimal. The POs obtained in this temperature interval differ in the content of fractions. For preparing hydraulic oils, it is appropriate to perform the oligomerization at 100°C, whereas a lower temperature, 80°C, is preferable for preparing heavy fractions.

We examined the effect of modifiers (Mg and $MgCl_2$) added to the CC on the propene conversion and on the fractional composition and properties of the oligomers obtained [kinematic viscosity at 50°C (ν_{50}), molecular weight (MW), iodine number (IN)]. The modifiers were added to the chosen optimal composition of the CC in an amount from 2.0 to 5.0 wt %. The propene oligomerization was performed at 60, 80, and 100°C. The fractional composition of the oligomer and its principal properties given in Table 1 show that addition of Mg into the CC increases the selectivity of formation of the light fraction boiling below 320°C, but an increase in its amount to 5.0% affects the fractional composition of the PO insignificantly. Thus, the minimal content of Mg (2%) is sufficient for performing the process so as to obtain the maximal

amount of the fraction boiling below 320°C. That is, the use of the Mg-containing CC is efficient for preparing lighter oils boiling below 320°C. With this additive, the amount of this fraction increases by a factor of 2, and the amount of the fraction boiling above 420°C decreases from 25–26 to 11–13%. It should be noted that addition of Mg to the CC leads also to a decrease in the temperature at which the PO starts to boil from 200 to 150–160°C, i.e., from this fraction it is possible to recover oligomers for preparing a component of propellants (of TS-1 or T-1 type) or diesel fuels boiling in the range 150–280°C or from the onset of boiling to 360–370°C.

We examined the effect of $MgCl_2$ added to the CC on the propene oligomerization. In this case, the resulting POs contain a large amount of high-boiling fractions, i.e., the use of CC containing $MgCl_2$ is appropriate if it is necessary to prepare bases of white oils of cable oil type, with a viscosity of 11 $mm^2\ s^{-1}$ and higher at 100°C.

The use of both modifiers does not decrease noticeably the propene conversion: It remains on the level of 95–96%. However, their content affects the process selectivity and the fractional composition of the POs. With the modifiers, the process temperature is lower than without them. This allows preparation of POs containing no tarry products which can be formed at an oligomerization temperature of 120°C.

A study of the structural-group composition of the oligomers obtained showed that the POs are mixtures of isoolefins with different positions of the double bond and following modes of monomer addition:

Head-to-head (H–H), 740 cm^{-1}

$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-$$

Head-to-tail (H–T), 780 cm^{-1}

$$-CH-\underset{\displaystyle CH_3}{\underset{|}{CH_2}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-$$

In the products, the double bond is located at carbon atoms forming the vinyl, vinylidene, di-, tri- and tetrasubstituted bonds. Similar structural fragments also characterize the PO fractions. The difference consists in the presence of isoolefins with definite structural fragments in different ratios, and correspondingly the main properties of the oligomers are different.

From the integral intensities of signals in the NMR spectra, we estimated the relative amounts of hydrocarbons containing different fragments with the double bond.

The composition of the PO prepared under the optimal conditions with the $AlCl_3$-based CC and with Mg and $MgCl_2$ modifiers at the oligomerization temperature of 80°C (Table 2) shows that the PO and its fractions differ in the content of hydrocarbons with different types of olefin fragments. This fact indicates that, by varying the CC composition and oligomerization temperature, it is possible to control the structural composition of the POs, so as to ensure the required physicochemical and service properties.

As seen from Table 2, introduction of Mg into the CC leads to a decrease in the content of tri- and tetrasubstituted structures, and oligomerization occus in the direction of formation of PO with vinylidene and disubstituted fragments. In addition, Mg controls the formation of the oligomer backbone at the expense of addition of propene units predominantly in the H–T fashion and acts as a chain-terminating agent. Therefore, the resulting oligomer is less viscous than that prepared without the modifier. Furthermore, the POs containing larger amounts of hydrocarbons formed by H–T linking have better viscosity–temperature properties at positive temperatures. The POs consisting of weakly branched hydrocarbons also have better antiwear properties.

To enhance the resistance of white oils to oxidation, oligomers or their fractions should be hydrogenated under such conditions at which addition of hydrogen to isomeric oligomer molecules would not involve changes in their structure and properties and would not be accompanied by side reactions such as degradation, hydroisomerization, etc.

The hydrogenation occurs at different rates depending on the surrounding of the double bond in hydrocarbon molecules. The PO hydrogenation is a sum of reactions of H_2 addition to hydrocarbons of different structures. Apart from the catalyst, the hydrogenation is affected by such parameters as temperature, pressure, and feed flow rate.

Taking into account these facts, we performed the hydrogenation in the temperature range 140–250°C and a pressure of 0.5–6.0 MPa. The feed flow rate was varied from 0.2 to 0.6 $l\ h^{-1}$. As the principal parameter of the product quality we took the iodine number, i.e., the amount of iodine (g) added to 100 g of product. We

Table 3. Iodine numbers of POs in relation to the pressure, temperature, and hydrogen flow rate

Pressure, MPa	IN, g I_2/100 g, at indicated temperature, °C			
	140	180	220	250
0.2 l h^{-1} (τ = 0.5 h)				
0.5	40.8	22.8	12.0	11.6
1.5	31.4	18.0	9.8	8.4
2.5	18.2	9.8	3.9	3.0
4.5	12.4	4.2	1.2	1.1
6.0	11.8	3.8	1.0	1.0
0.4 l h^{-1} (τ = 0.25 h)				
0.5	42.2	26.4	18.0	15.2
1.5	38.6	21.3	12.6	9.3
2.5	22.2	10.6	4.7	3.3
4.5	21.8	4.9	1.8	1.6
6.0	20.4	4.3	1.7	1.5
0.6 l h^{-1} (τ = 0.1 h)				
0.5	44.8	27.9	19.2	16.8
1.5	40.6	22.4	13.8	10.2
2.5	28.4	11.8	5.1	4.3
4.5	24.1	5.4	1.9	1.6
6.0	21.9	4.7	1.9	1.5

tested various pilot and commercial samples of catalysts containing Ni, Co, Mo, W, Pt, and Pd. Aluminum–platinum catalysts exhibited the best hydrogenating properties. Experimental data on hydrogenation of propene oligomer with an iodine number of 48 on the platinum-containing catalyst showed that the highest degree of hydrogenation was attained on this catalyst at temperatures of 220–250°C and pressures of 4.5–6.0 MPa (Table 3).

We also performed hydrogenation of close-cut PO fractions boiling in the intervals 225–325, 325–370, and >370°C [8]. The boiling limits of the fractions were chosen so that their composition corresponded to definite grades of oils with required characteristics. Hydrogenation of these samples was performed on Pt- and Pd-containing catalysts at 220°C and a pressure of 4.5 MPa, at a hydrogen flow rate of 50 l h^{-1}. We found that the hydrogenation was more efficient on pilot and commercial samples of platinum-containing catalysts. Therefore, for further experiments we chose platinum-containing catalysts. With these catalysts, the hydrogenation was the most efficient and was not accompanied by degradation and isomerization.

The properties of hydrogenated propene oligomers (HPOs) obtained on the Pt-containing catalyst are given in Table 4. In the course of hydrogenation, the density and molecular weight, as well as the viscosity at 100 and 50°C, do not change noticeably.

The hydrogenation under the conditions of our experiments was quite efficient: The iodine number after hydrogenation was as low as 0.64 g I_2/100 g.

We optimized the PO hydrogenation on the Pt-containing catalyst and determined the optimal parameters of the process: T = 220°C, P = 4.5 MPa, and G_m = 0.69 mol h^{-1}.

The isolated fractions were used for preparing white oils for various applications. In particular, from the HPO fraction boiling in the range 225–325°C we isolated two fractions: 225–285 and 285–325°C. The first fraction was examined as a base for AMG-10 oil,

Table 4. Principal properties of hydrogenated propene oligomers and their fractions

HPOs and their fractions	Kinematic viscosity, $mm^2 s^{-1}$		Molecular weight	Density at 20°C, kg m^{-3}	Iodine number, g I_2/100 g
	50°C	100°C			
Initial HPOs	14.6	4.0	350	829	0.64
Hydrogenated fraction 225–325°C	3.4	1.6	220	803	0.64
Hydrogenated fraction 325–370°C	10.2	3.6	340	812	0.64
Hydrogenated fraction > 370°C	60.4	11.0	436	833	0.64–1.0

and the second fraction, for RM and RMTs oils. The AMG-10 oil base obtained has the following properties:

Viscosity, $mm^2 s^{-1}$	
at 50ºC	2.08
at –50ºC	199.2
Open-cup flash point, °C	No lower than 92
Congealing point, °C	<–72
Evaporation loss at 125°C in 5 h, wt %	21.5

A sample of this oil was successfully tested in Aviatekhmas Joint-Stock Company as a component of AMG-10 oil. The base of the RM and RMTs oils had the following properties:

Viscosity, $mm^2 s^{-1}$	
at 50ºC	3.98
at –40ºC	301.4
Open-cup flash point, °C	No lower than 125
Congealing point, °C	<–62
Cloud point, °C	<–52

The properties of HPOs as oil bases meet the existing requirements.

The fractions boiling in the range 325–370°C and above 370°C met the requirements to brightening (Table 5) and cable (Table 6) oils.

With respect to the dielectric loss tangent, the oil based on HPOs considerably surpasses S-220 petroleum cable oil. The cable oil based on the HPO fraction 370–430°C has higher dielectric loss tangent and better viscosity–temperature characteristics. The HPO fraction boiling above 430°C can be used as a highly viscous cable oil with a viscosity of 45–50 $mm^2 s^{-1}$ at 100°C.

Fractionation of HPOs in other temperature limits allows isolation of fractions suitable for production of low-density polyethylene: solvent oil for ethylene polymerization; oil with a viscosity of 40 $mm^2 s^{-1}$ at 50°C for first step of compressors; and oil with a viscosity of 200 $mm^2 s^{-1}$ at 50°C for second step of compressors.

With respect to the viscosity, the HPO-based oils are similar to their petroleum analogs, and with respect to the flash point and congealing point the HPO-based oils even surpass them. Hydrogenated propene oligomers also exhibit high lubricating properties. They protect compressor parts from friction and wear, thus preventing its damage and prolonging its operation life.

Thus, we have prepared various kinds of white oils meeting the requirements of world standards.

CONCLUSIONS

(1) A wide set of white oils were prepared by oligomerization of C_3 olefin and hydrogenation of the resulting oligomers.

(2) The optimal process parameters of the oligomerization, ensuring the required fractional and hydrocarbon composition, molecular-weight distribu-

Table 5. Characteristics of brightening oils

Parameter	Konil 6517	S-9, TU (Technical Specification) 3810133-75	Brightening oil based on HPO fraction 325–370°C
Kinematic viscosity at 20°C, $mm^2 s^{-1}$	37.5–40.5	23–29	21
Density at 2°C, kg m^{-3}	880	865	813
Iodine number, g I_2/100 g	10–15	2.6	0.32
Open-cup flash point, °C	140	150	180
Congealing point, °C	–50	–45	–60
Content of water-soluble acids and alkalis, pH	6.0–7.0	7.0–8.0	6.0–7.0
Color	Colorless	Colorless	Colorless

Table 6. Characteristics of oils for high-pressure cable filling

Parameter	Requirements of GOST (State Standard) 8763–76 for S-220 oil	Cable oils based on HPO fractions	
		370–430°C	>370°C
Kinematic viscosity, $mm^2 s^{-1}$ at:			
100°C	No less than 11	11.1	11.8
50°C	No less than 50	64.2	69.8
20°C	No more than 800	466.6	748
0°C	No more than 5000	3205	4900
Acid number, mg KOH/g	No more than 0.002	Absent	Absent
Ash content, %	No more than 0.001	Absent	Absent
Content of water-soluble acids and alkalis, mechanical impurities, water	Absent	Absent	Absent
Closed-cup flash point, °C	No lower than 180	195	195
Congealing point	No higher than –30	–40	–36
Corrosion effect on copper plate, group	1	1	1
Nastyukov reaction	Negative	Negative	Negative
Dielectric loss tangent:			
in initial state	0.0020	0.00035	0.00041
after aging at 120°C for 300 h:			
without catalyst	0.009	0.0009	0.0052
in the presence of copper	0.120	0.0016	0.0630

tion, and properties of propene oligomers, were determined. The structural composition and properties of the oligomers can be controlled by varying the catalyst and the parameters of the oligomerization process.

(3) Hydrogenation of propene oligomers under the chosen conditions provides the required level of saturation of double bonds without altering the fractional composition and principal structural features of the oligomers. The white oils obtained on the basis of the isolated fractions of hydrogenated propene oligomers are similar to their petroleum analogs in the viscosity and flash point and considerably surpass the petroleum analogs in the congealing point and dielectric loss tangent.

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