

APPLICATION OF THE HYDROCRACKING PROCESS OF DISTILLATE OBTAINED FROM LOW-PARAFFIN OILS

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Abstract: One of the promising technological processes in the production of oils is the hydrocracking process. It is radical in destructive hydrogenation and change in the structure of raw material molecules to obtain oil products with new qualities that are absent in the original raw material.

The hydrocracking process in the processing of oil fractions and residues of Baku oils is especially necessary due to their high resin content. Therefore, the solution to this issue is of a topical nature.

In this paper, the possibility of using oil fractions – distillate D-11 – a mixture of Baku low-paraffin oils as a raw material for obtaining base oils, including high-index ones, was investigated.

Distillate D-11 from Azerbaijani oils was subjected to hydrocracking on an industrial catalyst GKD-205 under a pressure of 4-5 MPa, at volume rate of 0.5-1.0 h⁻¹ and at a temperature of 420 °C. The optimal process mode for the conclusion was determined in order to obtain the base of high-index oils: pressure of 5 MPa, temperature of 420 °C, volume rate of 0.5 h⁻¹ and amount of hydrogen of 1000 l/l of raw material.

The oil fractions obtained during the work (300-400 °C) do not require dewaxing, as a result of which the costs of oil production were reduced by half.

Without dewaxing, along with base oils VI-4 and VI-6, all-season motor oils M-4z/6V1 and M-6z/10V, turbine oils of the T-22, T-30, T-46, T-51 brands, and light cylinder oils 11, 24, AK-15, etc. were obtained. After dewaxing the oil fractions of hydrogenates, high-viscosity oils were obtained - vapors, which significantly surpass the quality of oils from unique Baku oils.

Keywords: low-paraffin oil, D-11 distillate, hydrocracking, hydrogenisate

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Introduction

In modern world oil refining, the most urgent and complex problem is increasing the depth of oil refining, which can be solved by using heavy oil residues – tars and fuel oils. The hydrocracking process is used as the main process for their processing [1-12].

The wide possibilities of the hydrocracking process, which provides a deep change in raw materials, make it possible to process residual oil fractions along with distillate fractions, which makes it possible to obtain not only motor fuels, raw materials for catalytic cracking, but also lubricating oil bases [13-23].

As is known, the efficiency of the hydrocracking process largely depends on the operating pressure. The lower the pressure, the

higher the economic efficiency of using the hydrogenation process [18, 24-33]. In view of the large resources of heavy oil residues from Azerbaijani oils, which do not find qualified application, a technology has been developed for obtaining a wide range of oils from them, including high-index ones, using an environmentally friendly process – hydrocracking under a pressure of 5-10 MPa [31-35].

It is known that one of the promising technological processes in the production of oils is the hydrocracking process. This process is radical for rational processing (destructive hydrogenation) and changing the structure of raw material molecules in order to obtain oil products

with new qualities that are absent in the original raw material.

The introduction of the hydrocracking process for processing oil fractions and residues of currently processed Baku oils is especially necessary due to their high resin content. With the existing technical base of the Baku Oil Refinery, where there are sufficient capacities for hydrogenation purification, the solution to this

issue is of particular importance [31-36]. Taking this into account, a study was conducted to examine the possibility of using oil fractions (D-11 distillate) of a mixture of Baku low-paraffin oils as raw materials for obtaining base oils, including high-index oils, components of fuels and liquids at various pressures and speeds [37-39].

Experimental part

The raw material used was industrial distillate (vacuum distillate type) obtained from a mixture of low-paraffin oils (fields of Oil

Rocks, Guneshli, and Mud Sopka), boiling in the range of 320-560 °C [40-42].

Fractional composition of distillate D-11 according to Bogdanov:

s.b.-320 °C	40 % – 450 °C	75 % – 510 °C
5 % – 394 °C	50 % – 460 °C	80 % – 514 °C
10 % – 416 °C	55 % – 477 °C	85 % – 520 °C
15 % – 430 °C	60 % – 489 °C	90 % – 526 °C
20 % – 437 °C	65 % – 497 °C	99 % – 560 °C
30 % – 447 °C	70 % – 503 °C	

Physicochemical properties of distillate:

Density at 20 °C, kg/m ³	916.7
Kinematic viscosity, mm ² /s, at:	
100 °C	11.74
50 °C	75.3
Viscosity index	72
Temperature, °C:	
flashes	208
pour point	-8
Color in NPA marks	8
Refractive index n_D^{20}	1.5072

Distillate D-11 from the Heydar Aliyev Oil Refinery was subjected to hydrocracking at the continuously operating pilot Shuykin unit of the ANAS OPP, on the industrial catalyst GKD-205 at a temperature of 420 °C, a pressure of 4-5 MPa, a feedstock volumetric feed rate of 0.5-1.0 h⁻¹ and a hydrogen flow of 1000 l/l of feed, the scheme of which is shown in Fig. 1 [43, 44].

Hydrocracking of the feedstock, preheated in heat exchangers 1 and 2 and mixed with H₂ gas is carried out in a multi-zone reactor 3 with a descending flow of the feed mixture. The liquid separated from the gas in separators 4 and 5 is heated in heat exchanger 6 and fed to distillation column 10 for the separation of light gasoline (b.s.-180 °C). Water vapor VI is introduced into

the bottom of column 10. The fraction boiling above 180 °C is heated in the coils of furnace 11 and separated in vacuum column 12 into fractions (180-300 °C), a light oil fraction (300-400 °C) and a heavy oil fraction (above 400 °C). In amine treatment unit 17, hydrogen sulfide is removed from the recirculating gas. The unit makes extensive use of air-cooled units – condensers and refrigerators. Between units 1 and 13, water is injected into the hydrocracking product stream to flush out deposits. The resulting fractions are collected in receiver 20.

The qualities of the D-11 distillate from a mixture of low-paraffin oils and its hydrogenates, obtained at a temperature of 420 °C, various pressures, and volume rates, are given in Table 1.

As can be seen from Table 1, increasing the process pressure leads to an improvement in the color, density, and other parameters of the hydrogenation product.

The color of the hydrogenation products improves from 8 to 5 NPA grades. Reducing the

process volumetric flow rate from 1 to 0.5 h⁻¹ at the same temperature (420 °C) leads to intensive destruction of the feedstock, and the viscosity, flash point, density, and other parameters of the hydrogenation products decrease sharply [27, 45, 46].

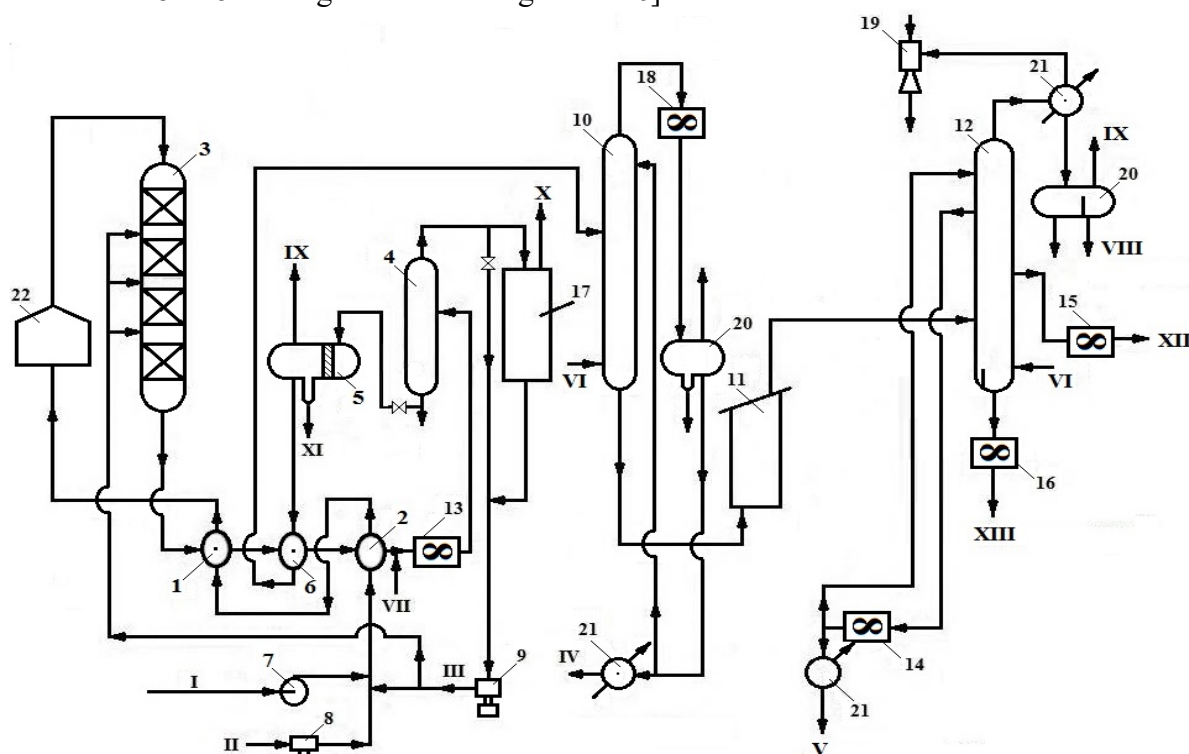


Fig. 1. Scheme of the unit for hydrocracking of distillates for the production of oils.

1, 2 – heat exchangers for heating purified oil; 3 – reactor; 4, 5 – separators; 6 – heat exchanger; 7 – raw material pump; 8 – fresh gas compressor; 9 – compressor of circulating hydrogen-containing gas; 10 – atmospheric column; 11 – tubular furnace in the fractionation section; 12 – vacuum column; 13-16 – air coolers; 17 – unit for cleaning circulating gas from hydrogen sulfide; 18 – condenser-refrigerator; 19 – ejector; 20 – receiver; 21 – refrigerator; 22 – tubular furnace. I – feedstock – distillate; II – fresh hydrogen-containing gas; III – circulating hydrogen-containing gas; IV – fraction b.s.-180 °C; V – liquid hydrocarbons; VI – water vapor; VII – water; VIII – fr. 180-300 °C; IX – gas to flare; X – hydrogen sulfide; XI – aqueous solution; XII – fr. 300-400 °C; XIII – fr. above 400 °C

Table 1. Qualities of distillate D-11 from a mixture of low-paraffin oils and its hydrogenates obtained at a temperature of 420 °C, various pressures and volume rates

Indices		Distillate D-11	Hydrogenisate	Hydrogenisate	Hydrogenisate
Pressure, MPa		–	4	4	5
Volume rate, h ⁻¹		–	1.0	0.5	0.5
Density at 20 °C, kg/m ³		916.7	909.3	904.2	902.1
Kinematic viscosity, mm ² /s	100 °C	11.74	8.47	5.02	6.26
	50 °C	75.3	47.0	20.62	25.73
	40 °C	–	77.58	30.9	39.58
Viscosity index VI		72.0	74.0	82.0	110.0
Temperature, °C	flashes	208	178	104	104
	pour point	-8	-12	-17	-12
Color in NPA marks		8	6	6	5
Refractive index n_D^{20}		1.5072	1.5050	1.4998	1.5010

Results and discussion

Oil fractions boiling at different temperatures were isolated and analyzed from the hydrogenation products obtained at different pressures and volumetric flow rates by atmospheric-vacuum distillation (Table 2).

In order to obtain a base for high-index oils, it is advisable to carry out the hydrocracking process under relatively low pressure (5 MPa), a temperature of 420 °C, a volume rate of 0.5 h⁻¹, and a hydrogen amount of 1000 l/l of feedstock.

Table 2. Qualities of oil fractions of hydrogenates obtained at a temperature of 420 °C, various pressures and volume rates

Indices	Fraction, °C											
	320-400			400-420			420-450			> 450		
Pressure, MPa	4	—	5	4	—	5	4	—	5	4	—	5
Volume rate, h ⁻¹	1.0	0.5	—	1.0	0.5	—	1.0	0.5	—	1.0	0.5	—
Density at 20 °C, kg/m ³	907.7	906.8	905.0	912.2	908.3	907.9	915.2	908.7	908.3	918.6	909.2	908.7
Kinematic viscosity, mm ² /c, at:												
100 °C	4.14	3.75	3.24	8.06	7.18	6.66	11.48	9.72	9.42	23.54	17.2	16.5
50 °C	15.99	13.84	11.02	46.43	38.52	33.99	88.87	62.95	60.12	194.4	131.94	119.51
40 °C	23.75	20.08	15.93	79.06	63.88	56.05	150.8	110.45	104.51	369.7	238.49	221.47
Viscosity index VI	70	71	73	58	60	63	45	53	55	82.5	70.0	78.0
Temperature, °C:												
flashes	184	180	173	229	226	220	249	248	242	293	285	292
pour point	-16	-20	-20	-8	-8	-4	-2	-6	-4	-2	-2	-4
Color in NPA marks	4½	2½ -	3½	8-	3½ -	4	8-	4	4½ +	dark	dark	dark
Refractive index n_D^{20}	1.5064	1.5037	1.5040	1.5074	1.506	1.505	1.508	1.5068	1.506	1.5083	1.5082	1.5064
Yield, % to process	23.77	27.36	18.83	18.72	15.14	20.13	28.57	20.69	22.22	22.01	25.03	31.86

Oil fractions with boiling ranges of 300-350 °C and 300-400 °C were isolated and studied from the hydrogenated distillate D-11.

It was shown that they are low-viscosity

oils with a high viscosity index (100) and meet the requirements of the standard GOST 33111-2014 for high-index industrial oils of the VI-4 and VI-6 types (Table 3).

Table 3. Physicochemical indices of fractions of 300-350 °C and 300-400 °C obtained from the hydrogenated distillate in order to obtain the base of VI oils

Indices	Fraction 300-350 °C	GOST R 59107-2020 for base oils of the VI-4 series	Fraction 300-400 °C	GOST R 59107-2020 for base oils of the VI-6 series
Density at 20 °C, kg/m ³	892.9	-	902.9	-
Kinematic viscosity, mm ² /c, at:				
100 °C	1.78	-	2.59	-
50 °C	4.37	3.5-4.5	7.29	5.5-7.5
40 °C	5.44	4.3-6.0	10.16	7.2-10.1
20 °C	10.39	-	22.27	-
Viscosity index VI	~150	-	99	95
Temperature, °C:				
pour point	-32	not higher -8	-28	not higher -10
flashes	140	not lower 125	150	not lower 145

Refractive index n_D^{20}	1.4994	-	1.5045	-
Color in NPA marks	2-	1.0	2	1.5
Acidity number, mg KOH/g	0.01	no more 0.05	0.02	no more 0.05
Ash content, %	absent	no more 0.05	absent	no more 0.05
Coking ability, %	0.02	no more 0.05	0.03	no more 0.05
Yield, % to process	6.61	-	20.00	-

It should be noted that the specified oil fractions do not require dewaxing, and, as a result, the production costs of such oils can be halved [20]. They can be used to obtain alloyed oils of the IGP series [47].

In order to obtain the base of high-index all-season oil of type M-4, the hydrogenation product of industrial distillate D-11, obtained at 420 °C, a feed volumetric feed rate of 0.5 h⁻¹ and a hydrogen supply of 1000 l/l of feed, was fractionated [29, 31, 35].

Fuel (up to 320 °C) and oil fractions boiling at 320-400 °C were isolated from the hydrogenation product, which was thickened with 2.48-4 % viscosity (T-2-670) additive (PMA with olefin copolymer) [48-53].

At the same time, a high level of viscosity-temperature properties of thickened oils is ensured, which meet the requirements of GOST 10541-2020 for oil M-4z/6B1 and oil M-6z/10V (Table 4).

Table 4. Characteristics of the base of thickened motor oils

Indices	Fraction 320-400 °C		GOST 10541-2020 for oil M-4z/6V1	GOST 10541-2020 for oil M-6z/10V
	+2.48 % T-2-670	+4 % T-2-670		
Density at 20 °C, kg/m ³	906.3	907.5	-	890.0
Kinematic viscosity, mm ² /c, at:				
100 °C	6.24	9.5	5.5-6.5	9.5-10.5
50 °C	23.81	32.28	-	-
40 °C	31.86	47.73	-	-
-18 °C	2091	7809	1100-2600	≤9000
-30 °C	10392	-	≤11000	
Viscosity index VI, not less than	133	145	125	115
Temperature, °C:				
pour point	173	183	no more 165	no more 190
flashes	-42	-37	no higher - 42	no higher - 40/-30
Color in NPA marks	4-	4	-	-
Refractive index n_D^{20}	1.5041	1.5041	-	-
Yield, % to process	18.83	18.83	-	-

The advantage of the hydrocracking process is that from the D-11 distillate under relatively easy conditions, it is possible to obtain the base of all-season oil with a yield of 18.83% by weight, calculated on the distillate (Table 4), and by compounding the oil fractions, it is possible to obtain various base oils with low solidification (Table 5).

Evaluation of the quality of fractions boiling at s.b.-180 °C, 180-320 °C, s.b.-240 °C, and 240-300 °C, obtained from hydrogenates, showed that they can be used as a solvent-liquid RZh-3 according to TU 38.101964-83, a component of jet fuel according to GOST 10227-2013, and a component of winter diesel fuel according to GOST 305-2013 [54-56].

Table 5. Qualities of oil fractions of hydrogenates obtained at a temperature of 420 °C, various pressures and volume rates

Fraction, °C	Pressure, MPa	Volume rate, h ⁻¹	Density at 20 °C, kg/m ³	Kinematic viscosity, mm ² /s, at:		Viscosity index VI	Temperature, °C:		Refractive index n_D^{20}	Yield, % to process
				100 °C	40 °C		flashes	pour		

								point		
320-400	4	1.0	907.7	4.14	23.75	70	184	-16	1.5064	23.77
–	–	0.5	906.8	3.75	20.08	71	180	-20	1.5037	27.36
–	5	–	905.0	3.24	15.93	73	173	-20	1.5040	18.83
GOST 32-74 for oil T-22	–	–	900.0	–	20.0- 23.0	70	180	-15	–	–
320-450	4	1.0	911.7	7.14	62.3	64	207	-6	1.5047	71.06
–	–	0.5	907.9	5.92	43.31	74	201	-12	1.5048	73.19
–	5	–	907.6	5.98	45.28	66	200	-7	1.5033	61.18
GOST 32-74 for oil T-30	–	–	900	–	–	65	180	-10	–	–
> 320 °C	4	1.0	915.0	9.53	95.55	76	213	-10	1.5051	93.07
–	–	0.5	908.5	7.76	68.41	72	208	-5	1.5058	98.22
–	5	–	908.0	8.16	75.12	70	205	-10	1.5053	93.04
GOST 32-74 for oil T-46	–	–	905.0	–	–	60	195	-10	–	–
GOST 32-74 for oil T-51	–	–	900.0	–	–	70	195	–	–	–
> 400 °C	4	1.0	916.0	13.1	179.7	50	254	-8	1.5075	69.3
–	–	0.5	908.7	11.47	131.4	60	250	-2	1.5070	70.86
–	5	–	908.3	9.43	94.65	71	215	-3	1.5050	74.21
GOST 26191- 84 on lightweight vaporizers 13	–	–	–	11.4- 14.5	–	–	180	-10	–	–
TU 0253-008- 58966428- 2005 for light cylinder oil 11	–	–	920	9-13	–	65	215	5	–	–
> 450 °C	4	1.0	918.6	23.54	369.7	82.5	293	-2	1.5083	22.02
–	–	0.5	909.2	17.2	238.49	70.0	285	-2	1.5082	25.03
–	5	–	908.7	16.5	221.47	78.0	292	-4	1.5064	31.86
TU 0253-008- 58966428- 2005 for light cylinder oil 24	–	–	940	22-28	–	35	240	20	–	–
SAE 90 for AK-15 oil	–	–	–	≥ 14.5	–	≤ 65	225	-5	–	–

The consolidated material balance of the process of obtaining fuels, oils, and liquids for industrial distillate D-11 by hydrocracking under optimal conditions ($T - 420\text{ }^{\circ}\text{C}$, $P - 5\text{ MPa}$, $v - 0.5\text{ h}^{-1}$, $\text{H}_2 - 1000\text{ l/l}$ of raw material) is presented below.

Taken, % wt.:		100
Distillate		
Received, % wt.:	I mode	II mode
Fraction to 300 °C	5.8	-
Fraction to 320 °C	-	6.97
including:		
s.b.-180 °C (RJ-3 or component of fuel T-2)	1.4	1.40
180-300 °C (component of diesel fuel «3»)	4.4	-
180-320 °C (component of diesel fuel «3»)	-	5.57
Fraction of lubricating oil		
including:		
300-400 °C (industrial VI-6)	20.0	-

320-400 °C (base of all-season motor oil M-4)	-	18.83
> 400 °C (cylinder light oil 11)	74.2	74.20
Total	100.0	100.0

Conclusion

Taking into account the above, we note that with the existing technical base of the Baku Oil Refinery, which has sufficient capacity for hydrogenation purification, research into the possibility of using oil fractions (D-11 distillate) of a mixture of low-paraffin oils as raw materials for obtaining base oils, including high-index ones, is of particular importance.

During the research into hydrocracking of D-11 distillate on the GKD-205 catalyst, the optimal mode was identified: pressure, 5 MPa; space velocity, 0.5 h⁻¹; temperature 420 °C.

It should be noted that the oil fractions (300-400 °C) obtained from the hydrogenate under the optimal mode do not require dewaxing and, as a result, the costs of oil production are reduced by half.

From the hydrocracking of the D-11

distillate, along with the base oils VI-4, VI-6, all-season motor oils M-4z/6V1 and M-6z/10V are obtained.

Also obtained oils without dewaxing – turbine oils of the T-22, T-30, T-46, T-51 brands and light cylinder oils 11, 24, AK-15, etc.

After dewaxing the oil fractions of hydrogenates boiling above 400 and 500 °C, high-viscosity oils - vapors - are obtained, significantly superior in quality to oils from the unique Baku oil oils.

It should be noted that the scheme proposed in this work ensures waste-free production of environmentally friendly fuels and renewable oils, and it is also significantly simpler than existing ones and can be used as the basis for oil refinery projects.

Conflict of Interest

The authors announced that there are no conflicts of interest regarding this current work.

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