RESEARCH OF HYDROCARBON COMPOSITION AND PHYSICAL AND CHEMICAL PROPERTIES OF LIGHT DISTILLATE FRACTIONS OF CASPIAN OIL

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ABSTRACT

This article presents the results of a study of the physical and chemical properties and individual hydrocarbon composition of gasoline and kerosene-gas oil fractions of the Caspian field, Atyrau region. The detailed group hydrocarbon composition and commodity physical and chemical characteristics of gasoline, kerosene and diesel fractions are determined, as well as the influence of the parameters of the main technological factors - temperature, pressure and volume feed rate of raw materials on the output and quality of the target product. The optimal variant of its processing with the production of commodity oil products is proposed. It is shown that the Caspian oil field paraffin medium, mainly consists of light hydrocarbons with high yields of gasoline fractions (36,2% wt.) and with a high content of hydrogen sulfide, sulfide and light mercaptan sulfur compounds, which require a special approach to their effective processing, and shows that in the process gidroliticheski processing of the received oil of the mixture oil of the Caspian Deposit significantly improves the physical and chemical properties: reduces sulfur, nitrogen and oxygen compounds. Light gasoline fraction (boiling point 62°C) Caspian oil is effectively used as a valuable raw material for the process of catalytic cracking at existing refineries of the Republic of Kazakhstan as a raw material for the process of catalytic isomerization, and the resulting product-isomerize is used as a component of commercial high-octane environmentally friendly automobile gasoline and for the production of hydrocarbon solvents, kerosene and diesel fractions, and after their hydrocatalytic processing is used as a component for the production of jet and diesel fuel.

Keywords: Physical and Chemical Properties, Gasoline Fraction, Hydrogen Sulfide, Distillate Fraction, Chromatograph, Catalytic Isomerization, Hydrocarbon, Petroleum Product.

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INTRODUCTION

The problem of studying the physical and chemical properties of oil from the promising Caspian field of the Republic of Kazakhstan is of great importance for finding the most rational ways to process them. The development of rational options for processing distillate fractions of Caspian oil allows us to effectively solve the problem of meeting the country's demand for high-quality motor and boiler fuels and raw materials for petrochemicals. There are no data in the scientific and technical literature describing the commodity and physical and chemical properties of light gasoline and medium distillate fractions of oil from the Caspian field. Therefore, the choice of optimal technological processes for the development of rational options for processing light distillate fractions of Caspian oil allows us to effectively solve the problem of meeting the country's needs for high-quality automobile, jet, diesel boiler fuels and oil and lubricants, as well as raw materials for petrochemicals. It should be noted that the potential reserve of the studied oil is very large, so specific and targeted special research is important and relevant.

EXPERIMENTAL

The object of this research is to select and develop the optimal technology for processing crude oil, a mixture of oil from the Caspian field. When studying the object, various standard methods of analysis for petroleum products were used following the relevant GOST-s.^{1,4}

Identification of potential content physical and chemical properties and commodity characteristics of individual distillate fractions of a given oil raw material using the laboratory installation for oil distillation ARN-2.

The ARN-2 oil rectification apparatus is designed for distilling oil to a temperature of 470-500 ° C to determine the potential content of petroleum products and their components in oil, as well as to obtain indicators for constructing distillation curves of the true boiling points of oil and its fractions, and to obtain oil fractions for studying their group hydrocarbon composition. The ARN-2 device consists of technological and electrical units mounted in a single metal frame. The processing unit is designed for distillation and consists of a cube with a capacity of 1 or 3 liters placed in the furnace, a distillation column, a condensation unit and receivers.

The electrical unit is designed for regulating and monitoring the process and consists of a recording potentiometer, an autotransformer, ammeters, and a control button.

Rectification column-nozzle type (nozzle) - spiral segments with a diameter of 5 mm and a height of 12 mm made of nichrome wire with a diameter of 0.5 mm. The column has a diameter of 50 mm and a length of 1016 mm. Equipped with electric heating and a thick layer of insulation. Temperature measurement is performed at three points (top, bottom, middle) using thermocouples, which are placed in pockets mounted in the column.

The linear separation capacity of the column corresponds to 20 theoretical plates. The lower part of the column is connected to the cube using a cap nut. For measuring the temperature of the cube is equipped with a pocket for a thermocouple.

The upper part of the column is connected to a condenser head consisting of a reverse refrigerator and a tap for selecting distillate, which then enters the receiver. At the place of distillate selection, a pocket for a thermocouple is installed in the refrigerator condenser, which records the temperature of the fraction selection. The heating of the cube and column is regulated by a laboratory autotransformer ammeters are included in the network to control the heating.

The individual and group hydrocarbon composition of various gasoline fractions was determined by chromatographic method using a gas chromatograph "CHROMATEK-KRISTALL 5000", shown in Fig.-1, following the standard ASTM D 6729.^{1,3}

Fig.-1: Gas Chromatograph «CHROMATEK-KRISTALL 5000»

The fractional composition of the initial straight-run gasoline and isomerization products, as well as reforming was determined using the AFSA-2 analyzer (series # 03051 2006), shown in Fig.-2 according to the guidelines "Determination of the fractional composition of gasoline on the AFSA-2 device".

The method consists of chromatographic separation of gasoline on a capillary column with a non-polar stationary phase, followed by registration of hydrocarbons by a flame ionization detector and automated processing of the obtained information using the software.

A representative sample of gasoline is introduced into a gas chromatograph equipped with a capillary column containing methyl siloxane as a solid phase deposited on the walls of a quartz capillary column.

Under the action of the carrier gas-helium, the sample passes through a column in which its components are separated. Components are detected by the flame ionization detector when they are eluted from the column. The detector signal is processed by an electronic data storage system or an integrating computer. Each resulting peak is identified by comparing its retention index in a table or visually by comparison with standard chromatographs.

Fig.-2: AFSA-2 Device

RESULTS AND DISCUSSION

The Caspian oil field is mainly characterized by a significant content of hydrogen sulfide and light mercaptan and sulfide sulfur compounds, which require an unconventional approach to their processing. The oil mixture of the Caspian field is characterized by a significantly high yield of gasoline fractions (36.2% by weight). The table shows a summary of the group hydrocarbon composition of light gasoline fractions (boiling point 62°C) of Caspian oil.²

Table-1: Group Hydrocarbon Composition of Light Gasoline Fraction (Boiling Point 62°C) of Caspian Oil

Number of Carbon Atoms	N-paraffins	ISO-paraffins	Naphthenes	Aromatic	Total
C ₃	0,032	-	-	-	0,025
C ₄	7,362	0,701	-	-	8,063
C ₅	20,923	16,859	1,393	-	39,175
C ₆	13,62	20,867	4,903	0,664	40,052
C ₇	2,53	4,554	3,314	0,405	10,813
C ₈	0,348	0,762	0,679	-	1,79
C ₉	-	-	0,056	-	0,056
total	44,816	43,753	10,344	1,069	99,982

Table-2: Physical Properties of Light Gasoline Fraction (Boiling Point 62°C) of Caspian Oil

Qualitative Indicators	Unit of Measurement	Value
Density	g / ml	0,6579
Net calorific value	kJ/g	44,6
Higher calorific value	kJ/g	48,5
Saturated steam pressure	mmHg Art.	22,14
Octane number	Motor method	51.2
Octane number	Research method	53.4
Fractional composition, TIC % of distilled fractions	°C	Boiling point
the beginning of the boil		-0,5
5%		1

10%		36,1
20%		36,1
30%		49,3
40%		49,3
50%		60,3
60%		63,3
70%		68,7
80%		71,8
90%		90,8
95%		90,9
end of the boil		118

Gasoline fractions of Caspian oil are characterized by low octane numbers (50-53). Due to the high content of mercaptans, they do not withstand testing on a copper plate, which requires the need for their purification when using isomerization and reforming processes as raw materials. The sulfur content in all distillates is high-0.12 - 0.29% wt., except for the boiling point fraction-120°C, the acidity is also high-4.1-6.3 mg KOH/100 cm³ of fuel. Gasoline fractions up to 200°C mainly consist of alkanes (50-85 %). The boiling point fraction-62°C is a good raw material for the isomerization process (the content of n-alkanes C₅-C₆ is 32% per fraction). Mercaptan sulfur in the Caspian oil mixture is distributed unevenly among the fractions. In fractions the beginning of boiling – 62°C its content is the highest (0.25-0.27% by weight), in heavy fractions it decreases. Due to the high content of volatile and environmentally harmful mercaptans in fractions, the quality requirements for Caspian oil for processing are significantly different from traditional ones. The table shows the results of the chromatographic analysis of the individual hydrocarbon composition of light gasoline fractions (boiling point-62°C) of Caspian oil, which is more effectively used as a raw material for the process of catalytic isomerization.^{8,9}

Table-3: Individual Hydrocarbon Composition of Light Gasoline Fractions (Boiling Point-62°C) of Caspian Oil.

No.	The Hydrocarbon Name	Wt. %	Rpm. %
1	propane	0,03	0,03
2	iso-butane	0,70	0,82
3	butane	7,21	8,11
4	t-2-butene	0,09	0,10
5	iso-pentane	16,48	17,32
6	pentane	20,83	21,66
7	2,2-dimethylbutane	0,38	0,38
8	cyclopentane	1,66	1,45
9	2,3-dimethylbutane	1,80	1,77
10	2-methylpentane	11,31	11,27
11	3-methylpentane	7,84	7,69
12	hexane	12,74	12,58
13	2,2-dimethylpentane	0,11	0,10
14	methylcyclopentane	3,67	3,19
15	2,4-dimethylpentane	0,26	0,25
16	benzene	0,76	0,56
17	3,3-dimethylpentane	0,08	0,07
18	cyclohexane	1,86	1,55
19	2-methylhexane	1,41	1,35
20	2,3-dimethylpentane	0,67	0,63
21	1,1-dimethylcyclopentane	0,24	0,21
22	3-methylhexane	1,89	1,79
23	c-1,3-dimethylcyclopentane	0,48	0,42

24	t-1,3-dimethylcyclopentane	0,42	0,37
25	3-ethylpentane	0,19	0,17
26	t-1,2-dimethylcyclopentane	0,89	0,77
27	heptane	2,31	2,20
28	methylcyclohexane	1,34	1,13
29	1,1,3-trimethylcyclopentane	0,10	0,09
30	ethylcyclopentane	0,15	0,13
31	2,4-dimethylhexane	0,06	0,05
32	ctc-124trimethylcyclo-pentane	0,11	0,09
33	tcc-123-trimethylcyclo-pentane	0,16	0,13
34	toluene	0,45	0,34
35	2,3-dimethylhexane	0,06	0,06
36	2-methylheptane	0,27	0,25
37	4-methylheptane	0,06	0,06
38	3-methylheptane	0,11	0,10
39	1c2t3-trimethylcyclopentane	0,32	0,27
40	t-1,4-dimethylcyclohexane	0,13	0,11
41	t-1,2-dimethylcyclohexane	0,09	0,08
42	octane	0,32	0,30
	Total	100,00	100,00

As can be seen from Table-3, the yield of the low-boiling gasoline part is significant, the content in the boiling point fractions-62°C of butane-pentane fractions-C₄-C₅ and pentane-hexane fractions - C₅-C₆, respectively, is 43.5 and 32.4% by weight. The sum of the heptane and octane fractions-C₅-C₆ total-2.65 mass.

Analysis of the individual hydrocarbon composition and physical and chemical properties of light gasoline fractions shows^{1,3} that the oil of the Caspian field is light, medium-paraffin, mainly a light hydrocarbon raw material with a significant content of hydrogen sulfide and light mercaptan sulfur compounds, which require an unconventional approach to their processing. The table shows the potential content of the composition of straight-run gasoline of Caspian oil.⁶

Table-4: Potential Content and Narrow Fractional Composition of Straight-run Gasoline of Caspian Oil.

No.	The Name Fraction, °C	The Output of Individual Fractions, % wt.	Total Output, % wt.
1	Boiling Point-62	5,31	5,31
2	62-70	1,20	6,51
3	70-85	3,01	9,52
4	85-100	3,41	12,93
5	100-120	5,12	18,05
6	120-130	3,21	21,26
7	130-140	2,61	23,87
8	140-150	3,11	26,98
9	150-160	2,11	29,09
10	160-170	2,91	32,00
11	170-180	2,31	34,31
12	180-190	2,21	36,52
13	190-200	2,41	38,93

Kerosene fraction 200-250°C and 250-300°C Oil of the Caspian field is mainly represented with a significant content of total sulfur (0.62 -1.24 % of turnover) mercaptan and sulfide sulfur compounds (49.2 and 37.8 % of the total turnover of sulfur-containing compounds) and the content of aromatic hydrocarbons (14.71 - 22.4% of the turnover), which require unconventional approaches to their processing and the use of the resulting oil product.^{5,7}

Table-5: Group Hydrocarbon Composition of the Broad Gasoline Fractions of Caspian Oil.

Fraction Selection Temperature, °C	Oil Yield, rpm l. %	Density at 20°C	Sulfur Content, %		Hydrocarbon Content, % rpm.		
			Com mon	Mercaptan	Aromatic	Naphthenic	Methane
65	7.72	636.1	160		0.81	4.3	95
65-100	9.23	704.3	64	51.6	4.03	30	66
100-150	14.4	747.2	67	42.5	17.3	34.9	50.4
150-200	13.35	781.2	0.46	52.2	21	24.4	54.5

Table-6 shows the Potential Contents and Fractional Composition of Straight-run Kerosene Fractions of Caspian Oil.

Table-6: Characteristics of Kerosene Fractions of Caspian Oil

Indicators	Unit	Fraction Selection Temperature, °C		Standard GOST-11244-65
		200-250	250-300	
Oil Yield	%, rpm	10.92	11.30	up to 50 %
Density at 20 ° C	kg/m	805.45	834.2	
Total Sulfur	%, rpm	0.62	1.24	0.1
mercaptan sulfur	%, rpm	49.5	37.8	
Aromatic Hydrocarbon Content	%, rpm	14.71	22.74	
Smoke-free Height Content	mm	24.52	19.12	25

Table-7: Characteristics of Diesel Fractions of Caspian Oil.

Indicators	Unit	Fraction Selection Temperature		
		250-300°C	300-350°C	350-370 °C
Oil Yield	%, rpm	11.54	10.21	3.12
Density at 20°C	kg/m ³	806.15	854.1	863.52
Sulfur Content	% rpm	0.61	2.08	3.08
Kinematic	mm ² /s	2.27	5.791	10.2
Temperature	°C	-27	3.1	17.2

CONCLUSION

Physical and chemical properties and individual hydrocarbon composition of gasoline and kerosene-gas oil fractions of the Caspian field, Atyrau region, Republic of Kazakhstan were studied. It is shown that the oil of the Caspian field is medium paraffin, mainly a light hydrocarbon raw material with a high yield of gasoline fractions (36.2% by weight) and a significant content of hydrogen sulfide, light mercaptan and sulfide sulfur compounds, which require a special approach to their effective processing. Light gasoline fractions (boiling point-62°C) of Caspian oil, effectively used as a raw material for the process of catalytic isomerization, and the resulting product-isomerizate used as a component of commercial high-octane environmentally friendly automobile gasoline and for the production of hydrocarbon solvents,

kerosene and diesel fractions after their hydrocatalytic processing used as a component for the production of jet and diesel fuel.

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