THE IMPACT OF FRACTIONAL COMPOSITION OF GAS OIL ON THE YIELD AND QUALITY OF CATALYTIC CRACKING PRODUCTS

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Abstract: *The impact of the depth of selection of narrow gas oil fractions of Azeri-Chirag-Guneshli oils on the yield and quality of catalytic cracking products was studied. The impact of fractional and group hydrocarbon composition on the main directions of cracking is analyzed. 5 types of gas oil fractions selected in the range of 200-360, 200-410, 200-440, 200-460, and 200-500°C were used as feedstock for catalytic cracking. The results of catalytic cracking of narrow gas oil fractions of Azeri-Chirag-Guneshli oils indicate a nonlinear nature of the dependences on the boiling point limits. The highest total yield of light oil products was obtained by cracking gas oil fractions boiling in the range of 200-410 and 200-440°C, reaching 60.5 and 60.8%, respectively. At the same time, the main contribution to this indicator was made by the gasoline fraction (31.5-33.2%). It was based on paraffin-naphthenic hydrocarbons. The yield of the diesel fraction changed symbiotically with the increasing weight of the fractional composition of the raw material, reaching maximum values of 9.9% during the cracking of the gas oil fraction, boiling in the range of 200-500°C. Based on a comparison of the ratio of iso-butane to iso-butylene, it was concluded that the cracking of gas oil at 200-440°C was accompanied by a significant contribution of bimolecular hydrogen transfer reactions.*
Keywords: *gas oil, Azeri-Chirag-Guneshli, catalytic cracking, fractional composition, group hydrocarbon composition.*
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Introduction

On September 20, 1994, the first international oil agreement was signed with foreign oil companies on the joint development of the Azeri, Chirag fields and the deep part of the Gunashli field (ACG) "Contract of the Century". The discovery of new deposits and the redistribution of the structure of reserves between them and old areas requires a detailed study of the possibilities for the rational use of new raw materials. At the Institute of Chemical Industry of the National Academy of Sciences of Azerbaijan in the laboratory "Oil Chemistry and Oil Technology," headed for many years by Dr. Tech. Sciences, corresponding member. NAS of Azerbaijan, hon. activities science, Prof. F.I. Samedova, detailed studies of the properties and composition of oils from each field were carried out using modern methods of analysis: UV, IR, PMR, EPR spectroscopy, mass spectral analysis, gas, and liquid chromatography, studies are presented qualities of Azeri oil and its light and oil fractions [1-3].

The influence of the depth of selection of narrow gas oil fractions of ACG oils on the yield of catalytic cracking products remains unstudied. This is of certain scientific and practical interest. It is known that with increasing boiling point of gas oil, i.e. As the raw material becomes heavier during the catalytic cracking process, coke formation increases and gasoline yield decreases. At the same time, these dependencies are nonlinear and change when using raw materials of different fractional and chemical compositions, which can be divided into 4 groups [4-6]:

1. Light raw materials – kerosene distillates, light gas oil fractions, distilled within 200-360°C.

2. Heavy raw materials - distillates, boiling in the range of 300-550°C or slightly narrower limits from 350 to 500°C.

3. Raw materials of a wide fractional composition are mainly a mixture of distillates of the first and second groups, with a starting temperature of 210-260°C and an end boiling point of 500-560°C, respectively.

4. Intermediate distillate feedstock with a boiling point of 250-470°C.

In industrial practice, the first group of raw materials is used mainly to produce base aviation gasoline. Whereas in the production of components of motor gasoline at catalytic cracking units, mainly raw materials of the second, third, and fourth types are used.

The purpose of this work is to study the influence of the depth of selection of narrow gas oil fractions of ACG oils on the yield and quality of catalytic cracking products.

Experimental part

The use of raw materials of a narrow fractional composition under industrial catalytic cracking conditions is not always possible. Even though there is a large amount of experimental data and the dependences of changes in properties have been obtained for mixtures of different types of oils, the results, as a rule, are scattered. There is no single universal model for predicting all properties of products and determining optimal recipes for mixing raw materials. Under these conditions, expanding the experimental base, especially for oils from new fields, is of undoubted interest.

5 types of gas oil fractions selected in the range of 200-360, 200-410, 200-440, 200-460, and 200-500°C were used as feedstock for catalytic cracking. The physicochemical properties of narrow gas oil fractions of ACG oils are given in Table 1.

Table 1. Physico-chemical properties of narrow gas oil fractions of ACG oils

Indicators	Boiling limits of raw materials, °C				
	200-360	200-410	200-440	200-460	200-500
Density at 20°C, kg/m^3	879.1	882.6	890.4	898.3	902.1
Kinematic viscosity at 20°C, mm^2/s	2.19	3.16	4.24	5.09	5.98
Molecular weight	274	280	299	317	322
Ash content, % wt.	-	-	-	-	0.001
Coking ability, wt.%	0.025	0.030	0.037	0.044	0.063
Sulfur content, wt.%	0.10	0.16	0.20	0.26	0.38
Group composition, %					
paraffinic-naphthenic hydrocarbons	59.1	65.4	65.2	58.4	59.6
aromatic hydrocarbons	36.9	29.8	29.2	35.2	33.1
RAS	4.0	4.8	5.6	6.4	7.3

The experiments were carried out in a catalytic cracking unit with a fluidized bed of catalyst at a temperature of 500, at a mass feed rate of 5 h-1 with a volume ratio of catalyst to raw material equal to 1: 2. The industrial zeolite-containing cracking catalyst OMNIKAT-210P was used as a catalyst [7-10].

The determination of the fractional and group hydrocarbon composition, the main characteristics of raw materials and liquid cracking products, was carried out by standard industry methods [11, 12]. The yield of cracking gas was determined by its volume and density, the yield of coke was determined by the gravimetric method based on the adsorption of dioxide by ascarid, the yield of liquid products (gasoline fraction n.c. - 195 ºC, light gas oil 195 - 350 ºC and residue > 350 ºC) according to the results of fractionation.

The sulfur content was determined using an ASE-2 X-ray fluorescence energy dispersive analyzer. The analysis of the hydrocarbon composition of cracking products was carried out using a gas chromatograph equipped with an Agilent 7890A/5975C mass spectrometer (USA). The mass fraction of unsaturated hydrocarbons was determined according to the GOST 2070-82 method using iodine bromide. Quantitative analysis of PAHs was carried out according to the STB method 13/17/05-04-2008.

Results and Discussion

The results of catalytic cracking of narrow gas oil fractions of ACG oils (Fig. 1) indicate a nonlinear nature of the dependences on the boiling point limits. The highest total yield of light oil products was obtained by cracking gas oil fractions boiling in the range of 200-410 and 200-440°C, reaching 60.5 and 60.8%, respectively. At the same time, the main contribution to this indicator was made by the gasoline fraction (31.5-33.2%). The yield of the diesel fraction changed symbiotically with the increasing weight of the fractional composition of the raw material, reaching maximum values of 9.9% during the cracking of the gas oil fraction, boiling in the range of 200-500°C. The results ob tained during the research indicated a nonlinear dependence of coke yield on the fractional composition of feed gas oils. In our opinion, two extreme points, in this case, are associated with the intensive occurrence of tertiary cracking reactions when using the lightest raw materials (this is also indicated by the high yield of hydrocarbon gas) and an increase in coking capacity and the content of resinous-asphaltene substances in the heaviest ones. The coke formation process occurs against the background of a decrease in the yield of the gasoline fraction. These results are in good agreement with the literature data [13-16].

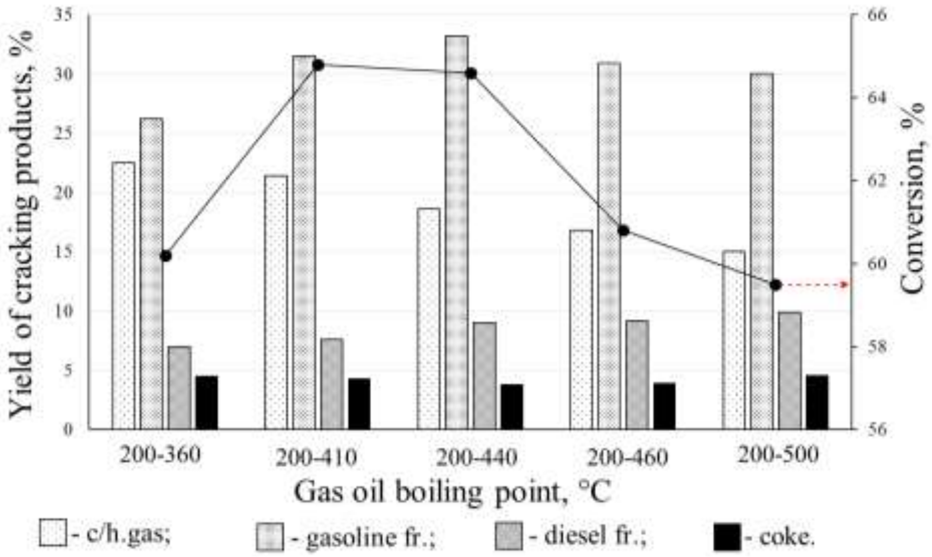

Fig.1. The influence of the fractional composition of ACG gas oil on the conversion (solid line along the additional axis) and the yield of catalytic cracking products.

An increase in the degree of conversion of raw materials with a heavier composition is associated with an increase in the content of the most reactive paraffin-naphthenic hydrocarbons in it. A subsequent decrease when using raw materials of a wide fractional composition (200-500°C) is expected due to the significant content of resin-asphaltene compounds in it, which have a high adsorption capacity, which leads to their blocking of active centers and their rapid deactivation. This is also indicated by the recorded high coke content (Fig. 1).

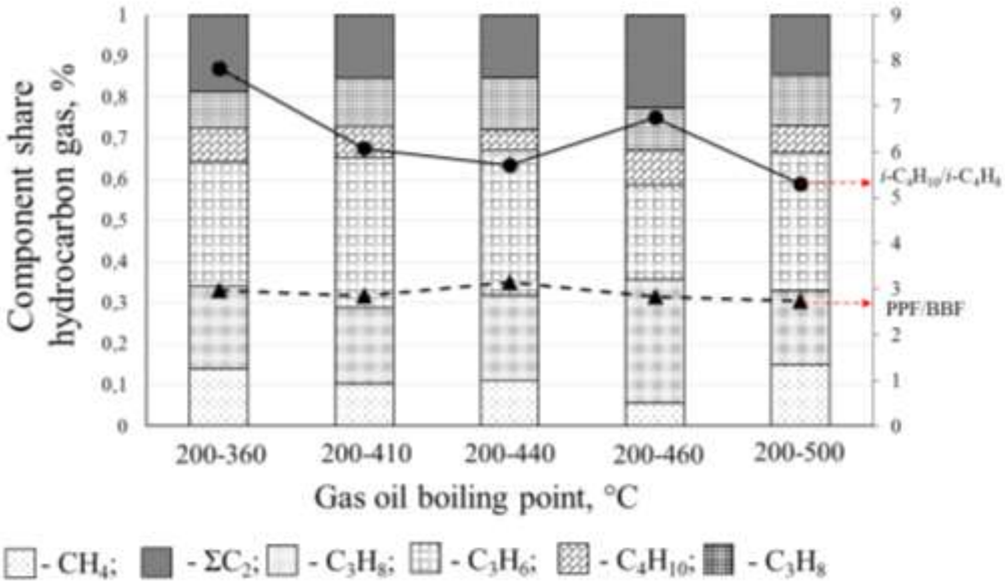

Fig.2. Composition of hydrocarbon gas from cracking narrow gas oil fractions of ACG oils

Denoting the indicators of the cracking process in conjunction with the group composition of raw gas oils (Table 1), it becomes obvious that in the case of a predominance of paraffin-naphthenic hydrocarbons in the initial oil fraction, the sequential-parallel reactions occurring during cracking lead to the predominant formation of lower molecular weight hydrocar bons.

It was of undoubted practical interest to study the qualitative composition of the cracking products of gas oils of ACG oils of various fractional compositions (Fig. 2, 3, Table 2). The proportion of hydrocarbon components of gas changes in the sequence (Fig. 2):

PPF (0.51-0.56) > EEF (14.7-22.7) > BBF (17-19.3)

The yield of dry gas noticeably depends on the fractional composition of the raw material, greatly increasing with increasing boiling point. Intense secondary reactions occurred during gas oil cracking at 200-440°C, as indicated by the PPF/BBF ratio. High values of the ratio of iso-butane to iso-butylene indicate a significant contribution to bimolecular hydrogen transfer reactions. The sensitivity of this indicator to composition is explained by the formation of hydrocarbons of iso-structure through intermediate tertiary carbocations. The latter, having great stability, easily enters the secondary cracking reactions, accompanied by the transfer of hydrogen and the formation of isobutane.

Table 2. Physico-chemical parameters of liquid cracking products

Indicators	Boiling limits of raw materials, °C				
	200-360	200-410	200-440	200-460	200-500
Gasoline fraction					
Density at 20°C, kg/m^3	0.760	0.761	0.766	0.762	0.769
Iodine number, I_2 g/100 g	72.3	87.8	87.2	92.7	99.4
Sulfur content, wt.%	0.031	0.021	0.013	0.017	0.032
Gas oil fraction					
Density	0.898	0.900	0.909	0.915	0924

at 20°C, kg/m^3					
Sulfur content, wt.%	0.30	0.38	0.24	0.31	0.42

The density of liquid light products of cracking gas oils of ACG oils changes linearly (Table 2). Gasoline is characterized by a high content of unsaturated hydrocarbons. The sulfur content in both gasoline and diesel fractions changed nonlinearly and had an extreme character.

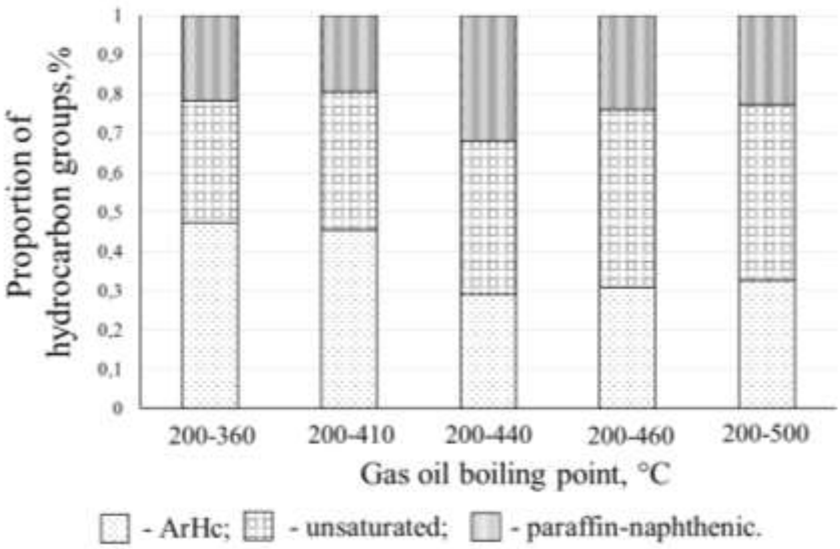

Fig. 3. Composition of hydrocarbon groups in gasoline cracking fractions of narrow gas oil fractions of ACG oils

The dependence of the content of aromatic and paraffin-naphthenic hydrocarbons in the composition of gasoline cracking fractions on an increase in the boiling point of the raw material was of an antibate and opposite nature, while that of unsaturated hydrocarbons was symbatic (Fig. 3). The gasoline fraction obtained during cracking of gas oil at 200-440°C differs from others in the maximum content of paraffin-naphthenic and minimum aromatic hydrocarbons, which indicates an intensive redistribution of hydrogen atoms in the molecules of compounds included in the final cracking products.

Conclusion

Thus, during a series of experiments on the catalytic cracking of narrow gas oil fractions of ACG oils, it was established that changing the boiling point limits of raw materials makes it possible to control the yield and quality of products. The boiling limits of gas oil fractions of ACG oils have been discovered, the cracking of which allows one to obtain the highest yield of hydrocarbon gas, gasoline, or diesel fractions. The group hydrocarbon composition and physicochemical properties of the resulting products also depend on the boiling point of the raw material.

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