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Directions of transformation of the stable gas condensate hydrocarbons on a zeolite catalyst under zeoforming conditions

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Abstract

Zeoforming of stable gas condensate was implemented on a laboratory catalytic unit, under conditions of varying technological parameters of the process (temperature, pressure, feedstock space velocity). The hydrocarbon composition of the feedstock and the obtained products was determined by the method of gas-liquid chromatography. The directions of transformation the stable gas condensate hydrocarbons on a zeolite catalyst were considered, and the influence of process technological parameters on the composition and properties of the obtained products was investigated. The optimal technological parameters of the process were determined from the viewpoint of using the obtained products in the blending of gasoline. Recipes for the blending of RON-92, RON-95 and RON-98 gasolines using the obtained zeoforming products as the main blending component have been developed. The gasolines obtained according to the developed recipes meet all the requirements of current standards.

Keywords: *Stable gas condensate; Zeolite catalyst; Directions of transformation gasoline; Octane number; Zeoforming; Temperature; Pressure; Feedstock space velocity.*

1. Introduction

The problem of rational use the products obtained during the extraction and treatment of oil and gas, with an increase the hydrocarbon production and requirement toughening for the utilization of by-products, is relevant and requires a systematic solution. One of these products is stable gas condensate (SGC), which is usually obtained as a by-product in the treatment of commercial gas in oil and gas fields [1]. The available application for this valuable hydrocarbon feed – adding to oil to reduce its viscosity [2] – is not rational. The study of the SGC properties and development the technologies for processing of this feedstock into valuable products, such as high-octane components of gasoline, is an extremely crucial task. Today, one of the most actively developing areas in the field of catalysis is the use of zeolite catalysts. Zeolites are used in the processes of cracking, hydrocracking, dewaxing, actively investigating the possibility of their use in other oil refining processes [3]. It is important to note that the advantages of zeolite catalysts are their environmental friendliness, profitability, and also resistance to catalytic poisons.

The process that allows to production the high-octane components of gasolines, using a zeolite catalyst, is called Zeoforming. The advantage of this process is the possibility of using a wide range of light hydrocarbons, including SGC [4]. However, like any hydrocarbon feedstock, stable gas condensates can vary significantly in composition (both in the content of various hydrocarbons and in the ratio of the contents of various hydrocarbons) depending on the place of production and production technology. Given the stringent requirements for the quality of motor gasolines (for example, the benzene content is not more than 1 % vol.), the fluctuations in the SGC composition, obviously, will require determining the optimal processing parameters in each case, to ensure a specified product quality [5]. For the effective processing of SGC on zeolite catalysts into components of motor fuels, research to describe the directions and mechanisms of occurring reactions and to identify patterns of influence of technological parameters, is needed.

Thus, the aim of this work is to study the directions of transformation the hydrocarbons of stable gas condensate on a zeolite catalyst, as well as to determine the regularities of influence the technological parameters on the composition and properties of obtained products.

2. Materials and methods

Hydrocarbon composition of the stable gas condensate and the obtained products was determined by the gas-liquid chromatography method using a "Chromatec-Crystal 5000" chromatograph with a quartz capillary column 25 m × 0.22 mm, stationary phase – SE-54, carrier gas – helium according to the method [6]. To calculate the research octane number (RON), motor octane number (MON), saturated vapor pressure (SVP) and density at 15°C, was used "Compounding" software [7], based on chromatography analysis results. The "Compounding" software was also used to develop recipes for blending gasoline of various grades.

3. Experimental

As an object of research in the work was used a sample of SGC obtained from one of the oil and gas condensate fields of Siberia. A zeolite catalyst KN-30 grade (manufactured by PJSC "Novosibirsk Chemical Concentrates Plant") was used to carry out Zeoforming of the SGC. Before testing, the catalyst was mechanically grinding, after which a 10 cm^3 sample of the catalyst was loaded into the reactor, where it was calcined for 8 hours at a temperature of 500°C in the flow of nitrogen.

The process temperature was varied from 325 to 425°C at 25°C intervals; process pressure was varied from 2.5 to 4.5 MPa at 1 MPa intervals; feedstock space velocity was varied from 2 to 4 h^{-1} at 1 h^{-1} intervals. Full technological parameters for all nine tests are presented in Table 1.

Table 1. Technological parameters of SGC Zeoforming process

No.	Temperature,°C	Pressure, MPa	Feedstock space velocity, h^{-1}
1	325	2.5	2
2	350		
3	375		
4	400		
5	425		
6	375	3.5	
7		4.5	
8		2.5	3
9		2.5	4

4. Results and discussions

The results of determining the characteristics and group composition of the studied SGC are presented in Table 2.

Table 2. Characteristics and group composition of the studied SGC

Characteristic	Value	Hydrocarbon group	Content, % vol.
RON	67.2	N-Paraffins	33.40
MON	64.0	Isoparaffins	44.40
SVP, kPa	65.5	Naphthenes	17.26
Density at 15 °C, kg/m^3	691.5	Olefins	1.68
Benzene, % vol.	0.17	Aromatics	3.26

From the obtained results, it is seen that paraffin hydrocarbons, in particular isoparaffins, prevail in the composition of the studied SGC, while the group with the minimum content is olefin hydrocarbons.

The results of calculating the characteristics of Zeoforming products, obtained under conditions of varying process temperatures, are presented in Table 3.

Table 3. Results of calculating the characteristics of Zeoforming products, obtained under conditions of varying process temperatures

Characteristic	Test number				
	1	2	3	4	5
RON	73.7	81.7	85.1	87.6	93.0
MON	70.4	77.1	79.9	81.9	86.5
SVP, kPa	85.8	119.6	117.2	90.8	86.1
Density at 15°C, kg/m^3	684.2	696.8	713.5	741.6	767.2
Benzene, % vol.	0.25	0.63	1.42	2.67	3.92

The results of determining the group composition of Zeoforming products obtained, under conditions of varying process temperatures, are presented in Table 4.

Table 4. Results of determining the group composition of Zeoforming products obtained, under conditions of varying process temperatures

Hydrocarbon group	SGC	Test number				
		1	2	3	4	5
N-Paraffins, % vol.	33.40	28.57	28.30	26.45	22.90	18.40
Isoparaffins, % vol.	44.40	49.92	47.35	45.34	39.79	31.43
Naphthenes, % vol.	17.26	13.18	9.74	6.94	5.78	9.01
Olefins, % vol.	1.68	2.34	2.68	2.19	2.54	3.85
Aromatics, % vol.	3.26	5.99	11.93	19.08	28.99	37.31

From the results of determining the hydrocarbon composition of Zeoforming products, obtained under varying process temperatures, it can be seen that with increasing process temperature, the content of n-paraffins and isoparaffins in the products decreases, and the content of olefin hydrocarbons increases. This tendency is explained in the carbonium-ion mechanism of hydrocarbon transformation reactions occurring on the surface of zeolite catalysts [8]. According to this mechanism, the monomolecular cracking and dealkylation reactions of high molecular weight compounds, that make up the feedstock, with the formation of low molecular weight hydrocarbons are primary. Also, with an increase in temperature, the content of naphthenes in Zeoforming products decreases, however, at a process temperature of 425°C, the naphthenes content increases, which can be explained by the formation of naphthenes through diene synthesis reactions, which is facilitated by the formation of low molecular weight olefins at high temperatures. The increase content of aromatic hydrocarbons in the product composition with increasing temperature is probably associated not only with the formation of aromatic hydrocarbons as a result of hydrogen transfer between olefins, olefins and paraffins [9], but also with the fact that cyclohexanes become less stable with increasing temperature and can undergoes dehydrogenation to aromatic hydrocarbons by transfer of hydrogen (which is also evidenced by an increase the content of benzene in the composition of the obtained products). An increase in the density of products with a simultaneous decrease in SVP and an increase in the content of aromatic hydrocarbons indicates the occurrence of aromatic hydrocarbons condensation reactions, building compounds with a higher molecular weight.

The results of calculating the characteristics of Zeoforming products, obtained under conditions of varying process pressure, are presented in Table 5.

Table 5. Results of calculating the characteristics of Zeoforming products, obtained under conditions of varying process pressure

Characteristic	Test number		
	3	6	7
RON	85.1	87.4	76.5
MON	79.9	82.6	71.8
SVP, kPa	117.2	151.1	62.7
Density at 15 °C, kg/m^3	713.5	706.9	724.9
Benzene, % vol.	1.42	0.06	0.60

The results of determining the group composition of Zeoforming products obtained, under conditions of varying process pressure, are presented in Table 6.

Table 6. Results of determining the group composition of Zeoforming products obtained, under conditions of varying process pressure

Hydrocarbon group	SGC	Test number		
		3	6	7
N-Paraffins, % vol.	33.40	26.45	25.42	22.95
Isoparaffins, % vol.	44.40	45.34	44.67	41.83
Naphthenes, % vol.	17.26	6.94	8.87	15.81
Olefins, % vol.	1.68	2.19	5.02	6.13
Aromatics, % vol.	3.26	19.08	16.02	13.28

The results of determining the group hydrocarbon composition of Zeoforming products obtained under conditions of varying the process pressure generally confirm the previously described directions of transformation the hydrocarbons of stable gas condensate on a zeolite. So, with increasing process pressure, the content of naphthenic hydrocarbons in the products increases, which can be explained by the fact that high pressure suppresses cracking reactions of naphthenes, and at the same time positively effects on the formation of naphthenes in reactions of diene synthesis. A decrease in the content of aromatic hydrocarbons with an increase in the process pressure evidenced to the fact that the reactions of the formation of aromatic hydrocarbon and hydrogen from olefins in hydrogen transfer reactions, in Zeoforming process occurring more actively then other type reaction.

The results of calculating the characteristics of Zeoforming products, obtained under conditions of varying feedstock space velocity, are presented in Table 7.

Table 7. Results of calculating the characteristics of Zeoforming products, obtained under conditions of varying feedstock space velocity

Characteristic	Test number		
	3	8	9
RON	85.1	84.1	83.1
MON	79.9	79.7	78.8
SVP, kPa	117.2	139.8	134.6
Density at 15 °C, kg/m^3	713.5	694.8	692.8
Benzene, % vol.	1.42	0.06	0.07

The results of determining the group composition of Zeoforming products obtained, under conditions of varying feedstock space velocity, are presented in Table 8.

Table 8. Results of determining the group composition of Zeoforming products obtained, under conditions of varying feedstock space velocity

Hydrocarbon group	SGC	Test number		
		3	8	9
N-Paraffins, % vol.	33.40	26.45	26.7	27.46
Isoparaffins, % vol.	44.40	45.34	47.14	46.55
Naphthenes, % vol.	17.26	6.94	10.54	11.17
Olefins, % vol.	1.68	2.19	4.33	4.76
Aromatics, % vol.	3.26	19.08	11.29	10.06

With an increase in the feedstock space velocity, the residence time of the feedstock in the reaction zone decreases and, as a result, the content of isoparaffinic increase and the content of aromatic hydrocarbons decrease. The obtained results (Table 7, 8) indicate that at a feedstock space velocity of more than 2 h^{-1}, the residence time of the feedstock-catalyst is insufficient for the formation of aromatic hydrocarbons. With an increase in the feedstock space velocity to 4 h^{-1}, the content of isoparaffins in the product also decreases, which indicates that at a feedstock space velocity of more than 3 h^{-1}, the contact time is also insufficient for isomerization reactions.

From the viewpoint of gasoline production, the most promising Zeoforming products (ZP) are the products No. 2, 3, 6 (relatively high RON, with a low content of benzene and low SVP). In this connection, at the next stage of work, the recipes for blending motor gasoline grades RON-92, RON-95, RON-98 based on ZP 2, ZP 3 and ZP 5 were developed. As additional blending components, toluene and methyl tert-butyl ether (MTBE) were used, as well as the original SGC. Characteristics of additional blending components are given in Table 9. The choice of additional components is justified by their relatively low cost, market availability and high RON.

The developed recipes for blending gasoline of various grades are presented in Table 10.

Table 9. Characteristics of additional blending components

Characteristic	Toluene	MTBE
RON	120.0	124.4
MON	103.3	109.5
SVP, kPa	7.6	40.3
Density at 15 °C, kg/m^3	867.3	735.0
Olefins content, % vol.	0.58	0.44
Benzene content, % vol.	0.47	0.00
Aromatics content, % vol.	97.26	0.01

Table 10. Recipes of blending gasoline grades RON-92, RON-95 and RON-98

Content, % wt.	Gasoline grades								
	RON-92			RON-95			RON-98		
Number of ZP	2	3	6	2	3	6	2	3	6
ZP	75.5	58.0	55.0	68.5	55.0	53.0	61.0	55.0	54.0
Toluene	24.5	26.0	24.0	31.5	27.0	30.0	30.0	28.0	29.0
MTBE	–	–	–	–	5.5	–	9.0	10.0	6.0
SGC	–	16.0	21.0	–	12.5	17.0	–	7.0	11.0

It is important to note that in all the proposed recipes for blending motor gasoline, the percentage of ZP exceeds 50 % wt., and the total share of ZP and SGC in the recipes exceeds 60 % wt. (for the most popular gasoline RON-92 brand an average of 75 % wt.).

The Table 11 presents the characteristics of various grades gasolines, obtained according to the developed recipes.

Table 11. Characteristics of various grades gasolines, obtained according to the developed recipes

Gasoline grades	RON-92			RON-95			RON-98			Requirements RON-92/ RON-95/ RON-98
Number of ZP	2	3	6	2	3	6	2	3	6	
RON	92.2	92.1	92.3	95.1	95.1	95.2	98.1	98.1	98.1	minimum 92.0/ 95.0/ 98.0
MON	83.9	83.3	84.2	85.9	85.7	86.3	88.4	88.0	88.7	minimum 83.0/ 85.0/ 88.0
SVP, kPa	92.2	80.4	98.7	84.3	76.9	93.5	78.9	75.2	93.4	35.0-100.0
Density at 15 °C, kg/m^3	738.6	750.0	742.2	750.6	753.5	752.5	751.4	757.2	753.5	725.0-780.0
Olefins, % vol.	2.27	1.76	3.41	2.15	1.65	3.32	1.96	1.59	3.27	maximum 18.00
Benzene, % vol.	0.59	1.00	0.17	0.59	0.96	0.18	0.53	0.96	0.17	maximum 1.00
Aromatics, % vol.	29.28	33.49	29.45	34.62	33.81	34.27	32.54	34.64	33.53	maximum 35.00

As can be seen from the results presented in Table 11, gasolines obtained according to the developed recipes, meet all the requirements of [10] and [11] for automotive gasolines.

5. Conclusion

It is established that with increasing process temperature, the content of n-paraffins and isoparaffins in the products decreases, and the content of olefin hydrocarbons increases. This tendency is explained in the carbonium-ion mechanism of hydrocarbon transformation reactions occurring on the surface of zeolite catalysts – monomolecular cracking and dealkylation reactions are primary. Increase the content of naphthenes, at a process temperature of 425°C, explained by the formation of naphthenes through diene synthesis reactions, which is facilitated by the formation of low molecular weight olefins at high temperatures. The increase content of aromatic hydrocarbons in the product composition with increasing temperature is probably associated not only with the formation of aromatic hydrocarbons as a result of hydrogen transfer between olefins, olefins and paraffins, but also with the fact that cyclohexanes become less stable with increasing temperature and can undergoes dehydrogenation to aromatic hydrocarbons by transfer of hydrogen (which is also evidenced by an increase the content of benzene in the composition of the obtained products).

It is shown that with increasing process pressure, the content of naphthenic hydrocarbons in the products increases, and the content of aromatic hydrocarbons decreases. This tendency is explained by the fact that high pressure suppresses cracking reactions of naphthenes, at the same time positively effects on the formation of naphthenes in reactions of diene synthesis, coupled with the fact that the reactions of the formation of aromatic hydrocarbon and hydrogen from olefins in hydrogen transfer reactions, in Zeoforming process occurring more actively then other type reaction.

It is established that with an increase in the feedstock space velocity, the content of isoparaffinic increase and the content of aromatic hydrocarbons decrease. The obtained results indicate that at a feedstock space velocity of more than 2 h^{-1}, the residence time of the feedstock-catalyst is insufficient for the formation of aromatic hydrocarbons; a feedstock space velocity of more than 3 h^{-1}, the contact time is also insufficient for isomerization reactions.

It is shown that, from the viewpoint of gasoline production, the most promising Zeoforming products are No. 2 (temperature 350 °C, pressure 2.5 MPa, feedstock space velocity 2 h^{-1}), No. 3 (temperature 375 °C, pressure 2.5 MPa, feedstock space velocity of 2 h^{-1}), No. 6 (temperature 375 °C, pressure 3.5 MPa, feedstock space velocity of 2 h^{-1}), because these products are characterized by relatively high octane numbers, with a low content of benzene and low SVP.

The recipes for blending motor gasoline grades RON-92, RON-95, RON-98 based on the most promising SGC Zeoforming products (the percentage of Zeoforming products exceeds 50 % wt.) were developed. Gasolines obtained according to the developed recipes, meet all the requirements of [10] and [11] for automotive gasolines. It is shown that the processing of SGC on a zeolite catalyst allow to obtain promising components of motor gasolines.

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List of symbols

SGC	*stable gas condensate;*
MON	*motor octane number;*
RON	*research octane number;*
SVP	*saturation vapor pressure, kPa;*
MTBE	*methyl tert-butyl ether;*
ZP	*Zeoforming product;*

References

[1] Shoaib AM, Bhran AA, Awad ME, El-Sayed NA, Fathy T. Optimum operating conditions for improving natural gas dew point and condensate throughput. Journal of Natural Gas Science and Engineering, 2018; 49: 324-330.
[2] Halimov EM, Kolesnikova NV, Hirayama A. Geologiya, geofizika i razrabotka neftyanyh i gazovyh mestorozhdenij. 2001; 11: 46.
[3] Shi J, Wang Y, Yang W, Tang Y, Xie Z. Recent advances of pore system construction in zeolite-catalyzed chemical industry processes. Chemical Society Reviews, 2015; 44(24): 8877-8903.
[4] Samborskaya MA, Gryaznova IA, Romanenkova VV, Cherednichenko OA. Optimal design of straight-run gasoline conversion on zeolite catalyst. Petroleum and Coal 2016; 58(7): 721-725.
[5] Belinskaya NS, Ivanchina ED, Dolganov IM, Belozertseva NE. Polzunovskij vestnik. 2019; 3: 102.
[6] EN 14517:2004 "Liquid petroleum products – Determination of hydrocarbon types and oxygenates in petrol – Multidimensional gas chromatography method".
[7] Ivanchina ED, Kirgina MV, Chekantsev NV, Sakhnevich BV, Sviridova EV, Romanovskiy RV. Complex modeling system for optimization of compounding process in gasoline pool to produce high-octane finished gasoline fuel. Chem Eng J., 2015; 282: 195 -205.
[8] Akhmetov SA, Serikov TP, Kuzeev IR, Baiazitov MI. Tekhnologiia i oborudovanie protsessov pererabotki nefti i gaza [Technology and equipment of the refining of oil and gas]. Saint-Petersburg, Nedra Publ., 2006. P. 657.
[9] Rovenskaya SA, Ostrovskiy NM Omskiy Nauchnyy Vestnik. 2003; 1 (22): 32.
[10] USS 32513-2013 "Automotive fuels. Unleaded petrol. Specifications".
[11] Technical Regulations of the Customs Union TU 01/11/2011 "On requirements for automobile and aviation gasoline, diesel and marine fuel, jet fuel and heating oil".

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