Article

Open Access

Development of Gasoline Blending Recipes Based on the Product Obtained by Processing of Stable Gas Condensate on Zeolite Catalyst

Andrey Altynov, Ilya Bogdanov, Elena Korotkova, Maria Kirgina

School of Earth Sciences & Engineering, Tomsk Polytechnic University, Tomsk, Russia

Received September 8, 2020; Accepted December 21, 2020

Abstract

The processing of stable gas condensate was carried out on a laboratory-catalytic unit in the change process conditions (temperature, pressure and the feedstock space velocity), also zeolite catalyst was used. It was shown that the obtained products are characterized by a high octane number, low content of aromatic and olefin hydrocarbons, as well as low content of benzene. The resulting recipes of gasoline fully meet the regulatory documentation requirements for commercial petroleum products. In addition, the optimal technological parameters of processing of stable gas condensate on zeolite catalyst, from the viewpoint of gasoline production, were determined.

Keywords: Stable gas condensate; Catalyst; Zeoforming; Zeolite; Gasoline; Blending recipe; Octane number.

1. Introduction

Production of ecologically and high-octane gasoline is a complex technological task for a number of refineries. This situation is due to the fact that despite the requirements tightening for the aromatic compounds content, in particular benzene. The most common process for production high-octane gasoline components in the Russian Federation remains catalytic reforming, while in other countries the largest share in the gasoline pool is the products of catalytic cracking, alkylation process, isomerization of light paraffins ^[1-3].

Commercialization of these processes requires significant investment. At the same time, in order to meet the environmental requirements for the benzene content in commercial gasoline, it is necessary to extract benzene from reformates or to modify the reforming process conditions, that eventually reduces the reformate octane number. A consequence of listed above factors is necessity using the additives or high-octane components for increasing octane number of commercial gasolines.

Not only aromatic compounds content requirements are increasingly stringent, but also sulfur content requirements in the fuels. That is why creating of more efficient feedstock hydrotreating technologies are needs ^[4-5]. At the same time, to solve this problem can be used, insensitive of sulfur, zeolite catalysts, with allow production components of gasoline.

Nowadays, by-products derived from oil production are generally used irrationally. In particular, stable gas condensate (SGC), which is a valuable feedstock, is burned in flare facility, returned back to the formation to maintain pressure, or added to oil for increase light fractions yield. At the same time, there is an increased interest in inexpensive and persistent zeolite catalysts ^[6-10]. In this connection, the study of the influence of process conditions on the products composition obtained during the processing of stable gas condensate on a zeolite catalyst is important scientific task.

The stable gas condensate used in the work, obtained from one of the West Siberian fields, is a by-product of the wide light hydrocarbons fraction (WLHF) separation process. In WLHF separation process in the field, the following products are obtained: commercial methaneethane fraction, commercial propane-butane fraction and stable gas condensate, containing C_{5+} hydrocarbons. One of the most promising applications of stable gas condensate is its use as Zeoforming process feedstock ^[11-12]. The Zeoforming process allows producing high-octane motor fuels by catalytic processing of different origin low-octane gasoline fractions on zeolite catalysts. The process advantages are the simplicity technological scheme and the used equipment; low capital costs for construction; the possibility of obtaining commercial gasoline through a single process; cost-effective and ecofriendly zeolite catalyst.

This work aim is to study the possibility of using stable gas condensate Zeoforming products (ZP), obtained under different technological conditions of the process, as a blended component for the production of gasoline.

2. Materials and methods

Zeoforming process implementation was carried out on a flow type laboratory catalytic unit. As a catalyst, a KN-30 brand zeolite catalyst (production of "Novosibirsk Chemical Concentrates Plant") was used. A 10 cm³ sample of catalyst with a bulk density of 0.638 g/cm³ was loaded into the reactor, where it was ignited for 8 hours at a temperature of 500°C in a nitrogen blanket.

The tests were carried out in the range of temperature variation from 375 to 425°C in increments of 25°C; in the range of pressure variation from 2.5 to 4.5 MPa in increments of 1 MPa; in the range of feed space velocity from 2 to 4 h^{-1} in increments of 1 h^{-1} . Seven tests were conducted. The test conditions are given in Table 1.

Parameter	ZP 1	ZP 2	ZP 3	ZP 4	ZP 5	ZP 6	ZP 7
Temperature, °C	400	400	400	400	400	375	425
Pressure, MPa	2.5	2.5	2.5	3.5	4.5	2.5	2.5
Feed space velocity, h ⁻¹	2	3	4	2	2	2	2

Table 1. Conditions of stable gas condensate Zeoforming process

The obtained products composition was investigated by gas chromatography analysis. Chromatographic analysis of the obtained products was performed on chromatograph "Chromatek-Crystal 5000" according to EN 14517:2004 "Liquid petroleum products – Determination of hydrocarbon types and oxygenates in petrol – Multidimensional gas chromatography method". Based on the obtained chromatograms with the help of the "Compounding" software (Tomsk Polytechnic University development) ^[13], the characteristics of the obtained products were calculated.

3. Results and discussion

Table 2 shows the composition of obtained products (where AH – aromatic hydrocarbons) and the results of calculation for characteristics of the obtained products (where RON – research octane number; MON – motor octane number; SVP – saturated vapor pressure).

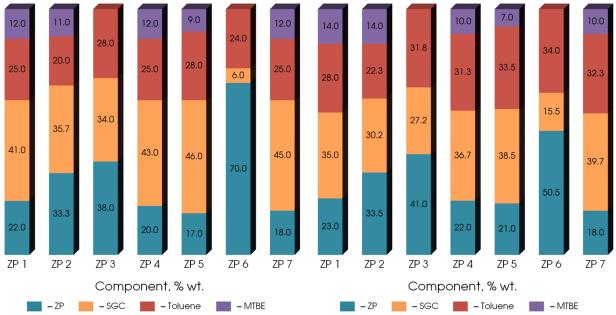
Product	RON poi	MON ints	SVP kPa	Density kg/m³	Olefins	Benzene % vol.	AH
ZP 1	84.2	77.5	97.7	738.8	4.30	3.50	24.07
ZP 2	88.2	82.5	167.0	687.4	4.40	2.40	16.28
ZP 3	88.8	83.0	190.4	688.5	6.30	0.10	12.70
ZP 4	85.8	79.4	149.3	706.0	6.70	3.40	20.14
ZP 5	89.1	81.1	182.5	710.6	3.00	3.20	19.98
ZP 6	82.5	77.3	123.6	690.4	4.80	0.10	10.26
ZP 7	87.4	79.5	108.4	732.7	3.60	4.20	25.25

Table 2. Characteristics and composition of stable gas condensate Zeoforming products

By analyzing the results, which are presented in Table II, it can conclude that the obtained products can be used as a gasoline blending component. This is because the products have relatively high RON (82.5-89.1 points) with a relatively low content of aromatic and olefin hydrocarbons (an average of 18.4 and 4.7 % vol.). In addition, the advantage of the products is the low benzene content.

The next stage of the work was development of the recipes for blending 92 RON and 95 RON brands of automobile gasoline based on the zeoforming products. Development of the recipes was carried out using the "Compounding" software.

In the developing of gasoline recipes, stable gas condensate, toluene, and methyl-tertbutyl ether (MTBE) was used as blending components. The choice of toluene as a blending component is explained by its relatively easy availability and low cost, choice of MTBE is explained its high octane number and the absence of aromatic hydrocarbons and benzene in its composition. Recipes for blending 92 RON and 95 RON brands of gasoline are presented in Figure 1, 2.



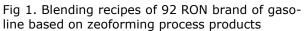


Fig. 2 Blending recipes of 95 RON brand of gasoline based on zeoforming process products

Tables 3, 4 shown characteristics of the gasoline, obtained from the developed recipes.

Table 3. Characteristics and composition of 92 RON brand of automobile gasoline, obtained by the c	le-
veloped blending recipes	

Recipe	RON po	MON ints	SVP kPa	Density kg/m³	Olefins	Benzene % vol.	AH
1	92.1	83.4	57.5	745.4	1.64	0.95	26.27
2	92.0	84.0	87.0	725.1	2.10	0.99	22.00
3	92.1	84.2	98.7	734.9	3.09	0.20	27.96
4	92.2	83.6	67.3	737.6	2.08	0.89	24.93
5	92.2	83.4	69.6	741.5	1.29	0.76	26.82
6	92.4	84.6	43.8	732.1	3.75	0.15	26.87
7	92.0	83.2	58.4	741.8	1.38	0.95	25.45
USSR 32513-2013 requirements	92.0	83.0	35.0- 100.0	725.0- 780.0	18.00	1.00	35.00

As can be seen from Tables 3-4, all gasoline produced by the developed recipes meet the requirements of USSR 32513-2013 "Automotive fuels. Unleaded petrol. Specifications" and TR TS 013/2011 "Customs Union Technical Regulations on requirements to automobile and aviation gasoline, diesel and marine fuel, jet fuel and heating oil".

Recipe	RON	MON	SVP kPa	Density	Olefins	Benzene	AH
Recipe	ро	points		kg/m³		% vol.	
8	95.1	85.7	55.2	752.8	1.65	1.00	29.23
9	95.0	86.4	84.8	731.2	2.09	1.00	24.06
10	95.0	86.5	99.9	742.4	3.29	0.21	31.70
11	95.0	85.8	65.4	749.0	2.22	0.99	30.90
12	95.0	85.5	71.2	752.1	1.34	0.10	32.49
13	95.1	86.3	76.0	748.6	2.99	0.20	33.60
14	95.0	85.5	54.3	754.5	1.36	0.98	31.89
USSR 32513-2013	92.0	83.0	35.0-	725.0-	18.00	1.00	35.00
requirements			100.0	780.0			

Table 4. Characteristics and composition of 95 RON brand of automobile gasoline, obtained by the developed blending recipes

From the data presented in Tables 3-4, it follows that with an increase in the temperature of the Zeoforming process (recipes No. 6, 1, 7 and No. 13, 8, 14 for 92 RON and 95 RON brands of automobile gasoline, respectively), the proportion of the zeoformate involved in the blend decreases. At a process temperature of 375°C, the involvement the most expensive blending component – MTBE in the gasoline blending recipes not required. With an increase in the pressure of the Zeoforming process (recipes No. 1, 4, 5 and No. 8, 11, 12 for 92 RON and 95 RON brands of automobile gasoline, respectively), the proportion of zeoformate involved in the blending recipe, decreases, at the same time, the proportion of stable gas condensate and toluene increases.

The consequence of the increase the feed space velocity of Zeoforming process (recipes No. 1, 2, 3 and No. 8, 9, 10 for 92 RON and 95 RON brands of automobile gasoline, respectively), the proportion of zeoformate involved in the blending recipe, increases, while the proportion of MTBE – decreases, and with the feed space velocity of 4 h^{-1} , it becomes possible to completely abandon of using MTBE in gasoline blending.

4. Conclusion

Zeoforming of stable gas condensate was carried out on a laboratory catalytic unit under the conditions of varying such technological parameters as pressure, temperature, and feed space velocity. The products obtained during the test are characterized by high octane numbers and low content of benzene, aromatic and olefin hydrocarbons.

With the use of the "Compounding" software recipes for blending 92 RON and 95 RON brands of automobile gasoline were developed. Stable gas condensate, toluene, MTBE and stable gas condensate Zeoforming process product were used as the blending component.

It was determined that the blending recipes of 92 RON and 95 RON brands of automobile gasoline on the base of ZP 6 are most preferred. It is characterized by maximum involvement of zeoformate, minimal involvement of stable gas condensate and the complete absence of MTBE in the blending recipe.

It was found that the optimal technological parameters for the stable gas condensate Zeoforming process implementation in terms of the production of automobile gasoline are temperature – 375° C, pressure – 2.5 MPa, feed space velocity – 2 h⁻¹.

Acknowledgements

The reported study was funded by RFBR according to the research project No. 20-38-90157.

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;
AH	aromatic hydrocarbons;

References

- [1] Liu Y, An Z, Yan H, Chen X, Feng X, Tu Y, Yang C. Conceptual coupled process for catalytic cracking of high-acid crude oil. Ind. Eng. Chem. Res. 2019; 58 (12): 4794-4801.
- [2] Ying L, Guoqing W, Xiaoying P, Guanjun G. Isobutane alkylation with 2-butene in novel ionic liquid/solid acid catalysts. Fuel. 2019; 252: 316-324.
- [3] Hidalgo JM, Zbuzek M, Černý R, Jíša P. Current uses and trends in catalytic isomerization, alkylation and etherification processes to improve gasoline quality. Cent. Eur. J. Chem. 2014; 12 (1): 1-13.
- [4] Tuktin B, Zhandarov E, Nurgaliyev N, Tenizbayeva A, Shapovalov A. Hydrotreating of gasoline and diesel oil fractions over modified alumina/zeolite catalysts. Pet. Sci. Technol. 2019; 37 (15):1770-1776.
- [5] Wu L, Liu Y, Zhang Q. Operational optimization of a hydrotreating system based on removal of sulfur compounds in hydrotreaters coupled with a fluid catalytic cracker. Energy Fuels. 2017; 31 (9): 9850-9862.
- [6] Aitani A, Akhtar MN, Al-Khattaf S, Jin Y, Koseoglo O, Klein MT. Catalytic upgrading of light naphtha to gasoline blending components: A mini review. Energy Fuels. 2019; 33 (5): 3828-3843.
- [7] Javdani A, Ahmadpour J, Yaripour F. Nano-sized ZSM-5 zeolite synthesized via seeding technique for methanol conversions: A review. Microporous Mesoporous Mater. 2019; 284: 443-458.
- [8] Ji Y, Yang H, Yan W. Strategies to enhance the catalytic performance of ZSM-5 zeolite in hydrocarbon cracking: A review. Catalysts. 2017; 7 (12):367.
- [9] Alipour SM. Recent advances in naphtha catalytic cracking by nano ZSM-5: A review Chin. J. Catal. 2016; 37 (5): 671-680.
- [10] Mohammadparast F, Halladj R, Askari S. The crystal size effect of nano-sized ZSM-5 in the catalytic performance of petrochemical processes: A review. Chem. Eng. Commun. 2015; 202 (4): 542-556.
- [11] Belinskaya N, Altynov A, Bogdanov I, Popok E, Kirgina M, Simakov DSA. Production of gasoline using stable gas condensate and zeoforming process products as blending components. Energy Fuels. 2019; 33 (5): 4202-4210.
- [12] Bogdanov IA, Altynov AA, Kirgina MV, Mardanov KEO. Directions of transformation of the stable gas condensate hydrocarbons on a zeolite catalyst under zeoforming conditions. Pet. Coal. 2020; 62(3): 792-798.
- [13] Ivanchina ED, Kirgina MV, Chekantsev NV, Sakhnevich BV, Sviridova EV, RomanovskiyRV. Complex modeling system for optimization of compounding process in gasoline pool to produce high-octane finished gasoline fuel. Chem. Eng. J. 2015; 282:194-205.

To whom correspondence should be addressed: Dr. Andrey Altynov, Division for Chemical Engineering, School of Earth Sciences & Engineering, National Research Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; E-mail: <u>andrey_altun@mail.ru</u>