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Petrol Production from Virgin Fractions of Oil and Gas Condensates with the Use of Zeoforming Process

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Abstract

Problems concerning the production of diesel fuel and motor petrol at small-scale installations intended for oil and gas condensate processing into motor fuel are considered. It is shown that for a large number of oil and gas condensate deposits the virgin diesel fractions correspond in their physicochemical characteristics to the requirements of standards for diesel fuel. In some cases, graded diesel fuel can be obtained by varying the fraction composition and/or using the corresponding additives. For the production of graded automobile petrol at small-scale installations, the most optimal process is Zeoforming, which is based on the use of a zeolite-containing catalyst. It is shown that varying the process conditions one may manufacture petrol of required grades (from AI-80 to AI-96, of summer and winter kinds) from low-octane hydrocarbon fractions of different origin without preliminary desulphurization or hydrofining and without any use of hydrogen-containing gas. In comparison with reforming, petrol obtained by Zeoforming Process is characterized by lower content of aromatic hydrocarbons, especially benzene.

INTRODUCTION

Oil and gas condensate are traditional primary raw materials for the production of motor fuel – petrol and diesel fuel. In spite of large production and enormous resources of this hydrocarbon raw material, the problem of reliable motor fuel supply to various regions is very important in Russia, especially for the regions of Extreme North and Kamchatka. The reason is that there often are many thousand kilometres from motor oil consumers to manufacturers. In addition, fuel can be supplied to some regions only seasonally, either by river or sea transport during the shipping season or by motor transport along winter roads, so there is the necessity in these regions to maintain a large reservoir for storing combustive-lubricating materials during off-season. This is the reason of additional substantial increase both in wholesale and consumer prices of motor fuel in these regions, which, in turn, causes an increase in the expenses for the performance of automobiles and tractors, and consequent increase in the price of motor transport services.

At the same time, many of these regions have their own natural resources of the hydrocarbon raw material – oil and gas condensate, from which one may manufacture motor fuel to provide the local automobile and tractor vehicles at small-scale installations (mini-plants) directly at the mines or in the vicinity of them; it is also possible to produce fuel oil which is not less necessary.

DIESEL FUEL PRODUCTION

The virgin diesel fractions (VDF) are obtained by oil or gas condensate rectification with the isolation of the corresponding fractions. In comparison with oil, gas condensate is economically more profitable raw material for the production of motor fuel because the mass fraction of light oil, that is, virgin petrol and

TABLE 1

Properties of virgin diesel fractions of some oil and gas condensate deposits of Russia and FSU countries

Deposits	Boiling range, °C	Temperature, °C		Density, kg/m^3	Content of total sulphur*, mass %	Cetane number
		Cloud point	Solidification point			
1	2	3	4	5	6	7
Gas condensate						
Astrakhanskoye	160−300	−30	−38	825	0.92	56
«	161−360	−4	−17	839	1.36	46.5
Berezanskoye	180−360	+15	−2	874		50
Beurdeshik	180−300	−20	<−20	834		54
Vuktylskoye	180−300		−36	806	0.04	56
Gugurutli	180−260	−20	<−20	808		47
Efremovskoye	180−330		−20	813	0.04	
Zhanazhol	170−340		−28	806	0.26	46
Zapolyarnoye (Senoman)	200−290	−65		872	0.012	
Karachaganak	170−310	−20	−25	824	0.58	57
Kovyktinskoye	133−295	−44	−61	758	0.04	51
Kirpichli	150−310	−3	−17	833		44
«	180−321	+2	−8	845		42
Luginetskoye	150−340		−40	789	<0.01	>56
«	200−340		−32	807	<0.01	>56
Markovskoye	300−360	−6	−22	803		63
Mastakh	132−306		−38.9	829	0.003	45.9
«	165−289	−48	−56.5	824	0.01	45.6
«	161−311	−26	−37.6	841	0.01	47.1
«	186−296	−28	−37	852	0.01	46.8
«	165−347		−6	853	0.01	49.4
Medvezhye (Senoman)	210−327	−68		869	0.012	37
Naip	180−300	−15	<−20		0.03	54
Punginskoye	180−310	−30	−38	808		40
Samburgskoye	188−355	−7	−26	826	0.045	51
Srednevilyuyskoye	120−290	−18	−41	816	0.01	45.0
«	156−279	−22	−35	809	0.01	41.1
Tedzhen	150−302	−14	<−15			54
Urengoyskoye (Valanzhin)	120−309		−45	784	0.0135	40
«	140−319		−36	799		45
«	175−298	−25	−37	827	0.01	47.6
Ust-Vilyuyskoye	200−320	−60		859		35
Shatlyk	150−344	+4	−3	797		54
«	180−346		−1	794	0.04	62
Shebelinskoye	180−306	−13	−30	807	0.02	58
Yuzhno-Soleninskoye	120−275	−32	−62	817	0.05	37.2
Oil						
Belozerskoye	150−350		−13	820	0.13	54
«	180−350		−9	829	0.14	50
Verkh-Tarskoye	130−330	−23	−28	795	0.1	46

TABLE 1 (Continued)

1	2	3	4	5	6	7
Vorobyevskoye	140–320		−27	824	0.03	55
«	140–350		−23	825	0.05	55
«	180–350		−17	836	0.07	54
Yurubchenskoye	117–341	−28	−36	789	0.04	54
«	120–288	−36	−45	783	0.03	51
Requirements						
of GOST 305–82		not higher than:	not higher than:	not larger than:	not larger than:	not lower than:
Grade L		−5	−10	860	0.2/0.5	45
Grade Z:						
for moderate climatic zone		−25	−35	840	0.2/0.5	45
for cool climatic zone		−35	−45	840	0.2/0.5	45
Grade A		not stand.	−55	830	0.4	45

Note. Here and in Table 3: the data were obtained from a large number of publications; they cannot be listed in whole due to the limited volume of the present paper.

*The first value is for kind 1; the second value is for kind 2.

diesel fractions, may reach 95–100 %, while in oil this value is 30–70 %.

To be used as motor fuel, the virgin diesel fractions should correspond to a number of requirements posed by the standard for diesel fuel. Both oil and gas condensate samples from different deposits can differ from each other substantially in-group, fraction composition and in physicochemical properties, so virgin diesel fractions obtained from them differ in their characteristics, too (Table 1). One can see that the mass fraction of total sulphur in VDF of oil and gas condensate from different deposits can very from thousandth of a per cent to 1.55 %, cetane ratio is 39–63 units, cloud point temperature varied from +15 to −60 °C, solidification point is from −1 to −62 °C and below.

In addition, it follows from the data shown in Table 1 that the virgin diesel fractions of the majority of gas condensate and oil deposits correspond to the requirements of actual State Standard GOST 305–82 in cetane number, cloud point and solidification point, total sulphur content and density. This allows one to consider these fractions as a potential diesel fuel of different grades.

Construction of mini plants of motor fuel can be reasonable also in the case when the quality of virgin diesel fractions does not meet the requirements of the standard in some parameters but these parameters can be brought up to the corresponding level with insignificant additional expenses or after the change in the fraction composition of the diesel fraction. For instance, if the cetane number of VDF is lower than 45 by 1–4 units, it may be increased up to the value required by the standard by adding ignition promoters [1]. In some cases, when VDF has a low cloud point and solidification point, cetane number may be increased by changing the fraction composition of the fuel toward heavier fractions (of course, within the level of standard requirement). This can be clearly seen with the example of VDF of the gas condensate from the Urengoy deposit (see Table 1). In the case of high cloud point and solidification point of VDF, depressor additives and paraffin dispersants are used to bring these characteristics down [1]. If the cetane number of VDF is high, with some excess, one may decrease the cloud point and solidification point by varying the fraction composition of the fuel toward light-weighed fractions (within the requirement of the standard), similarly to the VDF of gas condensate from the Mastakh deposit (see Table 1). It is also possible to use simultaneously several methods of those listed above.

It is also possible to decrease the cloud point and solidification point of diesel fractions as a result of their deparaffination carried out either with the use of selective solvents or carbamide, or by means of adsorption on A-type zeolites, or by means of catalytic processing [2]. However, these technologies implemented at mining miniplants bring about essential complication of the production, so, in our opinion, it is unreasonable to implement them. In the present work we also do not consider the question concerning the production of diesel fuel from sulphur-containing raw material. Sulphur can be removed from the raw material either by fuel demercaptanation with alkalis [2] or with the help of homogeneous or heterogeneous catalysts [3], or by deep catalytic desulphurisation using classical hydrofining processes. Small-scale production of diesel fuel from sulphur-containing raw material at the installations of this kind seems uneconomic because substantial expenses for the stage of purification of diesel fractions from sulphur would be required; hydrofining version requires the presence of hydrogen as well.

It should be noted that there are catalysts based on zeolite of the type of pentasil, which allow one to carry out sulphur removal from hydrocarbon fractions without using a hydrogen-containing gas [4–7]. When processing the diesel fractions with these catalysts, in addition to a decrease in total sulphur content, one also achieves a decrease in the cloud point and in solidification point [7, 8]. However, this is also accompanied by a substantial decrease in the cetane number of diesel fractions (Fig. 1), which allows one to process only the VDF having substantial excess in cetane number into the graded diesel fuel; this makes the raw material basis narrower.

In general, it follows from the above considerations that in the case if total sulphur content of the virgin diesel fractions from the majority of oil and gas condensate deposits corresponds to the requirements of the standard, one may use low-expense technologies to manufacture graded diesel fuel by varying the fraction composition and using different additives.

PETROL PRODUCTION

Modern gasoline has the octane number from 76 to 88 MM (from 80 to 98 IM), while the concentration of total sulphur in it should not

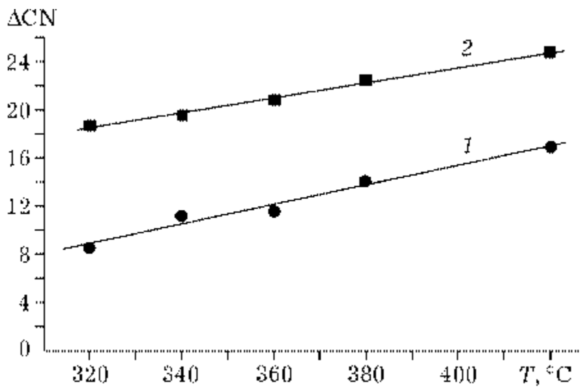

Fig. 1. Effect of reaction temperature on a decrease in the cetane number of *n*-paraffins C_9–C_{20} (ΔCN) for the transformation of virgin diesel fractions of oil from the Verkh-Tarskoye deposit (*1*) and gas condensate from the Zhanazhol deposit (*2*) on IK-30 catalyst. P = 1 MPa, $W = 2\ h^{-1}$; the cetane number of initial fractions is equal to 46.

exceed 0.015–0.10 mass %, depending on the standard. There are also limitations for the component composition and for the composition of antiknock additives (Table 2).

Similarly to the case of diesel fractions, the compositions and other quality characteristics of the virgin gasoline fractions (VPF) of oil and gas condensate from various deposits differ greatly (Table 3). The concentration of total sulphur in virgin gasoline varies within a broad range, depending on the deposit: from almost trace amount to 1% and above. The hydrocarbon composition changes within a broad range, too: the fraction of aromatic hydrocarbons varies from 1 to 28 mass %, naphthenes from 9 to 84 mass %, paraffin from 6 to 78 mass %. These variations of the hydrocarbon composition of virgin petrol lead to the variation of its octane number within a broad range: from 31 to 66 MM units; for a small number of deposits up to 72 MM (see Table 3). Because of this, the possibility of the direct use of virgin petrol fractions as a motor fuel is limited by the restrictions of actual standards, first of all due to low octane number.

In general, improvement of the antiknock properties, that is, an increase in the octane number of virgin petrol fractions, can be achieved using several methods: by adding antiknock compounds, by compounding with high-octane components (oxygen-containing compounds, alkylates, reformates, *etc.*); by using

TABLE 2

Requirements to unleaded automobile petrol

Petrol grade	Octane number, MM/IM, not less than	Content of sulphur, mass %	Content, vol. %, not more than:					Concentration, g/dm^3, not more than:		
			Aromatic hydrocarbons	Benzene	Olefine hydrocarbons	MTBE*	N-methyl-aniline [1]	Lead	Manganese	Iron [1]
According to GOST 2084–77:										
A-76	76/не норм.	0.10	55**	Not stand.	25**	–	–	0.013	–	–
AI-93	85/93	0.10	55**	Not stand.	25**	–	–	0.013	–	–
AI-95	85/95	0.10	55**	Not stand.	25**	–	–	0.013	–	–
According to TU 38.001165–97:										
AI-80	76.0/80.0	0.05	55**	Not stand.	25**	–	1.3	0.013	–	0.038
AI-92	83.0/92.0	0.05	55**	Not stand.	25**	–	1.3	0.013	–	0.038
AI-96	85.0/96.0	0.05	55**	Not stand.	25**	–	1.3	0.013	–	0.038
According to GOST R 51105–97:										
Normal-80	76.0/80.0	0.05	55**	5	25**	15**	1.3	0.010	0.050	0.038
Regulyar-91	82.5/91.0	0.05	55**	5	25**	15**	1.3	0.010	0.018	0.038
Premium-95	85.0/95.0	0.05	55**	5	25**	15**	1.3	0.010	–	0.038
Super-98	88.0/98.0	0.05	55**	5	25**	15**	1.3	0.010	–	0.038
According to GOST R 51866–2002:										
Regulyar Evro-92	83/92	0.015	42.0	1.0	21.0	15***	1.3	0.005	–	0.038
Premium Evro-95	85/95	0.015	42.0	1.0	18.0	15***	1.3	0.005	–	0.038
Super Evro-98	88/98	0.015	42.0	1.0	18.0	15***	1.3	0.005	–	0.038

*Methyl-*tert*-butyl ether.

**According to the complex of procedures of evaluation [9].

***According to GOST R 51866–2002, the volume concentration of oxygen-containing compounds, %, not more than: methanol, 3; ethanol, 5; isopropanol, 10; isobutanol, 10; *tert*-butanol, 7; C_{5+} ethers, 15; other monoalcohols and ethers, 10, but the mass concentration of oxygen is not more than 2.7.

TABLE 3

Composition and properties of virgin petrol fractions of different gas condensate and oil deposits of Russia and FSU countries

Deposits	Boiling range of fraction, °C	Density, kg/m^3	Content of total sulphur, mass %	Hydrocarbon composition, mass %			Octane number, MM
				Aromatics	Paraffins*	Naphthenes	
1	2	3	4	5	6	7	8
Gas condensate							
Astrakhanskoye	46–141	714	0.24				50.4
«	53–179	738	0.35				44
Berezanskoye	51–150						73.2
«	55–200						70.8
Beurdeshik	78–170	764		25	46	29	56.0
Bovanenkovskoye	46–118	707		17	47	43	71.6
Vasilkovskoye	58–169	732	<0.01	4	27/34	35	
Verkhnechonskoye**	l.b.–180	685	<0.01				45
«	l.b.–180	709	<0.01				53
Vuktylskoye	51–200						50.7
«	44–150						54.8
«	76–180	739		15	59	26	49
«	28–200		0.022	12	56	32	51.4
Gugurutli	70–160	761		21	47	33	54.2
Zhanazhol	40–170	733	0.29	13	–/29		54
Kalinovoye	35–146	724	<0.01	9	–/35		
Karachaganak	58–214	730	0.27	19	–/32		
Kirpichli	58–141	763		37	32	31	71.0
«	59–171	769		37	34	29	67.7
Luginetskoye	28–150	722		~1	~73	~26	55
«	28–200	728		~3	~75	~22	49
Markovskoye	39–150						50.2
«	41–200						45.0
Mastakh	66–158	755	0.02	14	14	72	70.0
«	45–177	737	0.002	15	15	70	67.0
«	40–136	735		13	9	78	70.1
«	43–163	736		12	7	81	69.1
«	45–177	737		10	6	84	67
«	34–167	721		4			76.8
Naip	100–174	777		27	37	36	57.7
«	98–140	768		29	35	36	62.5
Nekrasovskoye	44–150		<0.01				71.8
«	66–153	758	<0.01	29	18/18	35	70.7
Orenburgskoye	102–174	745		17	61	22	48.1
«	85–180	739	1.092	14	70	16	
«	36–154	688	1.15	16	–/31		
Pribrezhnoye	36–195	705	0.005	8	71	21	57
Punginskoye	47–150						68.4
«	59–200			2			66.5

TABLE 3 (Continued)

1	2	3	4	5	6	7	8
Samburgskoye	47–176	740	0.03	7	37/31	25	
«	79–185	747	0.03	11	62	27	47
Srednevilyuyskoye	45–146		0.006	15			
«	40–220	747	<0.01	18	–/23		
Sobinskoye	35–145	674		4	–/41		
Soleninskoye	48–149	739		6	–/9		
Sredneaziatskoye	105–182	776		25	42	33	56.1
Stavropolskoye	84–174	767		28	36	36	64.1
Urengoyskoye	42–150						66.0
«	47–200			10	–/29		60.8
«	28–143	647	0.1	5	–/25		65.0
«	43–137	712	0.1	2	–/22		67.0
«	31–201	744	0.1				56.0
«	28–109						73.0
Ust-Vilyuyskoye	40–150						73.6
«	45–200						72.0
Kharasaveyskoye	67–140	737	<0.01	<1	~33	~66	58.1
Shatlyk	67–149	732		18	66	16	50.2
«	86–175	743		12	78	10	31.2
Shebelinskoye	45–150	742		19	–/23		63.0
«	49–200						59.0
«	78–166	735					56–58
Oil							
Verkh-Tarskoye	35–175	685	0.02	4	–/34		64
Vorobyevskoye	н.к.–150	731	<0.01	12	32/25	31	
Vyngapurovskoye	31–190	702	<0.1	10	–/37		
Dzherskoye	28–180						55.5
«	28–200				–/28		53.5
Dolinskoye	28–180						56.6
«	28–200				–/20		50.0
Zhetybayskoye	28–180						37.0
«	28–200				–/33		31.0
Koturtepinskoye	28–180						57.0
«	28–200				–/15		51.5
Romashkinskoye	28–180						48
«	28–200				61		40
Samotlorskoye	28–180						53.4
«	28–200				–/28		51.6
Srendevasyuganskoye	35–160	695	<0.02				62
«	37–180	733	<0.02				59
«	28–180	708	0.05	7	30/32	31	
Troitsko-Anastasievskoye	28–180						72.0
	28–200				19		65.7
Ust-Balykskoye	28–180						39.6
«	28–200				–/25		34.8

TABLE 3 (Continued)

1	2	3	4	5	6	7	8
Ust-Tegusskoye	42–150	703		4	–/36		
Shaimskoye	28–180						47.8
«	28–200				56		41.5
Ekhabinskoye	28–180				–/9		67.2
«	28–200						64.0
Yurubchenskoye	35–115	671	0.011				51
«	37–153	683	0.012				48
«	36–146	686	0.013				46

Note. l. b. – low-boiling.

*Numerator shows the content of isoparaffins, denominator shows that of *n*-paraffins.

** From different horizons.

oil-processing and petrochemical procedures (reforming, isomerization processes, *etc.*).

Compounding

To increase octane number by adding antiknock additives and octane-increasing compounds to the virgin, that is, basic petrol seems in the first opinion to be the simplest and the most reasonable from the technological point of view. At present, antiknock and octane-increasing additives permitted for use in Russia in the production of automobile petrol are those based on: ferrocene – alkyl ferrocene compounds and dimethylferrocenylcarbinol (additives of the type of FK-3, FK-4); manganese compounds – manganese cyclopentadienyltricarbonyl and methyl cyclopentadienyltricarbonyl (Hitec-type additives), and aromatic amines (ADA, Ekstralin additives). With only one of these additives used in permitted amount (see Table 2), an increase in octane number of petrol does not exceed 2–6 units [1], which does not allow obtaining automobile petrol from VPF due to the low octane number. For example, using N-methylaniline, which is the most efficient substance for this purpose (ON = 250 MM and 280 IM [1]) for compounding basic petrol, in the case of its maximal admissible fraction in the final product, equal to 1.3 %, in order to obtain AI-80 type petrol, the octane number of the initial basic petrol should be not less than 74 MM (Fig. 2, curve *1*). Using at the same time two or three antiknock additives permissible in Russia one may reach an increase in the ON of virgin petrol by 6–8 units, which would only allow one to produce automobile petrol of AI-80 type from VPF in few very rare cases.

Automobile petrol of AI-80 and AI-91 grades may be produced from virgin petrol fractions by compounding with high-octane components. Among them, most readily available are various fractions of aromatic hydrocarbons and methyl *tert*-butyl ether (MTBE). However, it is necessary to take into account the existing restrictions for the concentration of both the aromatic hydrocarbons including benzene and MTBE in petrol (see Table 2). In addition, the production of automobile petrol from virgin

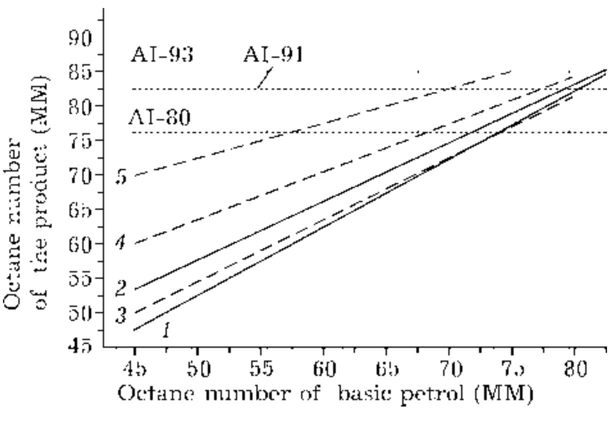

Fig. 2. Effect of the initial octane number of basic petrol on the calculated octane number of the product after compounding with high-octane components and octane-increasing additives: *1* – with N-methylaniline (with maximum permissible 1.3 vol. %); *2* – with methyl *tert*-butyl ether (with maximal permissible 15 vol. %); *3–5* – with 10 (*3*), 30 (*4*) and 50 vol. % (*5*) of the high-octane component – the aromatic fraction with ON = 95 MM.

petrol by compounding with high-octane components requires substantial amounts of the latter (see Fig. 2, curves *2*–*5*).

Thermocatalytic processes

A substantial improvement of antiknock properties of virgin petrol fractions of oil and gas condensates and a decrease in total sulphur content in them can be achieved by using thermocatalytic processes. This allows one not only to increase the octane number of petrol manufactured but also to transform sulphur from organic sulphur-containing compounds into hydrogen sulphide, which is then easily removed from the resulting petrol.

The main industrial process of obtaining high-octane petrol is reforming and its versions [10, 11]. The process is performed at a temperature within 450–500 °C in the atmosphere of hydrogen-containing gas. Reforming catalysts are extremely sensitive to sulphur- and nitrogen-containing compounds present in the raw material, so it is necessary to carry out preliminary deep hydrofining of the raw material. The resulting petrol fractions contain 50–70 mass % of aromatic hydrocarbons and a lot of benzene (concentration: 7–15 mass %). The benzene content of petrol obtained by reforming is much above the maximal permissible concentration (5 vol. %) admitted by the requirement of GOST R 51105–97 and 51313–99 to automobile petrol. This requires subsequent removal of the benzene fractions from the reformates by rectifying the latter. For remote regions, it may be reasonable to use reforming installations in medium-capacity miniplants of motor fuel only when processing sulphur-containing raw material (oil and gas condensate) when it is necessary to carry out hydrofining of the resulting diesel fuel from sulphur; it would not be reasonable from the economical viewpoint to use reforming in small-scale miniplants.

It is also possible to increase the octane number of petrol fractions by means of isomerization processes which are usually carried out in the atmosphere of hydrogen [10, 12, 13]. As a rule, catalysts used for this purpose are sensitive to sulphur-containing compounds in the raw material, so it is necessary to perform preliminary deep hydrofining of the raw material. Isomerization processes are most widely used to increase the octane number of narrow-boiling fractions containing mainly pentanes and hexanes and boiling away below 62–85 °C, in order to obtain high-octane component of petrol; for the isomerization of broad-boiling petrol fractions, octane number increases only by 4–6 units. In order to carry out the process in hydrogen, it is necessary to have its source, so the installations of isomerization of petrol fractions usually operate in combination with reforming installations. It is only reasonable to arrange isomerization installations incorporated into large-scale oil-processing plants equipped with reforming and hydrofining installations.

The Zeofoorming process is most suitable for realization in field miniplants of petrol production [14–18]. Due to the use of zeolite-containing catalyst of IK-30 type, there is no necessity to carry out preliminary hydrofining or purification of the raw material from sulphur. In addition, any hydrocarbon raw material boiling away below 120–150 °C can be processed into petrol of different grades (from AI-80 to AI-96) without any additional compounding or any use of antiknock additives (Table 4).

Zeoforming process

The Zeoforming process is based on the use of IK-30 type catalyst prepared on the basis of synthetic high-silica zeolite; the composition of

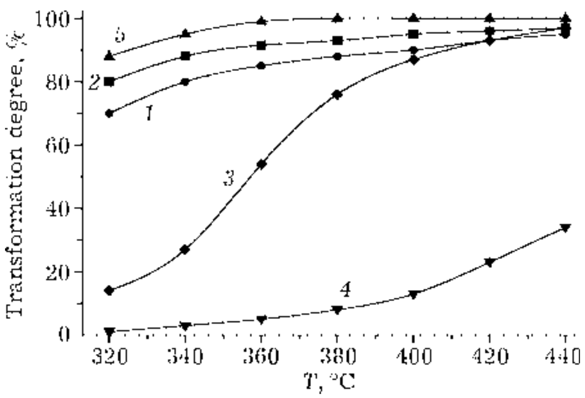

Fig. 3. Effect of reaction temperature on the transformation degree of individual hydrocarbons for Zeofroming processing of *n*-hexane (*1*), *n*-nonane (*2*), cyclohexane (*3*), isooctane (*4*) and hexene-1 (*5*) with IK-30-1 catalyst. P = 1 MPa, W = 2 h^{-1}.

TABLE 4

Yield of automobile petrol from Zeoforming processing of virgin petrol fractions of oil and gas condensates of different deposits

Deposit, oil	Nature of raw material	Boiling range, °C	Petrol yield, mass %		
			AI-80	AI-91	AI-95
Aganskoye	Oil gas condensate	28–135	78–81	59-64	50-55
Vasilkovskoye	Gas condensate	55–190	80–84	68–73	60–64
Vorobyevskoye	Oil	36–180	82–86	68–72	60–63
Verkh-Tarskoye	«	45–190	82–86	69–73	60–64
Vyngapurovskoye	«	31–190	84–86	69–73	62–64
West Siberian*	«	35–180	82–85	69–72	62–64
«	«	70–175	87–90	74–77	65–68
Zhanazhol	Gas condensate	40–170	88–90	75–77	67–70
Iraq*	Oil	34–140	84–88	70–74	62–65
Kaliningradskaya*	«	47–168	82–86	68–72	62–66
Kalinovoye	Gas condensate	35–146	79–83	66–70	57–61
Karachaganak	«	45–215	90–94	77–81	68–72
Luginetskoye	«	45–160	78–82	65–69	58–61
Mastakh	«	35–140	84–88	71–75	62–66
Mubarekskoye	«	35–190	90–93	78–81	69–72
«	«	35–250	90–93	85–88	77–80
Nekrasovskoye	«	45–150	86–89	71–73	64–66
«	«	36–180	89–93	73–77	65–69
Orenburgskoye	«	35–160	86–90	73–77	65–68
Pribrezhnoye	«	35–195	79–83	66–70	57–62
Samburgskoye	«	47–176	80–84	67–71	58–62
Sobinskoye	«	35–150	70–74	55–59	46–51
Soleninskoye	«	48–149	83–87	70–73	61–64
Srednevasyuganskoye	Oil	28–180	82–86	67–71	58–62
Srednevilyuyskoye	Gas condensate	40–220	92–95	80–83	70–74
Urengoyskoye	«	30–120	78–82	65–69	56–60
«	«	45–140	80–84	67–71	58–62
«	«	40–160	84–88	71–75	62–66
Chernoerkovkoye	«	36–185	79–83	66–70	57–62
Shebelinskoye	«	40–160	90–94	79–81	70–73

*Averaged oil.

the catalyst was developed at the Boreskov Institute of Catalysis, SB RAS [19–24]. The IK-30 type catalysts possess definite acidic and molecular sieve properties providing deep transformation of n-paraffins (the components with the lowest octane number) and olefins, moderate transformation of monomethyl paraffins and naphthenes. Strongly branched isoparaffins (the raw components with the highest octane number) remain almost non-transformed under the conditions of the process (Fig. 3).

In general, for the transformation of hydrocarbon fractions, the yield of petrol fractions decreases under a more rigid processing regime (for example, under elevated temperature) due to an increase in gas formation. However, the composition of the resulting petrol changes dramatically: concentrations of n-paraffins and naphthenes decreases while the fraction of high-octane components (isoparaffins and aromatic hydrocarbons) increases (Fig. 4). As a result, the

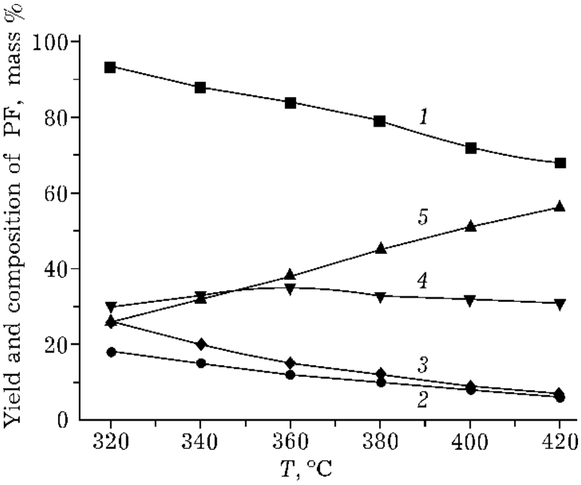

Fig. 4. Effect of reaction temperature on the yield and group composition of petrol fraction (PF) for Zeoforming processing of the virgin petrol fraction of the Srednevilyuyskoye gas condensate at the IK-30-1 catalyst (P = 1 MPa, W = 2 h^{-1}): *1* – PF yield; *2–5* – content of *n*-paraffins (*2*), naphthenes (*3*), isoparaffins (*4*) and aromatic hydrocarbons (*5*) in PF.

octane number of hydrocarbon fractions increases from 40–60 MM to 85–88.

The yield of petrol obtained in the Zeoforming process and resulting in fixed group composition and therefore in the fixed octane number depends on the composition of the initial raw material and may vary for processing virgin petrol fractions of oil and gas condensate from different deposits (see Table 4). Octane numbers of petrol itself are determined by its group composition; an individual dependence of the antiknock properties of petrol obtained by Zeoforming on the group composition exists for each type of the raw material (Fig. 5, *a* and *b*).

A specific feature of IK-30 type catalysts and, as a consequence, of the Zeoforming process itself, is the possibility to manufacture petrol with decreased content of aromatic hydrocarbons (Fig. 6, *a*), especially benzene (see Fig. 6, *b*) in comparison with reforming. The concentration of benzene is 0.5–5 mass % (after

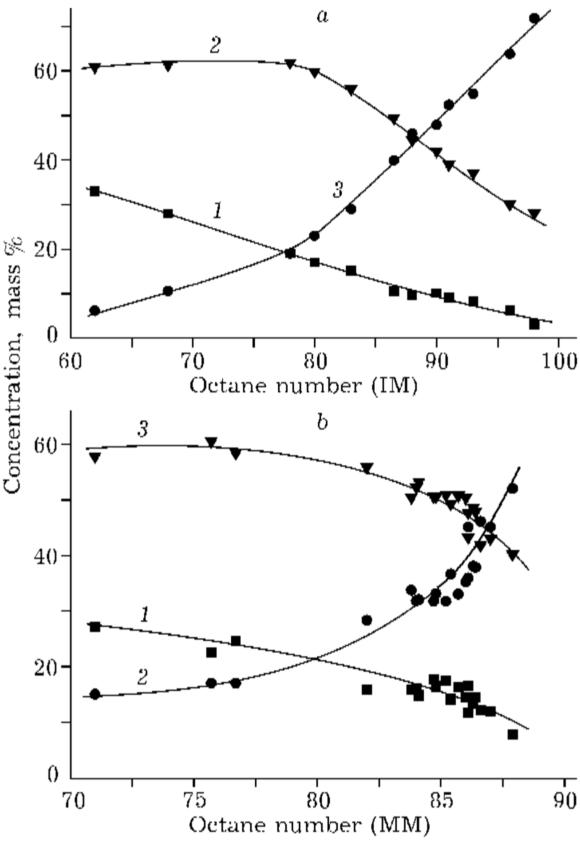

Fig. 5. Correlation between the octane number and group composition of petrol obtained by Zeoforming processing of virgin petrol fractions of the Urengoy gas condensate (*a*), oil from Glimar Refinery (*b*): *1–3* – concentration of *n*-paraffins (*1*), aromatic hydrocarbons (*2*) and isoparaffins + naphthenes (*3*) in petrol from Zeoforming.

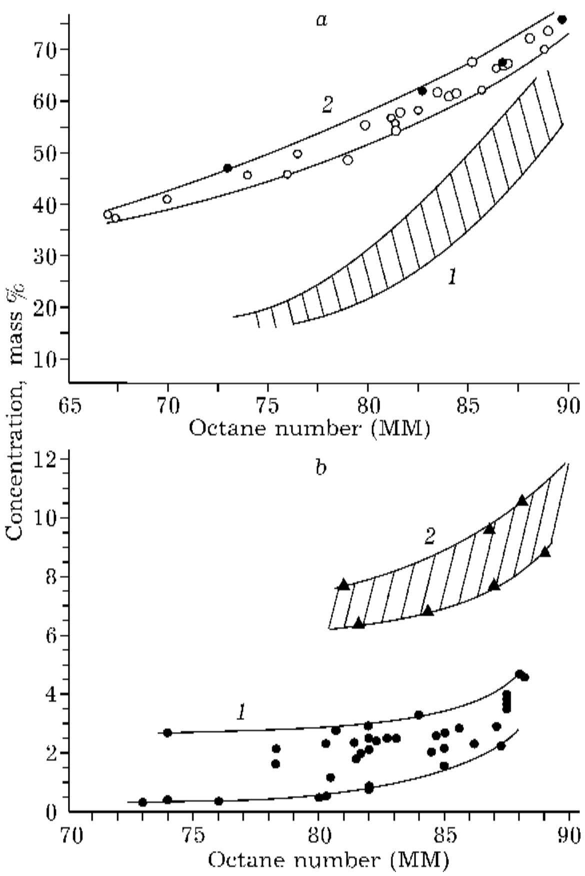

Fig. 6. Regions of changes in the concentrations of aromatic hydrocarbons (*a*) and benzene (*b*) in petrol obtained by Zeoforming (*1*) and reforming (*2*) depending on the octane number of petrol.

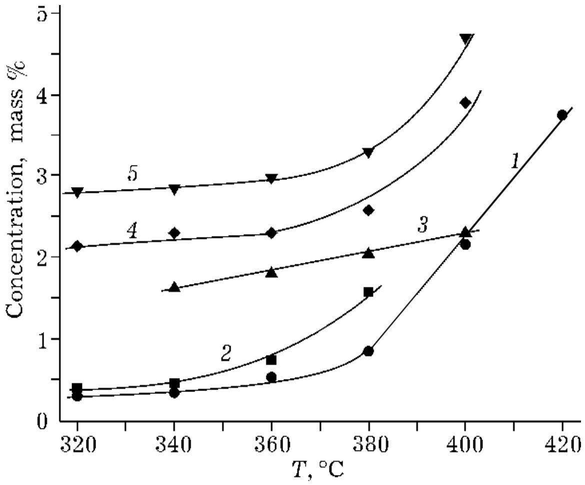

Fig. 7. Effect of reaction temperature on the concentration of benzene in petrol obtained by Zeoforming processing from different virgin petrol fractions at the IK-30 catalyst. P = 1 MPa, W = 2 h^{-1}; content of benzene in the initial raw material, mass %: 0.20 (*1*), 0.55 (*2*), 2.33 (*3*), 3.5 (*4*) and 3.83 (*5*).

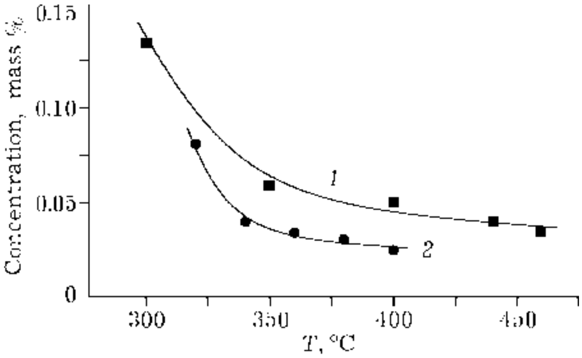

Fig. 8. Effect of reaction temperature on the residual concentration of total sulphur in liquid calalysates of Zeoforming for the transformations of virgin petrol fractions of the Orenburg (*1*) and Zhanazhol (*2*) gas condensates at the IK-30 type catalyst. P = 1 MPa, W = 2 h^{-1}; initial content of total sulphur, mass %: 1.15 (*1*) and 0.32 (*2*).

reforming, it is 7–15 %) and depends on the process conditions and on the nature of the initial raw material; however, even for severe regimes of petrol production it does not exceed 3–5 % and can be decreased even more with respect to benzene concentration in the initial raw material (Fig. 7). This is connected with different mechanisms of hydrocarbon transformations: with metal catalysts used in reforming, hydrocarbon transformation occurs according to the oxidation-reduction mechanism, while with the zeolite-containing catalyst of IK-30 type is follows the acid-base mechanism.

The IK-30 catalysts provide deep transformation of olefins, which allows one to obtain the products with low concentration of unsaturated hydrocarbons (0.5–2 mass %). Because of this, the resulting petrol is characterized by long induction period and, unlike for catalytic cracking, do not require any addition of antioxidants and stabilizers.

A substantial advantage of the catalyst used in Zeoforming is its stability to sulphurous compounds which are always present in one amount or another in oil and gas condensate. Sulphur-containing compounds from the raw material are transformed on IK-30 type catalysts into paraffin, aromatic hydrocarbons and hydrogen sulphide, which is then separated from petrol and the stage of separation and rectification together with hydrocarbon gases. This allows one to use sulphur-containing raw material to manufacture high-octane petrol corresponding to the standard requirements for total sulphur content (Fig. 8) without preliminary desulphurisation and without using hydrogen-containing gas.

The Zeofroming process was introduced into industry in Russia and abroad. On the basis of the developments of SEC Zeosit of IC, SB RAS (initial data and regulations for designing), at present in operation are:

– since 1992 at the Nizhnevartovsk GPP the first experimental industrial set-up [25] with a productivity of 5 thousand t/year, raw material: stable gas petrol;

– since 1997 at the Glimar Refinery (Gorliche, Poland), a set-up with the capacity of 40 thousand t/year, raw material: virgin oil petrol of gas condensate [26];

– since 2002 at the Virtuoz Concern (Azot Co., Rustavi, Georgia), a set-up with the productivity of 30 thousand t/year, raw material: various hydrocarbon fractions boiling within 35–220 °C.

Since one may obtain liquefied hydrocarbon gas (including SPBT (GOST 20448–90) and SPBT or PBA (GOST R 52087–2003) grades) at Zeoforming installations without any additional equipment, the target products of the installations listed above are automobile petrol grades AI-80, AI-92, AI-95, Eurosuper-95 and liquefied gas. At present, a number of Zeoforming installations with the capacity of

5 to 520 thousand t/g for different plants of Russia, Kirghizia, Ukraine and Saudi Arabia is at the stage of development and construction.

The technology of Zeoforming is rather simple; it is characterized by relatively low specific consumption of basic and auxiliary materials and is highly efficient form the economical point of view. This allows one to make and run Zeoforming installations of different capacities in miniplants manufacturing motor oil in remote regions in the vicinity of gas condensate and oil deposits in order to supply motor fuel (petrol and diesel fuel) to a given region.

CONCLUSIONS

In Russia, in spite of large resources and intense mining if hydrocarbon raw material, the problem connected with reliable supply of various regions of the country, first of all the regions of Extreme North, Siberia and Kamchatka, with motor fuel is essential because many thousand kilometres separate motor fuel consumers from its manufacturers.

It was shown at the laboratory, pilot and industrial levels that processing of petrol fractions into high-octane petrol with the octane number 80–95 IM may be performed with IK-30 type catalysts in Zeoforming Process. With Zeoforming installations without any additional equipment, one can manufacture also liquiefied gas of SPBT grade according to GOST 20448–90, as well as SPBT and PBA grades according to GOST R 52087–2003.

Relatively low performance expenses and capital investment into Zeoforming installations, as well as the simplicity of the process technology, its smaller fire and explosion risk (due to the absence of hydrogen), low sensitivity of the catalyst to the composition and quality of the raw material make the process profitable and more preferable for realization in small-scale installations with the productivity of 5–100 thousand t/year, located far from large oil processing plants and close to remote gas condensate or oil deposits, for supplying those regions with motor fuel (petrol and diesel fuel). Within refinery, it is possible to rub also Zeoforming plants with a higher capacity: up to 500 thousand t/year with respect to the raw material of Zeoforming.

The analysis of the quality of a large number of virgin diesel fractions was carried out. It was shown that in many cases the virgin diesel fractions of Siberian oil and gas condensate are already commercial products because they

Fig. 9. Zeoforming installation at OPP Glimar (Gorliche, Poland).

correspond to the requirements of the State Standard (GOST 305–82) to diesel fuel.

With the simultaneous catalytic transformation of petrol and diesel fractions in the same reactor, their processing results in a decrease in the yield and cetane number of diesel fractions, which, in addition to their quality worsening, leads also to unreasonable decrease in the resource of diesel fuel.

At present, a number of installations for the production of petrol and diesel fractions with the capacity of 5 to 520 thousand t/year are at different stages of development and construction at many enterprises of Russia, Kirghizia, Ukraine, Belarus and Saudi Arabia.

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