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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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CATALYTIC HYDRODEAROMATIZATION OF MOTOR FUELS AS A METHOD OF PRODUCING ECO-FRIENDLY FUELS

Abstract. The aim of the work was to study the process of hydrodearomatization of gasoline fractions and diesel fuels for the production of environmentally friendly fuels with a low content of aromatic hydrocarbons. Hydrogenation of two gasoline fractions of LLP Atyrau Refinery (AR) and LLP Pavlodar Refinery (PR) and two diesel fuels of PA and LLP PetroKazakhstanOilProducts, Shymkent (PKOP) on Rh-Pt/Al_2O_3 catalyst was studied. The influence of the technological parameters of hydrodearomatization process (pressure 1-5 MPa, temperature 25-200°C) on the content of benzene and aromatic hydrocarbons was studied. At temperatures of 50-200°C and hydrogen pressures of 2-5 MPa, benzene is completely removed from the fractions, and the amount of aromatic hydrocarbons is reduced by 1.5-2 times. Some operational properties (kinematic viscosity at 20°C, pour point and cloud point, flash point, density at 20°C, iodine number, aromatic hydrocarbon content) of the initial diesel fuels of PA and PKOP and after catalytic treatment were determined. In process of hydrodearomatization all operational indicators were improved and approached the standards for diesel fuel, and the cetane index increased by 1-2 units.

Keywords: catalyst, hydrogenation, hydrodearomatization, aromatic hydrocarbon, gasoline fraction, diesel fuel.

Introduction

In the world production of motor fuels, there is a constant tendency to tighten not only their operational but also environmental characteristics. One of the ways to improve the environmental characteristics of motor gasolines is to reduce the content of aromatic hydrocarbons, in particular, benzene. The problem of reducing the benzene content in motor gasolines is particularly acute for domestic oil refining. The content of benzene and aromatics in gasolines, significantly exceeding international standards (Euro 5 < 1% benzene and < 30% aromatics, Euro 6 - 0.1% benzene and 11% aromatics), is due to the predominant production of gasolines by reforming process.

The main reactions of hydrocarbons on the catalyst during the reforming process are the dehydrogenation of naphthenes and the dehydrocyclization of paraffin hydrocarbons, which lead to the accumulation of aromatic compounds with a high octane number in the reforming product. However, these compounds are the most toxic of all hydrocarbon groups and they form poisonous substances during combustion. Particularly dangerous is benzene, which forms benzopyrene during combustion, which, according to the degree of toxicity belongs to the first hazard class with a maximum permissible concentration - 0.000001 mg/m^3. Up to 58% aromatics are formed in reforming plants, and the benzene content can exceed 3% vol. This implies the task of development and implementing additional reformate processing processes in order to reduce the benzene content in it. Benzene reduction in reforming products is possible by the following methods [1-2]:

- hydrogenation of benzene with the formation of cyclohexane, leading to some decrease in the octane number of the component;
- extraction of pure benzene, cost-effective only with its further effective use;
- alkylation with low molecular weight olefins, which allows not only to solve the problem of benzene removal, but also to increase the yield of the target high-octane component;

- hydroisomerization of benzene to cyclohexane followed by isomerization to methylcyclopentane with a slight increase in the octane number and yield of the target component;
- transalkylation of benzene and aromatic hydrocarbons C_{9+}, leading to a decrease in the yield of the target product;
- fractionation of the reformate to obtain a set of fractions, then mixed in various proportions to achieve the desired result,
- reforming + hydroisomerization of benzene - hydrogenation of benzene to cyclohexane, followed by its isomerization to methylcyclopentane (RIGIZ).

The authors of RIGIZ [1] explain the benefits of hydroisomerization of cyclohexane to methylcyclopentane with a higher octane number of the latter 92, while cyclohexane has 88 units.

Diesel fuel in its composition has 15-30% aromatic hydrocarbons, 10-40% paraffin hydrocarbons and 20-60% naphthenic hydrocarbons. The high content of aromatic hydrocarbons reduces the value of the cetane number of diesel fuel and increases the emissions of particulate matter into the environment, adversely affects the ignition time, and increases the height of the non-soaking kerosene flame. For these reasons, reducing the content of aromatic hydrocarbons by hydrogenation is also relevant to improve the environmental friendliness of diesel fuels. In the process of hydrogenation, aromatic hydrocarbons are converted to naphthenic hydrocarbons, and the olefins found in fuels are converted to more stable paraffin or naphthenic hydrocarbons depending on their nature in the feedstock [3-4].

According to the regulation EN590:2010 in force in the European Union, the content of polycyclic aromatic hydrocarbons (PAHs) in diesel fuels should not exceed 8% wt. [3]. In the USA, the total content of aromatic hydrocarbons in diesel fuels is limited to 10% vol., and PAHs - 1.4% vol. [4]. The standards adopted in Sweden are the most stringent in the world: the volume fraction of aromatic hydrocarbons in diesel fuels should not exceed 5%, and PAHs - 0.02% [5].

Tighter requirements for motor fuels are observed in the CIS countries. According to the current Technical Regulations of the Customs Union of Russia, Belarus and Kazakhstan, diesel fuel may contain no more than 11% wt. PAHs.

The use of fuel purified from aromatic hydrocarbons (gasoline and diesel fuel) can significantly reduce its consumption, minimize the load on the engine and have minimal environmental impact.

A significant number of studies have been devoted to the problem of hydrodearomatization of oil products for the production of environmentally friendly fuels [6-16]. The most effective catalysts are metals of group VIII, which, in terms of activity for the hydrogenation of benzene, are arranged in the following order Rh> Ru >> Pt >> Pd >> Ni> Co.

In industry, both catalysts based on metals of group 8 and sulfide are used, but in the latter, hydrogenation of benzene and aromatic hydrocarbons is carried out under more stringent conditions. The most widely used carriers in the industry are active alumina, synthetic amorphous and crystalline aluminosilicates (zeolites). Two-stage of deep hydrodearomatization processes have become common in abroad in which NiW or NiMo sulphide catalysts are used in the first stage and more active acid supported bimetallic platinum-palladium catalysts in the second stage. The developers of two-stage processes are such largest companies as Shell, UOP, Criterion Catalyst.

Thus, in the literature on catalysis in recent years, there has been considerable interest to the process of hydrogenation of aromatics, which is largely explained by the practical application in the production of environmentally friendly fuels.

In previous works [17-20], it has been studied by us the catalytic hydrogenation of aromatic hydrocarbons, developed catalysts and process conditions for the hydrodearomatization process (removal of benzene and decrease in the content of polyaromatic hydrocarbons) of gasoline fractions of "Atyrau Refinery" LLP. The aim of this work is the catalytic hydrogenation of benzene, mono- and polyaromatic hydrocarbons in gasoline fractions of "Atyrau Refinery" LLP and Pavlodar Oil Chemistry Refinery (POCR LLP) , as well as diesel fuels POCR LLP and PKOP LLP (PetroKazakhstan Oil Products, Shymkent)

Experimental part

Bimetallic modified catalysts based on Group 8 metals (Pt and Rh) on aluminum oxide were prepared for hydrodearomatization of gasoline fractions and diesel fuels. At preparation of catalysts $RhCl_3{\cdot}3H_2O$,

$H_2PtCl_6{\cdot}6H_2O$ of "chemically pure" mark were used. Solutions of these compounds were applied by the adsorption method on the prepared carrier Al_2O_3. A mixture of aqueous solutions of two metals was applied at preparation of bimetallic catalysts. The catalyst samples were filtered off and dried at 100-110°C to constant weight. The reduction of supported catalysts was carried out in a quartz tube with electrical heating in a hydrogen stream at 200°C for 4 hours, then the catalysts were cooled in a hydrogen stream until room temperature.

The experiment was carried out on a kinetic installation - the autoclave of "Amar Equipment Ltd" in the isobaric-isothermal regime.

The chromatography method was used to determine content of benzene and aromatic hydrocarbons.

Results and discussion

Hydrodearomatization of the gasoline fractions was carried out on the prepared catalysts. Stable catalyzate of Atyrau Refinery (AR) and gasoline fraction Stable catalyszate of PCOP refinery. Both fractions were obtained as a result of reforming.

Table 1 presents data on the content of benzene 1.0 - 3.23% and aromatic hydrocarbons 55.04-58.68% in both fractions.

Table 1 - The content of benzene and aromatic hydrocarbons in the gasoline fractions of AR and PKOP

Name of fraction	Benzene content, mas. %	Aromatics content, mas. %
Stable catalyzate of AR	3.23	55.04
Stable catalyzate of PKOP	1.0	58.68

We studied the effect of the content of the active catalytic phase on the composition of the components of two gasoline fractions during hydrodearomatization on 0.2% Rh-Pt/Al_2O_3, 0.5% Rh-Pt/$Al_2O_3$and 1.0% Rh-Pt/Al_2O_3 catalysts.

Figure 1 shows the composition of the catalysis before and after the catalytic treatment of the gasoline fraction. The stable catalyzate AR at 50°C and 0.4 MPa. With an increase in the content of the active phase, the conversion of aromatic hydrocarbons increases, its content decreases from 55.05% to 34.7% for the catalyst 0.2% Rh-Pt/Al_2O_3, 32.5% for the catalyst 0.5% Rh-Pt/Al_2O_3 and 28.4% for the catalyst 1.0% Rh-Pt/Al_2O_3. On all three catalysts, benzene is completely removed from the fraction.

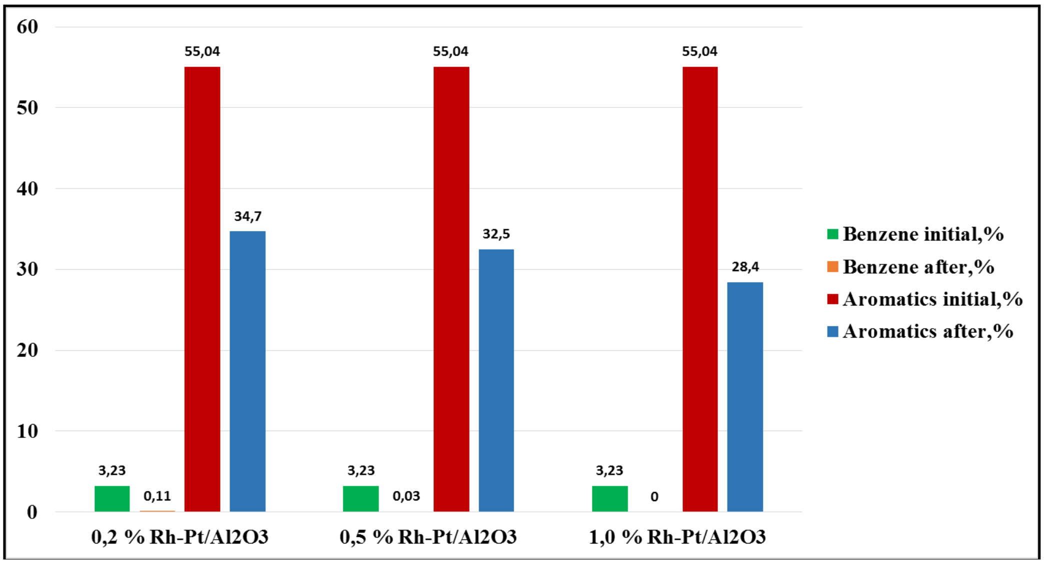

Figure 1 - Hydrogenation of the fraction Stable catalyzate AR on catalysts 0.2% Rh-Pt/Al_2O_3, 0.5% Rh-Pt/Al_2O_3 and 1.0% Rh-Pt/Al_2O_3 at 50°C and 0.4 MPa

Figure 2 shows the composition of the catalyzate before and after the catalytic treatment of the gasoline fraction. Stable catalysis of PKOP at 50°C and 4.0 MPa. On all three catalysts, benzene is completely removed from the fraction. With an increase in the content of the active phase, the conversion of aromatic hydrocarbons increases, its content decreases from 58.7% to 33.8% for the catalyst 0.2% Rh-Pt/Al_2O_3, 29.95% for the catalyst 0.5% Rh-Pt/Al_2O_3 and 29.0% for the catalyst 1.0% Rh-Pt/Al_2O_3.

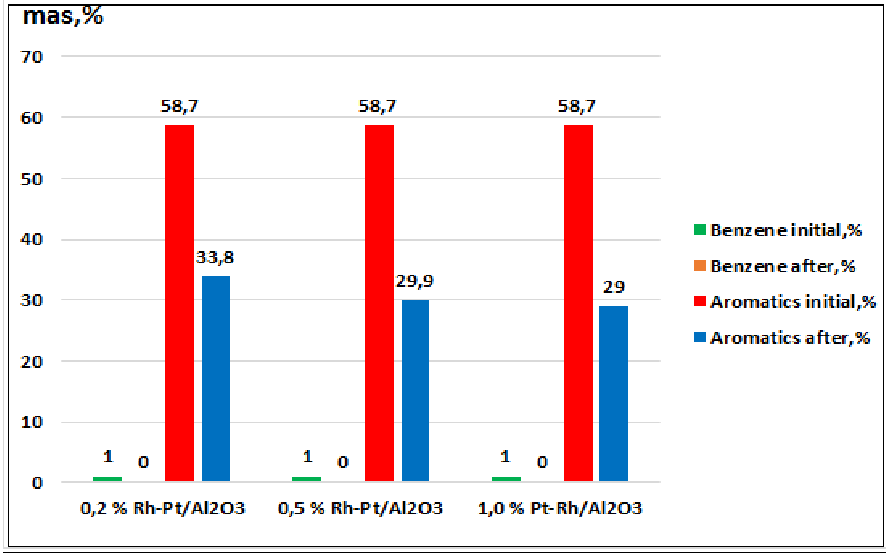

Figure 2 - Hydrogenation of the fraction Stable catalyzate PR on catalysts 0.2% Rh-Pt/Al_2O_3, 0.5% Rh-Pt/Al_2O_3 and 1.0% Rh-Pt/Al_2O_3 at 50°C and 4.0 MPa

The technological parameters (temperature and pressure of hydrogen) of the process of hydrodearomatization of two gasoline fractions were tested. The influence of temperature in the range of 25-200°C and hydrogen pressure of 1.0-5.9 MPa on the content of benzene and aromatic hydrocarbons was studied.

Table 2 presents data on the hydrogenation of a sample of gasoline. Stable catalyzate AR in the temperature range 25-200°C. In the entire temperature range, benzene is absent, i.e. its conversion was 100%. The content of aromatic hydrocarbons decreased from 55.04% to 20.54%. At 1.0-3.0 MPa, the benzene content decreases from 3.23% to 0.12-0.01%, and at 4.0-5.0 MPa, benzene was completely hydrogenated. The content of aromatic hydrocarbons with increasing pressure from 1.0 to 5.0 MPa decreases from 55.04 to 23.79%.

Table 2 - Hydrodearomatization of the fraction Stable Catalyzate AR at 0.5% Rh-Pt/Al_2O_3

Conditions		Benzene content, mas. %		Aromatics content, mas. %	
		Initial	After	Initial	After
P, MPa at 50°C	1.0	3.23	0.12	55.04	40.21
	2.0		0.05		36.92
	3.0		0.01		33.85
	4.0		-		29.73
	5,0		-		23,79
T, °C at 4 MPa	25	3.23	-	55.04	34.73
	50		-		29.73
	100		-		26.54
	150		-		23.91

Table 3 presents data on the hydrogenation of a sample of gasoline Stable catalyzate PR in the temperature range 25-200°C. In the entire temperature range, benzene is absent, i.e. its conversion was 100%. The content of aromatic hydrocarbons decreased from 58.68% to 25.74%. With a change in hydrogen pressure from 1.0 to 3.0 MPa, the benzene content decreases from 1.0% to 0.7-0.01%, and at 4.0-5.0 MPa, benzene was completely hydrogenated. The content of aromatic hydrocarbons decreases with pressure from 1.0 to 5.0 MPa from 58.68 to 29.05%.

Table 3 - Hydrodearomatization of the fraction Stable Catalyzate PR at 0.5% Rh-Pt/Al_2O_3

Conditions		Benzene content, mas. %		Aromatics content, mas. %	
		Initial	After		Initial
P, MPa at 50°C	1.0	1.0	0.7	58.68	50.21
	2.0		0.04		46.95
	3.0		0.01		33.85
	4.0		-		29.93
	5,0		-		29.05
T, °C at 4 MPa	25	1.0	-	58.68	34.93
	50		-		29.93
	100		-		28.76
	150		-		26.91
	200		-		25.74

Figure 3 shows data on the group composition of organic substances in two gasolines of the initial fractions and after hydrogenation over Rh-Pt(90:10)/Al_2O_3, P = 3 MPa, T = 50°C. For the Stable Catalyzate AR the benzene content in the initial state was 3.23 wt.%. After the reaction, benzene is absent, i.e. 100% benzene conversion. The amount of aromatics decreased from 55.04 wt.% to 23.79 wt.%.

It should be noted that the number of olefins decreased almost 2 times from 0.23% to 0.11 wt.%, this is very favorable for gasolines, since the presence of olefins leads to instability (the oligomerization and polymerization reaction proceeds).

The amount of paraffins slightly increased from 12.22 wt.% to 13.99 wt.%. And the content of isoparaffins increased from 27.16 wt.% to 36.81 wt.%. Apparently, the isomerization of paraffins to isoparaffins occurred. The content of naphthenes increased sharply from 2.12 wt.% to 25.3 wt.%.

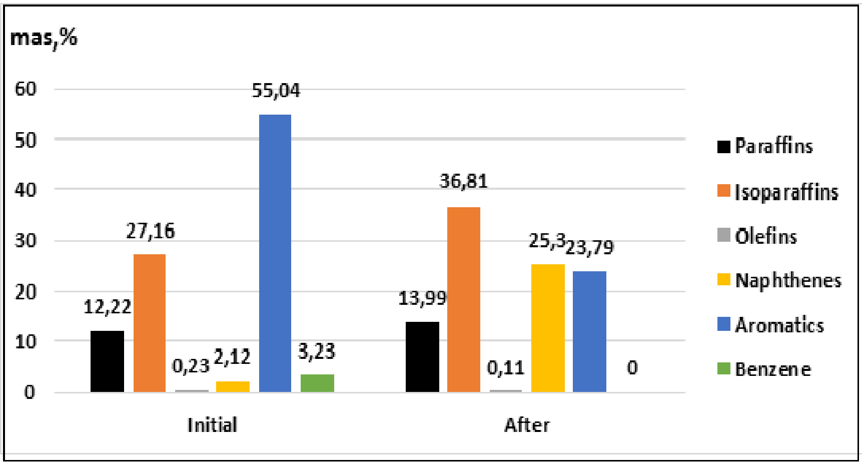

Figure 3 - Group composition of hydrocarbons of the Stable Catalyzate AR before and after catalytic treatment

Figure 4 showed that in the initial Stable Catalyzate PR there was 1.0 wt.% benzene; after hydrogenation benzene was not found in the catalyzate - i.e. it was completely hydrogenated. The aromatic content in the original gasoline was 58.68 wt.%, After hydrogenation it became 29.39 wt.%.

The amount of olefins decreased significantly from 10.2 wt.% to 0.51 wt.%, which leads to the stability of gasoline. In addition, the content of isoparaffins increased from 17.05 wt.% to 28.2 wt.%. This indicates the occurrence of the hydroisomerization reaction on this catalyst, which is favorable for the octane number.

The data on the octane number, density of the initial gasoline fractions before and after the catalytic treatment, shown by chromatographic analysis, are shown in Table 4. The octane number by the research method of the initial Stable Catalyzate AR is 83, after processing it decreased to 81. For the gasoline fraction, Stable Catalyzate PR octane number according to the research method before and after the experiment is 87. In this case also, the octane number has not changed. This indicates that the processing of gasoline practically does not reduce the octane rating. Densities slightly increased after treatment for both fractions, and the saturated vapor pressure decreased, which is understandable from the point of view of changing the hydrocarbon composition to a heavier region - naphthenes have a higher density and lower vapor pressure compared to aromatic hydrocarbons.

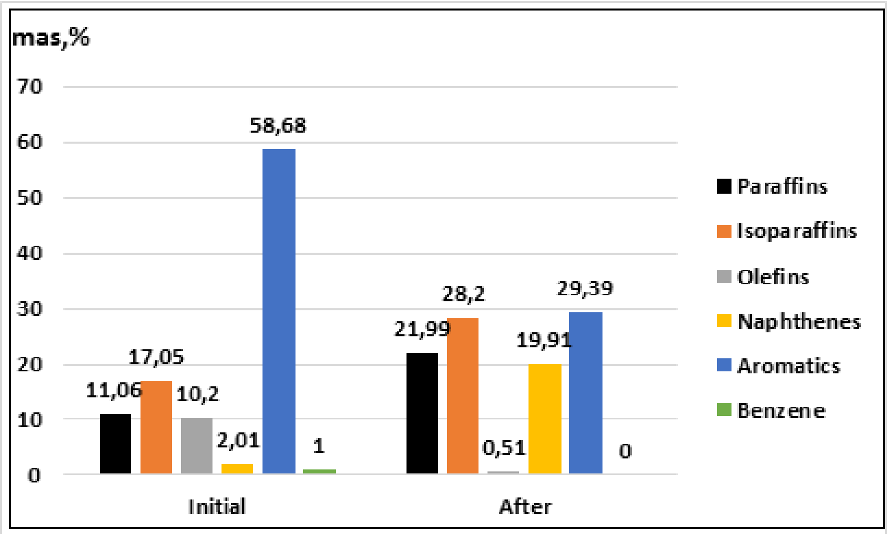

Figure 4 - Group composition of hydrocarbons of the Stable Catalyzate PR before and after catalytic treatment

Table 4 - Indicators of gasoline fractions before and after catalytic treatment

Name of fractions	Octane number		Saturated vapor pressure, kPa		Density at 20°C, g/l	
	initial	after experiment	initial	after experiment	initial	after experiment
Stable catalyzate AR	83	81	23.64	19.86	779.87	785.55
Stable catalyzate PR	87	86	24.65	19.39	789.4	793.50

It should be noted that the studied processes of hydrodearomatization of gasoline fractions were carried out under mild conditions – temperature 50°C compared with 160-330°C used in world industry. Under more stringent conditions, the process of complete hydrogenation of aromatic hydrocarbons can occur with the opening of the benzene ring, which is undesirable, because alkanes have a low octane number.

The same catalyst was tested during the hydrodearomatization of two diesel fuels obtained from PR and PKOP. In diesel fuels, olefins, mono- and poliomatic hydrocarbons can be hydrogenated. Table 5 shows the hydrogenation of PKOP diesel fuel (180-350°C) and PR diesel fuel (169-347°C). The change in the operational characteristics of diesel fuels during hydrogenation to Pt-Rh/Al_2O_3 is presented in table 5.

Table 5 - Physico-chemical indicators of diesel fuels of PR and PKOP in the process of hydrogenation

Condi-tions	Densi-ty at 20°C, g/cm^3	Cloud point, °C	Pour point, °C	Flash point in a closed crucible, °C	Kinematic viscosity at 20°C, mm^2/s	Aroma-tics content, %	Iodine number, gI_2/100g of fuel	Cetane index
Diesel fuel PKOP (180-350°C)								
Before hydrogenation	0.833	5	0	61	4.5	13.80	3.2	52
Pt-Rh/Al_2O_3	0.839	- 2	- 4	57	4,6	0.73	0	53
Diesel fuel PR (169-347°C)								
Before hydroge-nation	0.841	- 15	- 8	64	4.8	12.90	2.9	49
Pt-Rh/ Al_2O_3	0.850	- 18	- 12	58	5.0	0.68	0	51

In the presence of a Pt-Rh/Al_2O_3 catalyst, the density increases for PR fuel from 0.841 to 0.850 g/cm^3, and for PKOP fuel from 0.833 to 0.839 g/cm^3 (the norm for diesel fuel is 0.860 g/cm^3). Clouding and solidification temperatures decrease respectively for PR fuel increased from -15 to -18°C and from -8 to -12°C, and for PKOP fuel - from 5 to -2°C and from 0 to -4°C. The flash point in a closed crucible for PR fuel decreases from 61 to 57°C, and for PKOP fuel from 64 to 58°C, whereas according to the norm 55°C.

The viscosity of AR fuel increases from 4.8 to 5.0 mm^2/s and for PKOP fuel from 4.5 to 4.6 mm^2/s (according to the norm of 3-6 mm^2/s). The aromatics content (including mono- and polyaromatic hydrocarbons) for PR fuel decreases from 12.90 to 0.68%, for PKOP fuel from 13.8 to 0.73%. The iodine number indicates the presence of double bonds, i.e. the presence of olefins. For PR fuel, the iodine number decreased from 3.2 to 0 g I_2/100 g of fuel, for PKOP fuel it decreased from 2.9 to 0 g I_2/100g of fuel, which indicates that olefins were practically hydrogenated on the catalyst.

The cetane index increased by 1-2 units: for PR fuel from 49 to 51, for PKOP fuel from 52 to 53. The cetane index depends on the ratio of naphthenic and aromatic hydrocarbons, and in our case, the aromatics were hydrogenated to form naphthenic hydrocarbons.

Thus, the advantage of catalytic hydrodearomatization is the improvement of performance indicators and approximation to the standards for diesel fuels obtained at Kazakhstan refineries.

The technology of hydrodearomatization of automobile gasolines and diesel fuels is applicable for the production of eco-friendly fuels with a low content of aromatic hydrocarbons, which will reduce the volume of gaseous emissions and extend the service life of cars by 1/3, which will also bring economic benefits.

Conclusions

The process of hydrodearomatization of two gasoline fractions of AR and PR and two diesel fuels of PR and PKOP on the prepared Rh-Pt/Al_2O_3 catalysts was studied. The effect of the process parameters of the hydrodearomatization of gasoline fractions (pressure 1-5 MPa, temperature 25-200°C) on the content of benzene and aromatic hydrocarbons was studied. At of 50-200°C and 2-5 MPa, benzene is completely removed from the fraction, and the amount of aromatic hydrocarbons is reduced by 1.5-2 times. The group composition of gasoline fractions showed a decrease in the number of aromatic hydrocarbons, olefins and an increase in paraffins of the iso-structure, which indicates the occurrence of not only a hydrogenation reaction, but also hydroisomerization. Some operational properties (kinematic viscosity at 20°C, pour point and cloud point, flash point, density at 20°C, iodine number, aromatic hydrocarbon content) of the starting diesel fuel PR and PKOP and after catalytic treatment were determined. In the presence of a Pt-Rh/Al_2O_3 catalyst, all performance indicators improve and approach the standards for diesel fuel, the content of aromatic hydrocarbons decreased to 0, and the cetane index increased by 1-2 units.

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ЭКОЛОГИЯЛЫҚ ТАЗА ОТЫН АЛУ ӘДІСІ РЕТІНДЕ МОТОР ОТЫНЫН КАТАЛИЗДІК ГИДРОДЕАРОМАТИЗАЦИЯЛАУ

Аннотация. Жұмыстың мақсаты құрамында ароматты көмірсутектері төмен экологиялық таза отындарды өндіру үшін бензинді фракциялар мен дизель отындарын гидродеароматизациялау процесін зерттеу болып табылады. Атырау мұнай өңдеу зауыты Жеке Шаруашылық Серіктестігі (АМӨЗ) және Павлодар мұнайхимиялық зауыты Жеке Шаруашылық Серіктестігі (ПМХЗ) екі бензинді фракциясын және АМӨЗ мен ЖШС PetroKazakhstanOilProducts, Шымкент (ПКОП) екі дизельді отынын Rh-Pt/Al_2O_3

катализаторларында гидрлеу зерттелді. Гидродеароматизация процесінің технологиялық параметрлерінің (қысымы 1-5 МПа, температурасы 25-200^{o}С) бензол мен ароматты көмірсутектердің құрамына әсері зерттелді. 50-200^{o}С температурада және 2-5 МПа сутегі қысымдарында бензол фракцияда толығымен жойылады, ал ароматты көмірсутектер саны 1,5-2 есе төмендейді. ПМХЗ және ПКОП бастапқы дизель отындарының және катализдік өңдеуден кейінгі кейбір пайдалану қасиеттері анықталды (20^{o}С кезіндегі кинематикалық тұтқырлығы, қату және тұндыру температурасы, тұтану температурасы, 20^{o}С кезіндегі тығыздығы, йод саны, хош иісті көмірсутектердің құрамы). Гидродеароматизация процесі кезінде барлық пайдалану көрсеткіштері жақсарады және дизель отыны үшін нормаларға жақындайды,ал цетандық индекс 1-2 бірлікке ұлғайды.

Түйін сөздер: катализатор, гидрлеу, гидродеароматизация, ароматты көмірсутектер, бензин фракциясы, дизель отыны.

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КАТАЛИТИЧЕСКАЯ ГИДРОДЕАРОМАТИЗАЦИЯ МОТОРНЫХ ТОПЛИВ КАК СПОСОБ ПОЛУЧЕНИЯ ЭКОЛОГИЧЕСКИ ЧИСТЫХ ТОПЛИВ

Аннотация. Целью работы являлось изучение процесса гидродеароматизации бензиновых фракций и дизельных топлив для производства экологически чистых топлив с низким содержанием ароматических углеводородов. Изучено гидрирование двух бензиновых фракций ТОО Атырауский нефтеперерабатывающий завод (АНПЗ) и ТОО Павлодарский нефтехимический завод (ПНХЗ) и двух дизельных топлив ПНХЗ и ТОО PetroKazakhstanOilProducts, Шымкент (ПКОП) на Rh-Pt/Al_2O_3 катализаторе. Исследовалось влияние технологических параметров процесса гидродеароматизации (давление 1-5 МПа, температура 25-200^{o}С) на содержание бензола и ароматических углеводородов. При температурах 50-200^{o}С и давлениях водорода 2-5 МПа бензол полностью удаляется из фракции, а количество ароматических углеводородов снижается в 1,5-2 раза. Определены некоторые эксплуатационные свойства (кинематическая вязкость при 20^{o}С, температуры застывания и помутнения, температура вспышки, плотность при 20^{o}С, йодное число, содержание ароматических углеводородов) исходных дизельных топлив ПНХЗ и ПКОП и после каталитической обработки. В процессе гидродеароматизации все эксплуатационные показатели улучшаются и приближаются к нормам для дизельного топлива, а цетановый индекс увеличился на 1-2 единицы.

Ключевые слова: катализатор, гидрирование, гидродеароматизация, ароматические углеводороды, бензиновая фракция, дизельное топливо.

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