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# CATALYTIC TECHNOLOGY FOR REDUCING THE CONTENT OF AROMATIC HYDROCARBONS IN MOTOR FUELS

**Abstract.** The aim of the work was to study the process of hydrodearomatization of diesel fractions for the production of environmentally friendly fuels with a low content of aromatic hydrocarbons. The hydrogenation of two diesel fractions 180-350°C and 230-360°C of PKOP LLP (PetroKazakhstanOilProducts, Shymkent) has been studied. Rh-Pt/$Al_2O_3$ catalysts were used in the work. The influence of the technological parameters of the process of hydrodearomatization (hydrogen pressure 2-6 MPa, temperature 100-220°C) on the reaction rate, conversion and aromatic hydrocarbon content at the "aniline point" was investigated. To increase stability and resistance to poisoning with sulfur-containing compounds of petroleum fractions, the carrier was modified with chromium oxide and synthetic zeolite ZSM-5, which led to an increase in the reaction rate and conversion of aromatic hydrocarbons. Optimal conditions have been selected (temperatures 200-220°C, hydrogen pressure 4-6 MPa, solvent - ethanol, propanol, isopropanol) for hydrogenation of diesel fractions 180-350°C and 230-360°C on Pt-Rh-catalysts supported on alumina and mixed carriers. The content of aromatic hydrocarbons was reduced by 10-20%. Some operational properties of diesel fuel (kinematic viscosity at 20°C, pour point and cloud point and density at 20°C) of the initial diesel fractions and after catalytic treatment were determined, the effect of temperature and pressure on the change in these characteristics was investigated.

**Keywords:** catalyst, hydrogenation, hydrodearomatization, aromatic hydrocarbons, diesel fraction.

## Introduction

The constantly deteriorating of environmental situation in the world dictates the need for use of clean and quality fuel. Harmful compounds (carcinogens, in particular benzpyrene) are formed upon incomplete combustion of benzene and aromatic hydrocarbons. Aromatic hydrocarbons promote coking in the engine combustion system, which increases the $NO_x$ content in exhaust gases. For diesel fuels, the high content of polycyclic aromatic hydrocarbons reduces their cetane index; a lot of soot (black smoke) is contained in exhausts at combustion. The limiting value of aromatic hydrocarbons content according to the new EURO-5.6 specifications is less than 30%, benzene is less than 0.1%. One of the methods for improving the composition of fuels is their hydrodearomatization; olefins also hydrogenate at the same time, which reduce the stability of fuel as a result of their polymerization [1-6].

Development and introduction of the technology of hydrodearomatization of fuels and fuel fractions are relevant for the Republic, taking into account the high content of benzene (up to 5-7%) and aromatic hydrocarbons (up to 40-50%) in gasolines and diesel fuels, as the environmental situation in some regions raises concerns. The technological line for the proposed project is simple and the process can be carried out on the lines of oil hydrotreating at any refinery in Kazakhstan. The process technology is one-step and low-waste. Hydrodearomatization of fuels will help improve the performance properties of domestic gasolines, diesel fuels and will allow in a short time to cover the need for fuels with improved performance characteristics.

Many countries: Russia, United States, Great Britain, France, Germany, Japan, China, Poland, etc. are engaged in the problem of hydrodearomatizing of fuels [7-19]. Major trends in this field consist in

reducing the cost of catalyst (reduction of the noble metal content, selection of carriers and modifiers), increase stability and resistance to sulfur-containing compounds. In industry catalysts based on noble metals and sulfides are used, but in the latter, the process is carried out under more stringent conditions.

Recently Pt-Pd-catalysts have been intensively used for hydrotreatment of petroleum products, especially for reducing the content of benzene in gasolines and aromatics in diesel fuels, therefore, close attention of researchers has been riveted on them. The addition of Pd to $Pt/Al_2O_3$ leads to an increase in not only the activity, but also the stability in the hydrogenation of benzene. By varying the nature of the carrier and modifier the Pd catalysts with the addition of a second metal such as Cu, Ru or Pt a uniform distribution of metals in the pores, optimal acidity and stability against sulfur-containing compounds were achieved. Thus, in the literature of recent years on catalysis there has been considerable interest to the process of hydrogenation of aromatics, which is largely due to the practical use in the production of environmentally friendly fuels.

At present, Kazakhstan's refineries produce rather low-quality motor fuels, which are far from international standards. In addition to harmful emissions into the atmosphere, rapid deterioration of the details of equipment occurs due to the deposition of carbon during the combustion of such fuels. The service life of equipment is reduced by 30%.

In previous works [15-20] we investigated the catalytic hydrogenation of aromatic hydrocarbons and developed catalysts and technological regimes for the process of hydrodearomatization (removal of benzene and reduction of polyaromatic hydrocarbons) of gasoline fractions of ANPZ LLP (Atyrau Oil Refinery). Advantages of the these catalysts are a high conversion of benzene 99.5%, reduction of aromatic hydrocarbons content to 25%, high stability to poisoning with sulfur-containing compounds.The purpose of this work is the catalytic hydrogenation of polyaromatic hydrocarbons in diesel fractions of PKOP LLP (PetroKazakhstanOilProducts, Shymkent).

**Experimental part**

Bimetallic modified catalysts based on Group 8 metals (Pt and Rh) on aluminum oxide were prepared for hydrodearomatization of diesel fractions of PKOP LLP (Shymkent) - 180-350°C and 230-360°C with aromatics content of 30 and 39%, respectively.

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 “aniline point” method was used to determine the total content of aromatic hydrocarbons.

**Results and discussion**

Hydrodearomatization of diesel fractions of 180-350°C and 230-360°C was carried out on the prepared catalysts and the technological parameters (temperature and hydrogen pressure) were tested. The effect of temperature in the range of 100-200°C on the rate, duration of hydrogenation, and the content of aromatic hydrocarbons was studied.

Table 1 shows the data on the hydrogenation of the diesel fraction of oil 180-350°C. With increasing of temperature, the rate increases from 8.2 to 12.3 ml/min, the duration of the process decreases from 180 to 130 minutes. The aniline point increases from approximately <44 to <54. This indicates a decrease in the content of aromatic hydrocarbons by approximately 18% (the initial content of aromatic hydrocarbons is approximately 30%).

The effect of hydrogen pressure was studied in the range of 2.0-4.0 MPa. The change in reaction rate and duration at these pressure values is similar to the effect of temperature: the reaction rate increases from 8.2 to 10.1 ml/min, and the duration of the process decreases from 180 to 150 minutes (Table 1). The content of aromatic hydrocarbons is reduced by 15% as measured by the aniline point, which increases from <44 to <53.

Table 1 - Hydrogenation of the diesel oil fraction: 180-350°C on Pt-Rh/$Al_2O_3$ catalyst

| Conditions | Rate, ml/min | Duration, min | Aniline point | |
|---|---|---|---|---|
| | | | before | after |
| 100°C | 8.2 | 180 | <44 | <51 |
| 120°C | 9.0 | 169 | <44 | <52 |
| 140°C | 9.8 | 156 | <44 | <53 |
| 160°C | 10.2 | 149 | <44 | <54 |
| 180°C | 11.0 | 139 | <44 | <54 |
| 200°C | 12.3 | 130 | <44 | <55 |
| 2 MPa | 8.2 | 180 | <44 | <51 |
| 3 MPa | 9.1 | 165 | <44 | <52 |
| 4 MPa | 10.1 | 150 | <44 | <53 |
| ethanol | 8.6 | 170 | <44 | <54 |
| propanol | 7.8 | 195 | <44 | <51 |
| isopropanol | 8.2 | 180 | <44 | <51 |

Ethanol, propanol, and isopropanol were used as solvents. According to the reaction rate and duration of the process, ethanol is the best solvent. These solvents by reaction rate are arranged in a row: ethanol > isopropanol l> propanol.

And accordingly the speed values in this row are reduced from 8.6 to 7.8 ml/min, and the duration of the process is antibate increased from 170 to 195 minutes (Table 1). For all values of temperature, hydrogen pressure and solvent type, the rate of hydrogenation of the diesel fraction 180-350°C is greater than the fraction 230-360°C.

Pt-Rh/$Al_2O_3$ catalyst showed low activity for diesel fractions, which is associated with poisoning with sulfur-containing compounds (0.02%) contained in the fuel. Therefore, to increase its activity, the catalyst was modified in two ways: by introducing chromium oxide and zeolite ZSM-5. Chromium oxide increases resistance to poisoning by sulfur, and zeolite affects the formation of active surface phases, providing a sufficiently high concentration of strong proton donor and electron acceptor centers, thereby increasing the catalytic activity.

When hydrogenating diesel fuel with an aromatic content of 30-39% on catalysts modified by chromium oxide and zeolite, the reaction rate is higher than on an unmodified catalyst, the duration of the process is reduced. Conversion increases and is 10-13% (table 2).The content of aromatic hydrocarbons was determined by measuring aniline point. On modified catalysts, the aniline point after the reaction is <55, which indicates a decrease in the aromatic content. By all indications, a catalyst modified with zeolite is more active than unmodified and modified chromium oxide.

Table 2 - Hydrogenation of two diesel fractions on various catalysts

| Catalyst | Type of fraction | Content of aromatics,% | Rate, ml/min | Conversion, % | Duration, min | Aniline point | |
|---|---|---|---|---|---|---|---|
| | | | | | | before | after |
| Pt-Rh/ $Al_2O_3$ | Diesel fraction 180-350°C | 30 | 0.01 | 9 | > 360 | <44 | <54 |
| | Diesel fraction 230-360°C | 39 | 0.01 | 8 | > 480 | <42 | <53 |
| Pt-Rh/ $Al_2O_3$+ $Cr_2O_3$ | Diesel fraction 180-350°C | 30 | 0.05 | 10 | 280 | <44 | <55 |
| | Diesel fraction 230-360°C | 39 | 0.06 | 10 | 270 | <42 | <55 |
| Pt-Rh/ $Al_2O_3$+ ZSM-5 | Diesel fraction 180-350°C | 30 | 0.07 | 13 | 210 | <44 | <56 |
| | Diesel fraction 230-360°C | 39 | 0.08 | 12 | 200 | <42 | <56 |

For the same process the parameters of the regime (temperature and hydrogen pressure) were tested for some performance properties of diesel fuel, such as viscosity at 20°C, pour point and cloud point, and density at 20°C (Table 3). Table 3 shows the sample data for the Pt-Rh/$Al_2O_3$ catalyst.

In Table 3 the data of the initial diesel fuel before and after the catalytic treatment with the change of hydrogen pressure from 2 to 6 MPa and temperature from 180-220°C are presented. The characteristics presented are important operational parameters and are measured under laboratory conditions. The kinematic viscosity of the resulting product decreases from 3.15 to 2.86 $mm^2/s$ compared to the original fuel. Density is also reduced from 0.833 to 0.823 $g/cm^3$. The cloud point decreases from -19 to -27°C, and the pour point from -22 to -29°C.

Table 3 - Effect of hydrogen pressure and temperature on the properties of diesel fuel

| Conditions | Densityat 20˚C, $g/cm^3$ | cloud point, ˚C | pour point,˚C | Kinematic viscosity at 20˚C,$mm^2/s$ |
|---|---|---|---|---|
| Before treatment | 0.833 | -19 | -22 | 3.15 |
| 2 MPa | 0.830 | -21 | -25 | 3.00 |
| 4 MPa | 0.829 | -24 | -27 | 2.98 |
| 6 MPa | 0.823 | -25 | -28 | 2,86 |
| 180°C | 0.830 | -21 | -25 | 3.00 |
| 200°C | 0.828 | -25 | -27 | 2.72 |
| 220°C | 0.825 | -27 | -29 | 2.70 |

Table 4 shows some of the performance properties (physico-chemical indicators) of diesel fuel in the process of hydrogenation on three catalysts: Pt-Rh/$Al_2O_3$, Pt-Rh/$Al_2O_3$+$Cr_2O_3$ и Pt-Rh/$Al_2O_3$+ZSM-5.

Table 4 – Physico-chemical indicators of diesel fuel in the process of hydrogenation

| Conditions | Densityat 20˚C, $g/cm^3$ | cloud point, ˚C | pour point,˚C | Kinematic viscosity at 20˚C,$mm^2/s$ | Aniline point |
|---|---|---|---|---|---|
| Before treatment | 0.833 | -19 | -22 | 3.15 | <44 |
| Pt-Rh/ $Al_2O_3$ | 0.830 | -21 | -25 | 3.00 | <54 |
| Pt-Rh/$Al_2O_3$+$Cr_2O_3$ | 0.829 | -24 | -27 | 2.98 | <55 |
| Pt-Rh/$Al_2O_3$+ZSM-5 | 0.823 | -25 | -28 | 2.86 | <56 |

After treatment on developed catalysts, the fuel density decreases from 0.833 to 0.823. The cloud point and pour point are reduced, respectively, from -19 to -25 and from -22 to -28°C. Viscosity also decreases from 3.15 to 2.86 $mm^2/s$. The content of aromatic hydrocarbons, measured by the aniline point method, decreases from <44 to <56. The best results were shown by the Pt-Rh/$Al_2O_3$ + ZSM-5 catalyst, which had the lowest cloud point -28°C, pour point -28°C, viscosity 2.86 $mm^2/s$, as well as the content of aromatic hydrocarbons - aniline point <56.

Thus, the advantage of the prepared catalysts is in reduction the concentration of polycyclic aromatic hydrocarbons (PAHs) by 10–20% in diesel oil fractions. Diesel fuels obtained after hydrodearomatization have a lower cloud point and pour temperature, as well as kinematic viscosity. The catalysts have a high stability to poisoning with sulfur-containing compounds, which is especially important for diesel fuels in Kazakhstan.

The technology of hydrodearomatization of diesel fuels is applicable to the production of environmentally friendly fuels with a low content of aromatic hydrocarbons, has low energy consumption and high environmental friendliness. Reducing the amount of aromatic hydrocarbons in automotive fuels will reduce the amount of gaseous emissions and extend the service life of cars by 1/3, which will also bring an economic effect.

**Conclusions**

The process of hydrodearomatization of two diesel fractions of PKOP LLP (PetroKazakhstanOilProducts, Shymkent) of 180-350°C and 230-360°C on the prepared Rh-Pt/$Al_2O_3$ catalysts was investigated. The influence of the technological parameters of the process of hydrodearomatization (hydrogen pressure 2-6 MPa, temperature 100-220°C) on the reaction rate, conversion and aromatic hydrocarbon content at the “aniline point” was investigated.

To increase stability and resistance to poisoning with sulfur-containing compounds of petroleum fractions, the carrier was modified with chromium oxide and synthetic zeolite ZSM-5, which led to an increase in the reaction rate and conversion of aromatic hydrocarbons.

Optimum conditions have been selected (temperatures 200-220°C, hydrogen pressure 4-6 MPa, solvent - ethanol, propanol, isopropanol) for hydrogenation of diesel fractions: 180-350°C and 230-360°C on Pt-Rh-catalysts supported on alumina and mixed carriers. Some operational properties of diesel fuel (kinematic viscosity at 20°C, pour point and cloud point and density at 20°C) of the initial diesel fractions and after catalytic treatment were determined, the effect of temperature and pressure on the change in these characteristics was investigated.

In the presence of developed catalysts, the fuel density decreases from 0.833 to 0.823, cloud point and pour point decrease, respectively, from -19 to -25 and from -22 to -28°C, viscosity also decreases from 3.15 to 2.86 $mm^2/s$. The content of aromatic hydrocarbons is reduced by 10-20%. The best results were shown by the Pt-Rh/$Al_2O_3$+ZSM-5 catalyst, which had the lowest cloud point of -28°C, solidification of -28°C, viscosity 2.86 $mm^2/s$, as well as the content of aromatic hydrocarbons - aniline point <56.

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## МОТОР ЖАНАРМАЙЛАРЫНДА АРОМАТТЫ КӨМІРСУТЕКТЕРДІҢ ҚҰРАМЫН АЗАЙТУДЫҢ КАТАЛИЗДІК ТЕХНОЛОГИЯСЫ

**Аннотация.** Жұмыстың мақсаты ароматты көмірсутектердің аз мөлшері бар экологиялық таза жанармайды өндіруге арналған дизель фракцияларын гидродеароматизациялау процесін зерттеу болып табылады. «ПКОП» ЖШС-нің (PetroKazakhstanOil Products, Шымкент) екі дизельдік фракциясының гидрогенизациясы 180-350°С және 230-360°С-та зерттелген. Жұмыста Rh-Pt/$Al_2O_3$ катализаторы қолданылды. Реакция жылдамдығына, гидредероматизация процесінің технологиялық параметрлері (қысым 2-6 МПа, температура 100-220°С), «анилин нүктесінде» конверсия және ароматты көмірсутектердің құрамының әсері зерттелді. Мұнай фракцияларының құрамында күкірті бар қосындылармен улануы тұрақтылығы мен жалпы тұрақтылығын арттыру үшін тасымалдағыш хром оксидімен және ZSM-5 синтетикалық цеолитімен модификацияланды, бұл ароматты көмірсутектердің реакциясы мен конверсиясының жылдамдығын арттыруға әкелді. Алюминий оксидіне және аралас тасымалдағыштарға отырғызылған Pt-Rh-катализаторларында дизельді фракцияларды гидрирлеу үшін оңтайлы жағдайлар (температурасы 200-220°С, сутегі қысымы 4-6 МПа, еріткіш - этанол, пропанол, изопропанол) іріктелді. Ароматты көмірсутектердің құрамы 10-20% төмендейді. Дизель отынының кейбір пайдалану қасиеттері анықталды (20°С кезіндегі кинематикалық тұтқырлығы, қату және тұндыру температурасы және 20°С кезіндегі тығыздығы) және катализдік өңдеуден кейін, температура мен қысымның осы сипаттамалардың өзгеруіне әсері зерттелді.

**Түйін сөздер**: катализатор, гидрлеу, гидродеароматизация, ароматты көмірсутектер, дизельді фракция.

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# КАТАЛИТИЧЕСКАЯ ТЕХНОЛОГИЯ СНИЖЕНИЯ СОДЕРЖАНИЯ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ В МОТОРНЫХ ТОПЛИВАХ

**Аннотация.** Целью работы являлось изучение процесса гидродеароматизации дизельных фракций для производства экологически чистых топливс низким содержанием ароматических углеводородов. Изучено гидрирование двух дизельных фракций ТОО ПКОП («ПетроКазахстанОйлПродактс», г. Шымкент) 180-350°С и 230-360°С. В работе использовался Rh-Pt/$Al_2O_3$ катализатор. Исследовалось влияние технологических параметров процесса гидродеароматизации (давление 2-6 МПа, температура 100-220°С) на скорость реакции, конверсию и содержание ароматических углеводородов по «анилиновой точке». Для повышения стабильности и устойчивости к отравлению серусодержащими соединениями нефтяных фракций носитель модифицировали оксидом хрома и синтетическим цеолитом ZSM-5, что привело к повышению скорости реакции и конверсии ароматических углеводородов. Осуществлен подбор оптимальных условий (температуры 200-220°С, давление водорода 4-6 МПа, растворитель - этанол, пропанол, изопропанол) для гидрирования дизельных фракций: 180-350°С и 230-360°С на катализаторах Pt-Rh, нанесенных на оксид алюминия и смешанные носители. Содержание ароматических углеводородов снижается на 10-20%. Определены некоторые эксплуатационные свойства дизельного топлива (кинематическая вязкость при 20°С, температуры застывания и помутнения и плотность при 20°С) исходных дизельных фракций и после каталитической обработки, исследовано влияние температуры и давления на изменение этих характеристик.

**Ключевые слова:** катализатор, гидрирование, гидродеароматизация, ароматические углеводороды, дизельная фракция.

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