ABSTRACT

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6D073900 – Petrochemistry

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Demetallization and desulfurization of heavy oil residues to produce coke

The relevance of the topic.The main way to deepen oil refining is the processing of residues, which are becoming increasingly difficult and whose quality is deteriorating. Until now, an insurmountable technological barrier for deep and residue-free processing has been the problems associated with the increased content of not only metals in oils and oil residues, but also sulfur, which are irreversible poisons for catalysts, corrosive equipment. The processing of these residues with the use of catalysts leads to a rapid coking of the latter, their high consumption and a sharp increase in the cost of processing and, accordingly, the finished product.

At present, an increasing share in the country's fuel balance is occupied by sulphurous and high-sulfur oils, the processing residues of which are the source of petroleum coke production. Despite the fact that sulfurous coke finds independent application as a sulfonating additive to coal charge, the most valuable is coke with a sulfur content of less than 1.5 wt. %. The standard method for reducing the sulfur content of coke is the calcination method. Most petroleum coke refineries do not have sufficient calcining capacity and are forced to sell high sulfur coke at low prices. This is due to the fact that the bulk of coke with a sulfur content of 2% or more is not suitable for the electrode and unsuitable for the aluminum industry. Burning high sulfur coke fuels is environmentally damaging.

In this regard, the development of new technologies for processing heavy oil residues with the extraction of metal- and sulfur-containing compounds is an urgent scientific problem of the oil industry.

In addition, at the moment, the Republic of Kazakhstan does not produce petroleum coke with a total sulfur and metal content of less than one percent. The need for needle cokes is 250 thousand tons per year.

The aim of the research is to develop methods for demetallization, desulfurization and coking of vacuum fraction of the Pavlodar petrochemical Plant using adsorbents to reduce the content of sulfur and organometallic compounds.

Research objectives. To achieve this goal, the following tasks were solved:
- study of the composition, physico-chemical properties of the objects of research
- the initial vacuum fraction of the Pavlodar Petrochemical Plant and zeolite;
- manufacture and installation of a laboratory installation for demetallization and desulfurization of heavy oil residues;

- preparation of adsorbents based on zeolite modified with nanostructured compounds of vanadium, titanium, carbon and natural minerals and determination of their characteristics;
- testing of prepared adsorbents for the process of demetallization and desulfurization of vacuum fraction and establishing optimal process modes;
- isolation of vanadium-and sulfur-containing vacuum fraction compounds before and after the process of demetallization and desulfurization and establishment of their structure;
- coking of vacuum fraction after preliminary demetallization and desulfurization and determination of the physical and chemical characteristics of coke;
- issuance of practical recommendations for the processes of demetallization, desulfurization and coking of vacuum fraction of the Pavlodar Petrochemical Plant.

Research methods: The following modern laboratory instruments and equipment were used to conduct scientific research on the topic of the dissertation: Bruker Apex-Ultra (ESI) FT-ICR MS Fourier Transform ion-cyclotron resonance mass spectrometer, Xenemetrix X-Calibur energy-dispersive fluorescence X-ray spectrometer, Agilent Technologies atomic emission spectrometer with microwave plasma 4200 MR-AES, energy-dispersive Oxford Instruments Inca Energy Spectrometer, Q-1000/D Derivatograph, Bruker Optics ' VERTEX 70 IR spectrometer, Specord 210 pubs spectrophotometer, Tsvet-500 chromatograph with flame ionization detector, 3H-2000PS1 automatic analyzer, SEM FEI Quanta 3D 200i electron microscope.

The object of research is the heavy oil residue from the processing of a mixture of West Siberian oils at Pavlodar Petrochemical Plant LLP- vacuum fraction as a raw material of a delayed coking plant and adsorbents based on modified zeolite.

The subject of research is the processes of demetallization, desulfurization and coking of heavy oil residue- Pavlodar Petrochemical Plant vacuum fraction using the developed adsorbents.

The main provisions submitted for protection:

- a high degree of demetallization and desulfurization of the vacuum fraction of the Pavlodar Petrochemical Plant by thermal adsorption method using a zeolite-based adsorbent modified with vanadium oxide xerogel;
- the degree of demetallization and desulfurization of vacuum fraction with adsorbents based on zeolite modified with titanium compounds, nanocarbon and natural minerals;
- isolation and establishment of the structure of vanadium- and sulfur-containing compounds of the vacuum fraction of the Pavlodar Petrochemical Plant in the process of demetallization and desulfurization;
- development of a method for producing petroleum coke from the vacuum fraction of the refinery with preliminary demetallization and desulfurization by thermal adsorption method.

The main results of the study:

1. Adsorbents based on zeolite, modified vanadium oxide xerogel were prepared and the composition, structure and physico-chemical characteristics were established. The optimal technological parameters of the process of demetallization and desulfurization of vacuum fraction of Pavlodar Petrochemical Plant LLP in the presence of a zeolite adsorbent containing vanadium oxide xerogel were established: temperature 340 °C, pressure 1 atm, volume feed rate of raw materials 1 h^{-1}. As a result of the process, the degree of extraction of vanadium, nickel and iron was 90, 70 and 60%, respectively, and the sulfur content decreased from 1.97 to 1.36 %.
2. The method of demetallization and desulfurization of vacuum fraction on adsorbents based on a zeolite carrier modified with titanium, nanocarbon compounds and natural minerals such as serpentine, wollastonite, kaolin clay was tested. The test results showed the possibility of extracting 84-87 % of vanadium and nickel from vacuum fraction, the degree of desulfurization was 37 %. To reduce the metal content in the vacuum fraction composition, thermal adsorption treatment on kaolin clay with coke at a temperature of 350 °C for 3 hours is recommended, to reduce the sulfur content, thermal adsorption treatment on zeolite with wollastonite and coke at a temperature of 350°C for 3 hours.
3. The composition and structure of vanadium - and sulfur-containing organic compounds in the composition of vacuum fraction before and after the process of demetallization and desulfurization of vacuum fraction were identified and established. It was determined that after demetallization and desulfurization of vacuum fraction, the composition of etioporphyrins to $C_{29}H_{31}N_4VO$ and phylloporphyrins to $C_{31}H_{33}N_4VO$ changes.
4. Coking of demetallized and desulfurized tar of Pavlodar Petrochemical Plant LLP was carried out at a temperature of 490-510°C, the duration of the process is 8 hours. As a result of coking, the yield of coke and gasoline fractions increases to 34.4%, and the yield of coke distillate decreases.
5. The coke obtained from tar after preliminary demetallization and desulfurization has better indicators in terms of the mass fraction of volatiles (6%), ash content (0.25%), sulfur content (1.45%) and metals (0.008% V, 0, 0014% Ni, 0.0011% Fe). According to the indicated indicators, the coke sample meets the requirements for the KZA coke grade, first grade.
6. Practical recommendations of the processes of demetallization, desulfurization and coking of heavy oil residues for introduction into the technological scheme of the Pavlodar petrochemical plant were issued. For the production of coke with a low content of metals and sulfur, a technological scheme has been developed, including the process of demetallization and desulfurization of vacuum fraction at 340°C for 3 hours in the presence of zeolite modified with vanadium oxide xerogel, the process of coking vacuum fraction at 500°C for 8 hours.

Justification of the novelty and importance of the results obtained:

- a new method has been developed for demetallization of heavy oil residues using an adsorbent based on zeolite modified with vanadium oxide xerogel with a demetallization degree of vacuum fraction from Pavlodar Petrochemical Plant of 90%;

- new adsorbents based on zeolite modified with titanium compounds, nanocarbon and natural minerals have been prepared and their degree of demetallization and desulfurization of Pavlodar Petrochemical Plant vacuum fraction has been determined;
- for the first time, vanadium- and sulfur-containing compounds of vacuum fraction from the Pavlodar Petrochemical Plant were isolated and their structure was determined by mass spectrometry in the process of demetallization and desulfurization;
- a new method has been developed for producing petroleum coke from Pavlodar Petrochemical Plant vacuum fraction with preliminary demetallization and desulfurization by thermal adsorption method.

The theoretical and practical significance of the work lies in the fact that, on the basis of the results obtained, new methods of demetallization of heavy oil residues and the production of petroleum coke are proposed. The developed methods can be used to reduce the amount of sulfur and metal-containing vacuum fraction compounds and improve the performance characteristics of petroleum coke. The theoretical significance of the work lies in obtaining new data on the structure of vanadium- and sulfur-containing compounds in the composition of Pavlodar Petrochemical Plant vacuum fraction before and after demetallization and desulfurization.

The relationship of this work with other research works. The work was carried out within the framework of the project: No. AP05130830 "Development of technology for demetallization and desulfurization of heavy oil residues for coke production" under the program of the Ministry of Education and Science of the Republic of Kazakhstan for grant funding of fundamental and applied scientific research for 2018-2020.

The personal contribution of the doctoral student to the preparation of publications:

1. Article "Demetallization and desulfurization of heavy oil residues by adsorbents" in the journal "Petroleum Science and Technology": preparation and modification of sorbents, experiments on demetallization and desulfurization, analysis and processing of the results.
2. The article "Demetallization of heavy vacuum residuum by titanium-vanadium zeolite adsorbents" in the journal "Studia UBB Chemia": obtaining experimental data on demetallization and desulfurization of vacuum fraction from Pavlodar Petrochemical Plant with modified sorbents, analysis and processing of the results.
3. Article "Characterization of Vanadium and Sulfur Containing Compounds of Kazakhstan Petroleum Vacuum Residuum" in the journal "Periodica Polytechnica Chemical Engineering": preparation of a review and analysis of literature sources, obtaining and processing of analysis results at the China Petroleum University.
4. Article "Development of chemical adsorbents for demetallization and desulfurization of heavy oil residues" in the journal "Industry of Kazakhstan": preparation and modification of sorbents, demetallization and desulfurization of vacuum fraction by the developed sorbents.

5. The article "Nanocomposite for demetallization of heavy hydrocarbon raw materials" in the journal "Oil and Gas": analysis of the composition and properties of raw materials and products, processing and generalization of the results.
6. Articles “Thermal adsorption upgrading of heavy oil residues”, “Demetallization and deasphalting of heavy oil feedstock”, “Obtaining coke from heavy oil residues” in the journal “Combustion and Plasma Chemistry”: a review of literature sources, conducting experiments on coking, analysis and processing of results.
7. Patents for "Method for demetallization of crude oil" and "Method for producing coke": search and analysis of analogues and prototype, obtaining experimental data.
8. Materials of reports of scientific conferences and symposia: description and presentation of experimental data and analysis results.

Publications 18 publications have been published, including 3 articles in international publications indexed in the Web of Science or Scopus databases, 5 articles in republican journals from the List of recommended publications, 2 patents for the method of demetallization and production of coke from heavy oil residues, 8 reports in conference materials.

The structure and scope of the dissertation. The dissertation consists of an introduction, 6 chapters, a conclusion and appendices. The work is presented on 118 pages of typewritten text, contains 25 tables, 29 figures. The list of sources used includes 129 titles.