Qualitative and quantitative indicators of coked products, sorption characteristics

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Abstract. Coke is a by-product of petroleum. Currently, petroleum coke is mainly used in the metallurgical industry. However, due to the large amount of carbon in its composition, obtaining a carbon adsorbent from coke is one of the important tasks. Due to its structural and mechanical strength, the production and industrial use of carbon sorbent from coke is important. Especially carbon adsorbents with micro-, meso- and macropores can be used in the regeneration of oils used in various industries. It improves the physicochemical properties of industrial and engine oils.

1 Introduction

The production of petroleum coke supplies raw materials to industries such as aluminum (for the production of anode mass and baked anodes), the electrode industry (for the production of structural graphite and electrodes); chemical (in the production of ferroalloys, silicon and abrasive materials). In non-ferrous metallurgy, coke is used as a reducing agent in smelting non-ferrous metals from ores [1-3].

The quality of petroleum coke is determined by coking raw materials and its production technology. Coke must meet the requirements of consumers, which differ depending on the purpose of the coke [2].

Thus, due to the deterioration of the quality of the obtained metal and environmental pollution, the aluminum industry limits the ash content, the mass fraction of sulphur and vanadium in coke.

The sorption properties of microporous carbon, silica-alumina adsorbents with high sorption properties are currently attracting a lot of interest. In particular, a group of scientists is conducting research on sorption processes based on thermodynamic laws [4-22].

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2 Materials and methods

Coke is obtained by heating the post-asphaltene process at 500-600°C. After that, it is treated under special thermal conditions and coke is activated.

3 Results and discussion

The decrease in the yield of heavy coked gas oil with an increase in pressure is explained by the slowing down of the evaporation of the reactive structural units of complex molecules, the increase in their concentration in the liquid phase, and the precipitation of polycondensation products from the vapor phase, the surface of the coke particles, which leads to a decrease in the yield of liquid products and an increase in the yield of coke.

Thus, the coking pressure makes it possible to fully use the potential of the coking components present in the coking raw materials, which are not involved in the process under normal coking conditions. In the study of the influence of the density of Fergana oil tar, asphalt raw materials mixture and the cracking of sulphurous oil residues on the yield of coking products, it was shown that the yield of liquid products decreases with the weight of raw materials. It is known that as the density of low-sulphur and high-sulphur tars increases, the kerosene content of naphthenic hydrocarbons in them decreases and aromatic substances increase.

The increase of asphaltenes in coking raw materials reduces the yield of heavy gas oil of coking. It is known that in highly aromatic environment, as polycyclic aromatic hydrocarbons are involved in thermocondensation processes, the solvent power of the environment decreases, rapid coagulation occurs - sharp precipitation of asphaltenes leads to a significant increase of carbides in the system, more asphaltenes pass into coke than coking distillate. Figures 1-2 graphically show the fit of the predicted calculated data to the experimental data for the density of light oil and the release of heavy oil.

In the coking of heavy oil residues of direct distillation, about 30% of sulphur compounds undergo thermal degradation before the formation of hydrogen sulfide, for residues of secondary origin, 12% are converted to gases in the form of hydrogen sulfide. The main part of organic sulphur obtained with raw materials is distributed between coke and distillates (70% for residues of direct distillation, up to 90% for residues of secondary origin). The sulphur content in distillates obtained from the coking of oil residues increases sharply from the gasoline fraction to the light gas oil fraction, and slightly increases after switching to the heavy gas coking fraction.

Under the conditions of coking under pressure, the group chemical composition of distillates changes. At the same time, heavy gas oil (above 350), paraffin naphthene and light aromatic hydrocarbons are reduced compared to a similar gas oil fraction obtained by coking the same feedstock under atmospheric conditions. In gasoline fractions, on the contrary, the percentage of paraffin naphthenic hydrocarbons increases.

The results of the study showed that the coking pressure has almost no effect on the sulphur content of the coke, which mainly depends on the properties of the raw materials. With a change in coking pressure from 0.3 to 0.6 MPa, the sulphur content of coke is in the range of 1.41-1.47% by weight (the change is no more than 4%).

Currently, it is generally accepted that the amount of sulphur in coke mainly depends on the composition of the raw materials used and its origin. Coke, depending on the nature of the oil, contains 20-35% of all sulphur in the initial residue.

With the increase of paraffin-naphthenic hydrocarbons in coking raw materials, the amount of sulphur in coke increases. This is due to the following reasons.

In the process of carbonization of residues with a high content of long aliphatic chains, the intensity of release of decomposition products significantly exceeds the rate of destruction of organic sulphur compounds in the raw material, which contributes to the transfer of most of the sulphur to coke. So, in the coking of aromatic tars, 20-27% of the sulphur of the raw material goes to coke, and for paraffin tars with low coke productivity, 26-32% of sulphur goes to coke. Therefore, the depth of decomposition of sulphur compounds during coking of oil residues, which determines the ratio of sulphur in coke to sulphur in raw materials, depends on the nature and depth of chemical changes of all components of raw materials and their mutual chemical composition.

Factors contributing to the "slow" transfer of sulphur from raw materials to coke include the following - long duration of the raw material in the coking stage in a plastic state without carbon formation, a high percentage of aromatics as a good solvent of the dispersed phase, high thermal stability of the raw material, with reagents that prevent the formation of solid cross-links processing etc. At the same time, the formation of coke from aromatic and more thermostable raw materials, characterized by the greater solubility of the dispersion medium, occurs at higher temperatures, where more sulphur compounds of the raw materials are decomposed before the formation of a solid carbon matrix. Figures 3-4 graphically show the adequacy of predicted calculated data to experimental data on sulphur yield and content of coke.

As a result of the analysis of the obtained regression equations on the qualitative and quantitative indicators of coking products, it is clear that in order to obtain a high amount of distillation products and improve the quality indicators, it is necessary to reduce the pressure and increase the share of low-sulphur products of secondary origin, in particular, TSP.

In order to obtain high-quality and larger amounts of coke, it is necessary to increase the pressure and increase the aromaticity of the coking raw materials, while the sulphur content of the coking raw materials is low. Increasing the aromaticity of the raw material is achieved by processing the gas oil fractions, in addition to the combination of the raw material with the most aromatic component. Calculation of qualitative and quantitative indicators of coking products using one-factor linear regression equations. selected coking pressure. As a result, it is possible to determine in advance how economical it is to use oil residues as raw materials for coking.

Regeneration of industrial and engine oils was carried out using coal sorbent obtained by thermal method of foaling obtained petroleum coke. The obtained results are presented in the following tables.

The result of the experiment was tabulated as shown in Table I.

Samples	viscosity 400C (Pa*s)	specific gravity	Total acid number	Color
New oil	□58.98	0.960	0.52	Yellow green
Used oil	32.81	0.865	0.66	Black
A	53.16	0.932	0.54	Yellow
В	41.23	0.884	0.64	Pink
С	39.94	0.882	0.62	Pink
D	37.80	0.880	0.61	Brown
Е	40.41	0.883	0.59	Light brown

Table 1. Properties of produced, fresh and regenerated oil

Table 2 shows the properties of new, used and reconditioned motor oils using industrial bleaching earth and activated carbon as polishing agents.

Table 2. Formulations of materials using industrial bleaching earth and activated carbon for bleaching under the same and different conditions by changing the amount of acid used

Formulas	Used engine oil volume (ML)	Acid treatment (ml H ₂ SO ₄)	Adsorbent	Hydrated lime	Bleaching temperature (0C)
A	300.00	30.00	Industrial bleaching earth	4.00	110.00
В	300.00	20.00	Industrial bleaching earth	4.00	110.00
С	250.00	30.00	Industrial bleaching earth	4.00	110.00
D	300.00	30.00	Activated clay	4.00	110.00
E	250.00	30.00	Activated clay	4.00	110.00

The viscosity, specific gravity, and total acid number (standard grade) of new oil at 400C are 58.98 cP, 0.960, and 0.52, respectively, while the used oil is 32.81 cP, 0.865, and 0.66, respectively.

Recovered by treating the oils chemically (acid treatment) and filtering, which increases the viscosity of the oil. In addition, treating the oil with industrial bleaching earth or activated carbon increased its viscosity.

4 Conclusion

Mathematical relationships of qualitative and quantitative indicators of coking products of "Fergana NQIZ" LLC to the quality of coking raw materials were obtained in the form of one-factor equations of linear regression.

The presented one-factor linear regression equations describe the experimental data with sufficient accuracy.

These equations created to predict the qualitative and quantitative indicators of coked products for the conditions of "Fergana NQIZ" LLC allow to optimally design the delayed coking process block and determine the economic efficiency of the enterprise's oil residue processing.

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