ANNOTATION
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(Phd)

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Hydrogenation processing of distillate fractions of coal liquefaction for obtaining motor fuels

Distillates produced at coal hydrogenation have a special composition. They contain phenols, nitrogen bases, and unsaturated hydrocarbons. In this regard, coal distillates cannot be used directly as commercial fuels. The removal of heterocyclic compounds from raw materials and effective hydrogen peroxide in the process of coal liquefaction, as well as for the production of motor fuel, should be carried out using hydrotreating, catalytic reforming and hydrocracking processes.

The dissertation is devoted to the study of effective hydrogenation processes in the hydroprocessing of coal distillate products by removing oxygen, nitrogen, sulfur and unsaturated compounds from raw materials in order to improve the quality and improve the quality of motor fuel components.

All studies were conducted for the first time, the results are presented as a single article in journals with a non-zero impact factor according to the information database of Thomson Reuters and Scopus, nine articles in journals recommended by the Committee for Control of Education and Science, and also in the form of 10 abstracts in international, national scientific-practical conferences and symposia.

Relevance of the research topic. About 90% of the world's potential energy resources are solid fuels (coal, slate, peat, and bitumen), among which coal predominates. Chemically processed coal is the main raw material for ferrous and non-ferrous metallurgy, the liquid product of coal processing (resins) is a source of various coke chemical products. Coal is the most common fossil fuel in the world. It is much cheaper and has a clearly high cost of energy consumption with high heat generation and electricity production for the production process.

Since coal consists of various organic elements, it can be used to produce electricity, gas and liquid fuel, chemical raw materials, metallurgical coke, activated carbon, building materials, etc.

Coal hydrogenation is one way to increase the yield of motor fuels. This is expedient during hydrothreatment of diesel fuel, which meets the standard requirements for motor fuels produced during oil refining in the presence of a wide-pore aluminum-molybdenum-coke catalyst (AC-24) in studies of the processing conditions of motor fuel components of coal liquefied products.

In recent years, stringent conditions for motor fuels have been introduced in accordance with European standards. Therefore, it is important to carry out processes in a mild conditions. It should be noted that coal distillate contains unstable nitrogen, acid compounds and hydrocarbons that do not polymerize,

which, in turn, affects the quality of motor fuel. So, the resulting gasoline cannot be used as motor fuel; therefore, the hydrogenation process must be carried out.

The coal is important energy carrier at the cutting edge of the future, which petroleum and natural gas reserves are decreasing, and plays the important role in the world economy. Due to the variety of organic compounds in coal, it is possible to produce on its basis electricity, gas and liquid fuel, chemical raw materials, metallurgical coke, activated carbon, building materials and many others.

Given the need to develop and implement highly efficient waste-free technologies focused on environmental and resource-saving standards, the rational use of coal as energy is becoming a state-level problem.

One of the ways to increase the production of motor fuels is the hydrogenation treatment of coal in the presence of a catalyst. Coal distillates contain a significant amount of heteroatomic compounds, unsaturated and aromatic hydrocarbons, which negatively affect the quality of motor fuels. Consequently, motor fuel cannot be used directly as commercial fuel, i.e. it is necessary to carry out hydrotreatment processes.

Professor J. Kairbekov, together with his colleagues, has been engaged in intensive research over the past 20 years in the field of hydrogenation of hydrocarbon fuels, synthetic fuels and liquefied coal distillates. The dissertation is intended for the use of Mo-catalyst components in the subsequent hydrotreatment reaction of motor fuels (gasoline, diesel fraction) produced by hydrogenation in the presence of a bauxite catalyst in order to further develop and optimize these studies.

The main problem is to determine the kinetic structure of coal distillates and the number of thermal effects and the individual chemical composition of coal distillates to determine the chemical composition of heteroatomic compounds in the process of hydrotreating coal liquefaction products.

The purpose of the dissertation. The development of effective hydrogenation processes for the processing of coal distillates by removing oxygen, nitrogen, sulfur and unsaturated compounds from raw materials to improve the quality and quality of motor fuel components.

To achieve this goal, the following tasks were set:

- increasing the yield of liquid products by methods of preliminary mechanochemical activation, γ-irradiation, coal ozonation of the Mamyt deposit;
- determination of kinetic and thermodynamic parameters of the process of hydrogenation of coal by the method of equilibrium kinetic analysis (EKA);
- determination of the optimal technological parameters for the hydrotreatment of coal distillates with a boiling point up to 360 °C in the presence of Mo-containing catalysts;
- a study of the composition of gasoline fractions from coal distilltaes by modern physicochemical methods, as well as determination of the group and individual composition of hydrocarbons in the hydrogenate;
- development of the process flow diagram for the production of low-sulfur motor fuel of coal distillates using hydrogenation processes;

- to study the kinetics of removal of heteroatoms and unsaturated compounds from coal liquefaction products and determine the magnitude of the thermal effect when hydrofining coal distillates.

Objects of study: coal of the Mamyt deposit and coal distillates with a boiling point up to 360 ºC.

The subject of scientific research.

The liquefaction of the Mamyt coal in the presence of natural bauxite as a catalyst, hydrotreating and hydrogenation of coal distillates with boiling point of up to 360 ºC in the presence of Mo-containing catalysts and hydrogenation of aromatic hydrocarbons of hydrotreated raw materials in the presence of a PdS/Al2O3 catalyst (palladium).

Research methods.

The following research methods were used in this work: IR spectroscopy, electron paramagnetic resonance, radiation, nuclear magnetic resonance, gas chromatographic analysis, elemental analysis, as well as the nonlinear regression method in the mathematical package of the program Maple13.

The source base and research materials are made up by 179 sources of literature on ozonation, mechanical activation and irradiation of γ-radiation of coal, hydrogenation and hydrotreating in the presence of a Mo-containing catalyst of coal distillates obtained by liquefying coal, as well as other areas of natural science related to the topic of this study.

Scientific novelty:

This dissertation for the first time:

- by mathematical processing of experimental data by nonlinear regression method showed that the preliminary addition of an iron-containing catalyst modified with elemental sulfur, ozonation, activation of coal by mechanochemical treatment and radiation irradiation leads to a change in the paramagnetic characteristics of coal, an increase in the concentration of free radicals, which leads to an increase in the yield of liquid products. A comparative analysis showed the reproducibility of the yield function of liquid products from two variables and experimental data;
- the kinetic and thermodynamic parameters of the catalytic hydrogenation of coal of the Mamyt deposit were determined by the method of equilibrium kinetic analysis (EKA);
- shows an increase in the yield of gasoline and diesel fractions as a result of hydrotreatment of coal distillates in the presence of 5% Mo/Ni-Re catalyst:
- the process flow diagram for the production of low-sulfur motor fuel of coal distillates using hydrogenation processes was developed;
- the possibility of reducing the amount of nitrogen, oxygen, phenolic compounds as a result of the hydrotreatment of coal distillates with a boiling point up to 360 °C in the presence of 5% Mo/Ni-Re catalyst was shown;
- it was suggested that the hydrogenation reaction of heterotome and unsaturated compounds of coal distillates with a boiling point of 180-360 ° C are characterized by first-order equations;

- the value of the thermal effect of hydrotreating coal distillates with a boiling point of 180-360 ° C was determined.

The theoretical significance of the study. The scientific basis for the integrated processing of coal of the Mamyt deposit has been developed, and the laws of the mechanism of transformation of the organic mass of coal in the catalytic hydrogenation process have been established. For the first time, it was determined that the hydrogenation reactions of coal distillates with a boiling point of 180-360 °C are characterized by a first-order reaction, and the thermal effect of the hydrotreating process corresponds to 200-220 kJ/kg depending on the content of raw materials

Practical value.

New ways of processing coal of the Mamyt deposit were proposed and a method of coal hydrogenation using natural bauxite as a catalyst to produce a synthetic liquid product was developed. Methods have been developed to increase the reactivity of coal by mechanical, radiation exposure methods and the ozonolysis method. The high-quality motor fuel was produced through hydroprocessing.

The kinetic and thermodynamic parameters of the process of catalytic hydrogenation of coal were determined by the method of equilibrium kinetic analysis. An effective 5% Mo / Ni-Re catalyst has been developed, which allows you to obtain a high yield of liquid products (gasoline and diesel fractions) by coal hydrogenation and reduce the amount of nitrogen, oxygen, and phenolic compounds. The magnitude of the thermal effect and the sequence of the hydrogenation of heterotomic and unsaturated compounds of coal distillates were determined. The obtained values of the thermal effect can be used to assess the chemical composition of the reactions that occur during the design and hydrogenation of the corresponding technological apparatus.

The main provisions to be defended:

- creation of optimal conditions for the process of catalytic hydrogenation of coal at the Mamyt deposit when producing liquid products;
- to increase the yield of liquid products by methods of preliminary ozonation, mechanization and irradiation of coal;
- determination of kinetic and thermodynamic parameters of the process of hydrogenation of coal by the method of equilibrium kinetic analysis (EKA);
- the condition of hydrotreating in the presence of a Mo catalyst, coal distillates with a boiling point up to 360 °C;
- development of a process flow diagram for producing motor fuel components of brown coal at the Mamyt deposit;
- study of the kinetics of heteroatomic and unsaturated compounds of coal distillates and determination of the magnitude of the thermal effect.

The main results of the dissertation research are published in 20 scientific papers, including:

- in one paper published in an international scientific journal having a non-zero impact factor according to the information base of the companies Scopus and Thomson Reuters;

- in nine papers published in magazines recommended by the Committee for the Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in ten abstracts of reports at foreign and national, international conferences and symposia.

The structure and scope of the dissertation.

The dissertation includes an introduction, three sections, a conclusion, as well as a list of sources used containing 179 items. The dissertation is presented on 123 pages, contains 41 figures and 42 tables.

Based on the results of the dissertation research, the following conclusions were made:

For the first time, a new highly active catalyst based on bauxite modified with elemental sulfur was produced for the coal hydrogenation process of the Mamyt deposit, and the possibility of increasing the yield of liquid products from 62.5% до 69.6%. was shown. The nonlinear regression method was applied to the results of the gyrogenation process, the relationship between the yield of liquid products, pressure and the amount of elemental sulfur was established.

1. A new approach was proposed for the production of motor fuels using methods of ozonation, mechanical and radiation treatment of source coal, and it is shown for the first time that:

- as a result of coal ozonation, the yield of liquid products increases by 9.6%. Ozonation of coal leads to a change in paramagnetic properties, an increase in the concentration of free radicals, and as a result, the yield of liquid products increases.
- during mechanical processing of coal for 30 minutes, the yield of liquid products reaches a maximum value (69.2%).. Using the nonlinear regression method, a functional relationship has been established between the time of mechanical activation and the concentration of free radicals. The extremum was determined by two arguments of the function.
- with preliminary radiation exposure of coal from 50 kGy to 150 kGy, the yield of liquid products increases from 63.5% to 71.7%. The functional relationship between the concentration of free radicals, exposure time and the yield of liquid products was established.

2. The group composition of the hydrotreated gasoline fractions of coal from the Mamyt deposit was determined. Paraffin and isoparaffin hydrocarbons, aromatic compounds and their derivatives, olefin and naphthenic hydrocarbons were determined using the method of chromatographic analysis. The composition of the gasoline fraction was also determined by ^{13}C and ^{1}H NMR and IR spectroscopy.

3. Hydrotreating of coal distillates was carried out in the presence of 5% Mo/Ni-Re at a hydrogen pressure of 6.0 MPa and a temperature of 400 ^{o}C. It was shown that, in the composition of the hydrotreated product, the content of phenolic compounds and nitrogen compounds decreased in up to 6 times, and the sulfur content decreased in up to 14 times, and nitrogen - 15 times.

4. The kinetic and thermodynamic parameters of the catalytic hydrogenation of coal of the Mamyt deposit were determined by the method of equilibrium kinetic analysis (EKA).

5. It was shown that the hydrogenation reaction of heterotome and unsaturated compounds of coal distillates with a boiling point of 180-360 °C are characterized by first-order equations.

6. The value of the thermal effect during hydrotreatment of coal distillates with a boiling point of 180-360 °C, which corresponds to 200-220 kJ/kg depending on the content of raw materials, was calculated.

Assessment of the completeness of solutions to the tasks set.

The goals and tasks set in the dissertation are fully solved:

- new ways of processing coal were proposed;
- the physico-chemical characteristics of coal and coal distillates with boiling point of up to 360 ^{0}C;
- individual and group compositions of the gasoline fraction were determined;
- optimal conditions for catalytic hydrogenation were determined;
- the value of the thermal effect of hydrogenation was calculated;
- kinetic and thermodynamic parameters of hydrogenation were determined.

So, the objectives of the dissertation research have been achieved — effective processes for the hydrogenation of coal distillates have been developed to increase the yield of motor components and improve the quality of motor fuel components, as well as the removal of oxygen, nitrogen, sulfur and unsaturated compounds from coal distillates

Assessment of technical and economic efficiency proposed in the dissertation. The solutions proposed in the dissertation can be attributed to the fact that the hydrogenation of coal distillates of various fractional components is important for obtaining low-sulfur motor fuels with high octane and cetane numbers in the general scheme of an industrial enterprise for the production of synthetic liquid fuels. A special role is to obtain motor fuels with low sulfur content. The use and justification of a new catalytic system for producing motor fuel with low sulfur content from coal distillates represents the scientific and practical significance of the method for processing coal hydrogenation products that has no analogues with domestic and foreign analogs. In this way, synthetic motor fuel with a filtration temperature of at least -26 °C can be produced, which corresponds to the EN 590 standard for all winter motor fuels without squeezing the situation.