Manuscript

Almansoori Ahmed Chead Auda

DEVELOPMENT OF METHOD FOR REMOVING SULFUR AND SULFUR-CONTAINING COMPOUNDS FROM OIL

18.04.01- Chemical Technology
Author's Abstract
Master's thesis
for obtaining Master's qualification

Tambov 2018

The thesis is prepared at the Department “Chemistry and Chemical Technologies” of Tambov State Technical University

ACADEMIC ADVISOR: **Konstantin V. Bryankin**
Doctor of Technical Sciences, Associate Professor

REVIEWER:
Head of the laboratory
«Tambovnefteprodukt», Tambov **Svetlana I. Zaitseva**

Thesis defense will be held on June 28, 2018 at 10 o'clock at the meeting of the State Certification Commission of Tambov State Technical University at the address: room 17, 1, Leningradskaya str., Tambov, 392020,Russia.

The thesis can be found in the library of the university.

Author’s abstract was prepared on May 25, 2018.

Secretary of the State Examination Commission **M.Yu.Subocheva**

Translation from Russian into English is made
by interpreter of International Relations Office
of Tambov State Technical University
Julia A. Nesterova

Translation is correct

Head of International Relations Office Larisa V. Mikheeva

GENERAL DESCRIPTION OF THE THESIS

Relevance of the subject: The increasing use of petroleum raw materials for the production of motor fuels today is accompanied by restrictions on oil production. As a result, there is an increase in the volume of low-quality raw materials containing in its composition a high mass fraction of high-boiling heteroatomic compounds, the presence of which in commercial fuels is undesirable, because it reduces their quality due to their corrosion activity, chemical aggressiveness and toxicity.

In order to reduce sulfur-containing compounds in oil, absorption, extraction, alkaline treatment processes are used. These methods are technologically complex, energy-consuming and have high water consumption. Wastewater treatment of such industries is technologically complex, involves the formation of a huge amount of sludge and is expensive.

The method of adsorption purification of hydrocarbons using active components of natural origin containing minerals with a rich composition and low cost due to its availability becomes very promising in these conditions. This method does not require high capital and operating costs.

Thus, the development of new sorption materials for the purification of petroleum raw materials is of great scientific and practical importance.

The aim of the thesis: is to develop a method to reduce the concentration of sulfur-containing compounds in oil.

To achieve this aim, the following tasks were formulated and solved:

1. To develop a method for reducing the content of sulfur and sulfur-containing compounds in oil.
2. To develop and produce an experimental facility for the study of the process of oil desulfurization.
3. To study the effect of catalysts in the nanostructured form on the reduction of sulfur content in oil.
4. To make compositions of catalysts in the nanostructured form initiating the process of destruction of sulfur-containing compounds in oil.
5. To produce oil matrices that contribute to the destruction of sulfur-containing compounds in it.
6. To study the effect of matrixes on the process of oil desulfurization.
7. To study the effect of the obtained oil matrices on its hydrocarbon composition.
8. To determine the effectiveness of the developed method of destruction of sulfur-containing oil compounds.

9. To evaluate the effectiveness of the effect of the obtained oil matrices on its chemical composition.

10. To develop technical solutions for industrial implementation of the method reducing the concentration of sulfur-containing compounds in oil.

Research methods: Aiming at studying the process of oil desulfurization it is necessary to develop techniques of the following processes:

- manufacture of oil matrices;
- manufacture of ash structures of natural origin components included in the filter;
- method of analysis of the surface, size and elemental composition of matrixes and nanostructured components that are parts of the filter;
- method of activation of the filter components;
- method of purification of sulfur-containing compounds in motor fuels;
- method of determination of fuels hydrocarbon composition.

Scientific novelty:

The method of adsorption of sulfur-containing compounds in oil using oil matrices, components of natural origin and catalysts in the nanostructured form in the filter as a sorbing agent is proposed.

Practical value:

- experimental facilities were developed and manufactured for the study of the process of oil desulfurization using oil matrix, natural components and catalysts in the nanostructured form in the filter;
- methods for obtaining ash structures and matrixes were developed;
- methods of analysis were adopted, which allow to obtain reliable information about the surface, granulometric and elemental composition of matrixes, ash structures and catalysts in the nanostructured form;
- methodology for studying the process of oil desulfurization using matrices of oil and natural origin components is developed;
- compositions of oil matrices and natural origin components providing the maximum reduction of the concentration of sulfur-containing compounds in oil were compiled.

Publications: Three articles are published on the results of this research.

Structure and volume of the paper: The thesis consists of an introduction, three chapters, conclusion, list of sources, including 35 titles, The main part is presented on 100 pages of typewritten text, contains 15 figures, 32 tables and 4 appendices.

THE CONTENTS OF THE MASTER'S THESIS

In the introduction the relevance of developing a method to reduce the concentration of sulfur-containing compounds in oil is substantiated, as well as the advantage of the proposed method with respect to existing methods of oil purification.

In the first chapter the following aspects are considered: physical and chemical properties, classification composition and classification of oil by its properties and the presence of sulfur; classification and properties of organic sulfur compounds contained in oil; the influence of sulfur and sulfur compounds on ecology and structural materials; the existing methods of reducing the sulfur content in oil (hydrotreatment, demercaptanization, biodesulfurization, extraction, adsorption, oxidative desulfurization, etc.); methods for monitoring normalized oil indicators.

According to the results of the literature analysis, the conclusion was made about the prospects of the application of the adsorption method of oil purification from organic sulfur compounds using as sorbents of natural origin minerals.

The use of x-ray fluorescence analysis to determine the sulfur content in oil is justified.

The second chapter is devoted to the experimental study of the process of oil desulfurization using oil matrices, transfer structures, natural origin minerals and catalysts in the nanostructured form.

To conduct research to assess the impact of the compositions of the oil matrices, natural origin minerals and catalysts in nanostructured form in the process of oil desulfurization an experimental facility for carrying out the following works were developed and manufactured:

1) Obtaining ash structures of working media (oil, components of natural origin: soil, clay, sand, iron oxide, material containing metals in nanostructured form)

Ash structures of working environment were obtained by combustion in a muffle furnace at 600 C.

Oil was combusted several times in a muffle furnace at a temperature of 600 ° C to produce ash. The mass of fresh oil in each subsequent combustion increased in an amount of 10% of the previous state.

2) Analysis of the structure, surface and elemental composition of matrixes and minerals of natural origin.

The elemental composition was determined by x - ray fluorescence method on the EDX-3600 spectrometer. The surface analysis was performed on an inverted metallographic microscope Axiovert 40 MAT.

The following analyzed ash structures subjected to x-ray fluorescence analysis are used: oil, minerals of natural origin: soil, clay, sand, iron oxide, material, containing metals in nanostructured form.

The analysis of samples was carried out automatically according to a given program, which allowed to determine both the full elemental composition of the analyzed material and the percentage-mass content of a particular component in it.

As a result of x-ray fluorescence analysis, the content of the following elements in the ash structures affecting the quality and regulatory indicators of fuels was determined. (Tables 1-7).

Tab. 1 Basic elements included in the oil matrix and their quantity.

Oil						
Element	Ni	Co	Cu	Fe	W	S_2
Quantity (%)	16.5	10.19	7.61	13.18	4.52	14.14

Tab.2 Basic elements included in the ash structure of soil and their quantity.

Soil						
Element	O_2	Si	Fe	Ni	Ca	S_2
Quantity (%)	25.9	15.13	32.08	1.8	1.54	2.91

Tab.3 Chemical composition of the compounds included in the sand and their quantity.

Sand						
Chemical compounds	SiO_2	Fe_2O_3	Al_2O_3	MgO	CaO	SO_2
Quantity (%)	69.40	6.82	7.05	0.25	1.79	0.1

Tab. 4 Chemical composition of clay compounds and their quantity

Clay						
Chemical compounds	SiO_2	Fe_2O_3	Al_2O_3	MgO	CaO	KO_2
Quantity (%)	54.61	6.3	15.22	3.14	5.36	5.91

Tab. 5 Compounds of iron oxide

Iron oxide					
Elements	Количество (%)				
Fe	49.25	49.21	49.21	49.24	49.23
O2	49.17	49.09	49.16	49.11	49.13

Based on the obtained data, the matrix structures were composed.

3) Obtaining recycling matrix structures and activation of components of natural origin;

The matrix structure was created by calcination of the oil ash, a material containing metals in a nanostructured form, in a muffle furnace.

The oil matrix for the application in the filter was activated after each use of the filter cassette.

Activation of the filter components of natural origin was carried out by their calcination in a muffle furnace at a temperature of 300 ° C

4) Determination of sulfur content in oil was carried out by x-ray fluorescence analysis (GOST R 51947-2002 Oil and petroleum products. Determination of sulfur by energy dispersive x-ray fluorescence spectrometry);

To determine the sulfur content in oil, the hardware - software complex "SPECTROSCAN S" was used.

5) Determination of the effect of oil matrix and each filter component on the removal efficiency of sulfur-containing compounds.

The obtained structure of the oil matrix and activated natural origin compounds were alternately mixed with sulfurous oil containing 1.9% sulfur, and determined the effect of each component on the sulfur content in oil (table 6). The experimental facility is shown in figure 1. The process was carried out at temperatures of 15° and 25 ° C.

Tab. 6 The effect of oil matrices, natural components of the filter and process temperature on the sulfur content in the oil

Components	Sulfur concentration in oil (mg/kg)					
	Initial concentration of sulfur in the original oil 1950 mg/kg					
T(ºC)	25 ºC			35 ºC		
1	2	3	4	5	6	7
Oil matrix	786.98	791.25	780.25	635.45	641.28	625.33
Soil	899.87	854.13	873.52	832.25	841.63	840.54
Sand	1028.36	1046.56	1035.28	1010.14	1013.27	1015.64
Clay	1125.36	1157.37	1132.24	1104.49	1107.48	1100.55
Iron oxide	1367.13	1352.24	1358.47	1300.16	1302.59	1303.58
Metals in nanostruct.form (Fe, Co Cu, Ni, Zn, Si, Al, W)	726.31	732.19	721.59	714.36	715.64	710.39

It is experimentally proved that the increase in the process temperature by 10 °C improves the efficiency of oil desulfurization. Basing on the experimental data obtained, it was decided to use all the components considered for the sulfurization process and collect them in the form of filter cassettes.

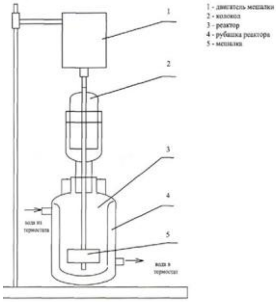

Fig. 1 Experimental facility to determine the effect of matrices on oil desulfurization.

6)Basing on the obtained data on the effect of the oil matrix and the components of natural origin, filter cassettes were collected;

The filter consists of two cassettes. The experimental facility is shown in Fig.2

The first cassette

1. Oil matrix

The second cassette

2. Material, containing metals in nanostruc-tured form
3. Soil
4. Clay
5. Sand
6. Iron oxide
7. Metals in nanostructured form (Fe, Co Cu, Ni, Zn, Si, Al, W)

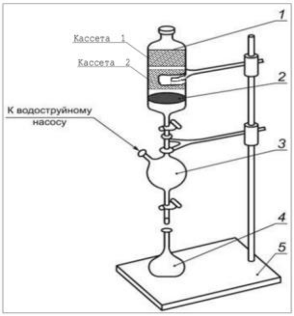

Fig. 2 Experimental facility for oil desulfurization

1 – filter separating funnel, 2 — grid separating filter layers, 3 - receiver, 4 - measuring flask with a capacity of 50 cm^3, 5 – holder.

7) oil desulfurization using the structure of diesel fuel matrixes and components of natural origin;

The prepared components (oil matrix, earth, clay, material containing metals in a nanostructured form, sand, iron oxide, metals in a nanostructured form) were placed in a separating funnel. Each layer was separated by a grid. Then oil was poured through the layer in two filters with the same filling.

The first filter model

After each oil filtration, a new matrix was made and placed as the upper layer. Oil was filtered 7 times to determine the capacity and absorption ability of the filter. Table 7.

Tab. 7 Influence of filter filling structure on desulfurization

Number of filtration cycles	Concentration of sulfur and sulfur containing compounds in oil (mg/kg)	
	Initial concentration of sulfur in the original oil 1950 (mg/kg)	
	Before regeneration	After regeneration
1	1856.12	2069.574
2	1159.48	1292.82
3	958.34	1068.549
4	756.59	843.5979
5	691.24	770.7326
6	589.13	656.88
7	523.36	583.5464

In the course of experimental studies, it was found that multiple cycle of oil filtration through the filter, using matrix structures reduces the sulfur content and its components by 20 times after each cycle. The sixth and seventh cycles showed that the filter lost its ability to recycle sulfur and sulfur-containing compounds. Regeneration of the filter layers was carried out by calcining them in a muffle furnace at a temperature of 300 ° C. After calcination the filter was re-assembled using the structure of matrixes, after the first and seventh cycles of filtration.

The second filter model

In the second model of filter the cassette initially consisted of oil matrixes from the first to the seventh filtration cycle.

The efficiency of oil desulfurization by means of filtration after the regeneration of the filter components using matrixes after 1-7 cycles of filtration are presented in Table 8.

Tab 8. The efficiency of oil desulphurization using matrixes in the oil after the 1-7 cycles of filtration.

Number of filtration cycles	Concentration of sulfur and sulfur containing compounds in oil (mg/kg)		
	Initial concentration of sulfur in the original oil 1950 (mg/kg)		
1	523.36	526.15	521.64
2	524.69	525.14	521.31

After regeneration the filter worked similarly to the initial state. The use of matrix structures (the first — seventh cycles) reduced the sulfur content by 3.6 times for two cycles of filtration.

8) The influence of oil contact time with filter components was determined;

Oil was filtered through the filter components by gravity and by means of forced supply. Tab.9

Tab.9. The influence of oil contact time with filter components on the change in elemental composition

	Concentration of sulfur in oil (mg/kg)					
Number of filtration cycles	Initial concentration of sulfur in the original oil 1950 (mg/kg)					
Time	67 min			35 min		
1	524.15	526.94	522.42	524.15	526.94	522.42
2	412.52	415.32	410.79	412.52	415.32	410.79

Analysis of experimental research results to determine the influence of the contact time with the filter components on the concentration of sulfur-containing compounds in oil showed the absence of this dependence.

9) Determination of each filter component amount on the desulfurization process. Tab.10

Tab. 10. Influence of each filter component amount on the sulfur concentration in oil

	Concentration of sulfur in oil (mg/kg)					
Number of filtration cycles	Initial concentration of sulfur in the original oil 1950 (mg/kg)					
Mass	2 grams			1.5 grams		
1	524.15	526.94	522.42	526.93	529.73	525.19
2	412.52	415.32	410.79	414.71	417.52	412.97

It is experimentally proved that the decrease in the mass of the filter components by 2.0 grams led to an increase in the sulfur concentration on average of 5 mg/kg. The change in the mass of each component of the filter does not affect the desulfurization process. The time of oil filtration through the filter layers is reduced by 10 minutes (from 67 to 57 minutes).

It was experimentally proved that the oil matrix and the components of natural origin, which are part of the filter, reduce the sulfur content by 72 %. The amount of sulfur in the oil filtrate allows to improve its classification according to GOST 51858-2002 from granular to low-sulfur.

The third chapter is devoted to the study of the mechanism of sorption of organic sulfur compounds by filter components and the development of the technology of oil desulfurization, calculations of material and thermal balances.

Organic sulfur compounds are natural components of crude oil.

Basic metals included in the filter components: Ni, Fe, Cu, Co, Zn, Si,Al, W, Ca, Mg, K, Pb, Cr. All metals form oxides at room temperature.

Taking into account the principle of geometric correspondence, the following ranges of Me-O bond lengths of possible sorbents (calculation by valence angle and Van-Der-Waals radius) are accepted. (Tab.11)

Tab. 11 Ranges of Me-O bond length of possible sorbents

Name	Bond	Bond length (Å)	Range of Me-O bond length of sorbents (Å)
Hydrogen sulphide	S-H	1.33	1.76 ÷ 2.19
Mercaptans	S-H и S-C	1.33 1.82	1.76 ÷ 2.19 2.41 ÷ 3.02
Sulfides or thioethers	S-C	1.8	2.4 ÷ 3.0
Disulfides and polythioether	S-C	1.75	2.3 ÷ 2.93
Thiophene	S-C	1.74	2.28 ÷ 2.89
Thiophane	S-C	1.8	2.4 ÷ 3.0

1. Sorption of hydrogen sulfide and mercaptans in S-H bond by metal oxides (Cu, Si, Al, W, Mg, Cr, Zn, Co)
2. Sorption of mercaptans in S-C bond by metal oxides (Ni, Fe, Ca, Cr)
3. Sorption of sulfides in S-C bond by metal oxides (Ni, Fe, Ca, Cr)
4. Sorption of disulfides in S-C bond by metal oxides (Ni, Fe, Ca, Cr, Co)
5. Sorption of thiophenes in S-C bond by metal oxides (Fe, Ca, Pb, Co, Cr)
6. Sorption of thiophanes in S-C bond by metal oxides (Fe, Ca, Cr, Ni)

Based on the research of the effectiveness of reducing the sulfur content in the oil and analysis of process parameters impact (temperature, contact time of the raw material components of the filter) a sketch technological scheme of crude oil desulfurization was proposed (figure 3).

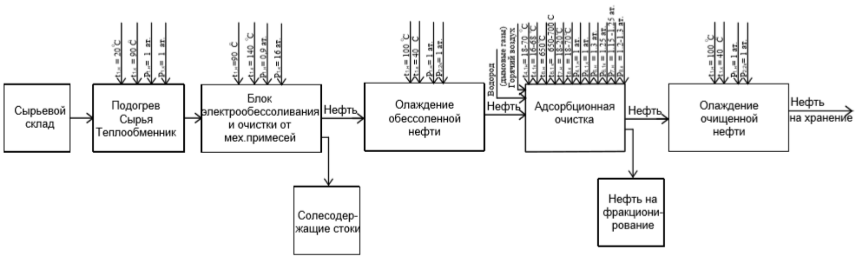

Fig. 3 Sketch technological scheme of oil desulfurization.

THE MAIN CONCLUSIONS AND RESULTS OF THE RERSEARCH

1. The method of adsorptive oil desulfurization using matrixes of oil and components of natural origin was proposed.

2. Experimental facilities for studying the oil desulfurization process using matrix structures of oil and filter components of natural origin were designed and manufactured.

3.The techniques to research the process of oil desulfurization with the use of oil matrix and filter components of natural origin were developed.

4. The methods of obtaining oil matrices and activation of the natural origin components of the filter are developed.

5. The analysis of elemental composition of matrixes and natural filter components structure was carried out.

6. The research determined the influence of oil matrix elements and each filter component on the concentration of sulfur-containing compounds in oil, which decreased from 1.95 to 0.59%.

7. The influence of the temperature of the oil filtration process on the removal of sulfur-containing compounds is studied. Temperature increase by 10 ° C allowed to increase the efficiency of adsorption of sulfur-containing compounds from oil by 12.3%.

8. The first modification of the filter cassettes, consisting of oil matrix structures and natural filter components, showed a decrease in the concentration of sulfur-containing compounds from 1.95% to 0.58% from the first to the seventh filtration cycle.

9. An experimental study on the regeneration of the filter components showed the possibility of its repeated use.

10. The second modification of the filter, consisting of an oil matrix (using a matrix of six cycles of filtration) and filter components of natural origin showed a decrease of concentration of sulfur-containing compounds in oil from 1.95 to 1.4 % for two filtration cycles.

11. The influence of the contact time of oil with the filter components was investigated. The reduction of oil contact time from 67 to 57 minutes did not have a significant impact on the reduction in the concentration of sulfur-containing compounds in the filtrate.

12. The influence of filter components mass on the removal of sulfur-containing compounds was studied. The decrease in the mass filter by 0.55 gram led to the increase in the concentration of sulfur-containing compounds of 15.6 mg/kg. Thus, mass of filter components has no significant effect on the concentration in the filtrate of sulfur-containing compounds. The time of oil filtration through the filter layers is reduced by 10 minutes (from 67 to 57 minutes).

13. The oil matrices were made and the ingredients of natural origin that reduce the concentration of sulfur-containing components in the oil by 68 % are proposed.

14. Based on experimental studies of reducing sulfur-containing compounds in oil, a mechanism of sorption of organic sulfur compounds by metal oxides, which are part of the oil matrix and filter components of natural origin, was developed.

15. The sketch technological scheme of oil purification from sulfur-containing compounds was proposed.

16. Based on the sorption mechanism and the sketch scheme of oil purification from sulfur-containing compounds, calculations of material and thermal balances of production were carried out.

17. The fundamental technological scheme of desulfurization was developed.

LIST OF PUBLICATIONS

1. K.V. Bryankin, A.Ch.A. Almansoori, Ye.H.M. Alaamery Mineral composition of filter elements for the process of adsorptive oil desulphurization and products of its processing. Proceedings of the All-Russian Scientific and Technical Conference “Actual Problems of Oil and Gas Complex Development” , 2018.

2. A.I. Leontueva, A.V. Vyzhanov, N.N. Balobaeva, Ye.H.M. Alaamery, A.Ch.A. Almansoori. Desulfurization of oil and oil products by adsorption method using matrixes. Gas and Oil Technologies, 2018, №5 (116).

3. A.I. Leontieva, A.V. Vyzhanov, N.N. Balobaeva, K.H.K. Al-Fadhli, A.Ch.A. Almansoori. Desulfurization of diesel fuel by adsorption method. 2018. №7.

4. K.V. Bryankin, K.H.K. Al-Fadhli, A.Ch.A. Almansoori Adsorbent for sulfur removal from sulfur-containing oil products. Proceedings of the Third All-Russian Scientific Conference (with international participants) “Actual Problems of Theory and Practice of Heterogeneous Catalysts and Adsorbents”, 2018.