A removal of sulfur-containing compounds from fuel oils using a naturally occurring iron oxyhydroxide FREE

Oleg Andrienko; Natalia Kobotaeva ✉; Tatyana Skorokhodova; Elena Marakina; Victor Sachkov

Check for updates

View Online

Export Citation

CrossMark

09 December 2023 12:24:22

A Removal of Sulfur-containing Compounds from Fuel Oils Using a Naturally Occurring Iron Oxyhydroxide

Oleg Andrienko[1,2], Natalia Kobotaeva[1, 3,a)], Tatyana Skorokhodova[1,3], Elena Marakina[1,b)] and Victor Sachkov[1]

[1]*National Research Tomsk State University, 36 Lenina Avenue, 634050 Tomsk Russia*
[2]*Zuev Institute of Atmospheric Optics of the Siberian Branch of the RAS, 1 Zuev Square, 634021 Tomsk Russia*
[3] *Institute of Petroleum Chemistry of the Siberian Branch of the RAS, 4 Akademichesky Avenue 634055 Tomsk Russia*

[a)]Corresponding author: nat@ipc.tsc.ru
[b)]vioes@mail.ru

Abstract. The paper deals with removing sulfur-containing compounds (SCC) from a fuel oil during oxidative desulfurization in the presence of a naturally occurring iron oxyhydroxide. A natural iron oxyhydroxide is obtained by deferrization of underground water. Iron oxyhydroxide activated at 100, 200, 250, 350, and 700°C, is used as a catalyst. The process of removing SCC from the fuel oil includes two steps: oxidation using hydrogen peroxide and a catalyst and extraction of oxidized sulfur compounds with aqueous acetonitrile. A temperature of 45 °C and the duration of 60 minutes at a sulfur:oxidant molar ratio of 1:3…1:5 have been found out as the optimal condition for the oxidation process. A correlation is made between the activation temperature of the catalyst and the degree of sulfur removal from fuel oil. It is established that the use of catalytic samples of iron oxyhydroxide treated at a temperature of 200 or 250 °C is most preferred. The optimum catalyst content in the reaction mixture is 2.0 wt.%. According to the above steps and conditions, the degree of removal of sulfur from the fuel oil in the course of a sequential removing SCC from the fuel oil is 92.3 wt.%.

INTRODUCTION

In recent years, as the largest deposits of light and low-sulfur hydrocarbon raw materials have depleted, the proportion of extracted and refined heavy high-sulfur oils and gas condensates in the total oil production in the Russian Federation has significantly increased. As a result, the total sulfur content in the residues of processing of such feedstock will increase, and therefore, today certain problems are facing the world both in the recycling of oil and gas condensate residues and in their use as fuels. It should be noted that in the course of refining more than 60% of sulfur compounds goes into the fuel oil, which is widely used as boiler fuel in electric power plants. Fuel oil ranks fourth after oil, gas and diesel in Russia's export structure. In 2015, Russia exported 71.3 million tons in the amount of 15.5 billion dollars.

However, the widespread use of fuel oils with high sulfur content in the power industry involves some problems. Fuel oils for power plants contain from 3 to 5% of total sulfur [1-3]. Combustion of sulfur fuel oils contributes to the intensive ash fouling of boiler heating surfaces and corrosive and aerosive wear of its heat-recovery surfaces. The ash fouling results in a decrease of boiler capacity by 20%. At the same time, heat losses with the outgoing gases increase by 25%, which results in an increase in the specific fuel consumption by 10% and in the doubled electric power consumption for blast and draft [2, 3]. Flue gas emitted during combustion of sulfurous fuel directly in boilers of large thermal power plants contains a large percentage of sulfur oxides, including SO_3. This reduces the efficiency of a boiler, as it increases the dew point, which suggests the formation of sulfurous acid – the strongest corrosive agent – in the flue gas.

The result of the combined effects of these toxic compounds are a soil acidification, corrosion of buildings and facilities located in the area adjacent to power plants, and harmful effects on flora and fauna.

In this regard, fuel oils with high sulfur content must be cleaned from sulfur before burning in boiler furnaces. The main classes of sulfur compounds contained in fuel oil are alkylaryl sulfides, diarylsulfides, thiacyclanes, benzothiacyclic groups, dibenzothiacycanes, thiophenes, benzothiophenes, dibenzo, and naphthothiophenes [4].

The hydrotreating process is widely used in industry for the removal of sulfur compounds but this process is ineffective for the removal of some heterocyclic compounds, such as thiophene, dibenzothiophene and their derivatives. Alternative methods for removing sulfur-containing compounds from petroleum products are extractive desulfurization, oxidative desulfurization, adsorption desulfurization, and biodegradation.

Oxidative desulfurization is a promising technology in view of its widespread use and compatibility with the technologies of extraction, adsorption and biodesulfurization. In [5] it is reported that a combination of oxidation and extraction could yield 90% removal of sulfur from oil fuels (from gasoline to fuel oil). The most applicable industrial oxidation process is the oxidation with peroxide and hydroperoxides in the presence of transition metal compounds as catalysts [6].

Hydrogen peroxides with transition metal salts, which form with them peroxo complexes, could be used for the oxidation of alkylaromatic sulfides to the corresponding sulfoxides and sulfones. Vanadium [7] or niobium [8] are the examples of such hydroperoxides. In [9] the oxidation of dibenzothiophene with hydrogen peroxide in the presence of a titanium-containing catalyst in a model mixture was studied. The degree of removal of dibenzothiophene from the model mixture with n-octane was 90%. A number of molybdenum-based catalytic systems for the oxidative desulfurization of sulfur-containing compounds with hydrogen peroxide was proposed in [10]. The use of such a catalyst at 333 K allows reducing the sulfur content in the fuel from 320 to 10 ppm. The oxidation of following model sulfur compounds: 2-methylthiophene, 2,5-dimethylthiophene, benzothiophene, dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene by hydrogen peroxide over a vanadium catalyst was studied in [11]. A two-phase system with an interphase carrier, which is tetraamido-macrocyclic ligands linked with iron Fe-TAML was used in [12]. The method allows to remove to 75% of sulfur from the feedstock after additional treatment with silica gel. During the process, alkylbenzo- and alkyl dibenzo-thiophenes are oxidized with the Fe/TAML/H_2O_2 system, which accelerates the adsorption of sulfur compounds over silica gel.

For the oxidative desulfurization of oil feedstock with hydrogen peroxide, Ti, V, W, Mo, Co/Mn, Ag [13], Au [14], Re [15] catalysts were used. The Fenton catalyst (ferric chloride (II) and copper sulphate) was used in [16].

Current technologies of oxidative desulfurization compared to technologies of hydrodesulphurization are simple, but still quite expensive, especially when it comes to the removal of large amounts of sulfur. The relatively high cost of methods of oxidative desulfurization is due to the cost of oxidative reagents (hydrogen peroxide, organic peroxides), consumable catalysts, or high energy intensity.

The search for new, cheaper catalysts for the oxidation of sulfur-containing compounds of petroleum and petroleum products leads to the consideration of the use of iron oxyhydroxide (IOH), which is the basis of the waste of water treatment – a deposit after water deferrization.

Earlier, such systems were used as an active sorbent to remove petroleum products and phenols from water. These wastes were also used as catalysts for the oxidation of oil hydrocarbons [17, 18].

The use of waste of water treatment plants as a mixture of oxyhydroxides and iron oxides seems to us quite relevant for removing sulfur-containing compounds from fuel oil in the process of oxidative desulfurization.

The purpose of the paper was to find the optimal conditions for the oxidative desulfurization of fuel oil to remove sulfur-containing compounds (SCC) using a natural iron oxyhydroxide as a catalyst and the correlation between the thermal activation of a catalyst and the degree of SCC removal from the fuel oil during the oxidative desulfurization.

EXPERIMENTAL PART

The feedstock used was the residue of West Siberian oil of the CJSC Chernigov Refinery (Russia) at 370-560 °C, with a total sulfur content 1.04 wt.%. The sulfur content in the feedstock and desulfurized petroleum oil stock was determined by burning in a lamp in the presence of oxygen according to GOST RF 19121-73 [19]. The principle of method consists in burning a fuel oil sample in a platinum holder (basket) of the cork of the Sheniger flask with an oxygenated absorption solution. Upon burning, the absorption solution was titrated with a solution of barium nitrate in the presence of an indicator until a stable color appeared. By analogy, a "blank" experiment was

conducted (without a weighed fuel oil sample) under the same conditions and the total sulfur content in the analytical sample of fuel oil was calculated. The degree of desulfurization of feedstock was calculated by the formula (1):

$$X = \frac{(\omega_0 - \omega_k)}{\omega_0} \cdot 100\%, \tag{1}$$

where X is the degree of sulfur removal,%; ω_0 is the initial sulfur content, wt%; ω_k is the sulfur content in the feedstock after the desulfurization (residual content), wt%.

Before starting the removal of SCC from fuel oil, the catalysts were prepared. Preparation of catalytic samples was carried out as follows: dry material was ground in a porcelain mortar, sieved through a sieve with a cell size of 0.3 mm (to separate large inclusions) and subjected to thermal activation at 100, 200, 250, 350, 700 °C for 3 hours at each temperature value. Conventionally, the samples were marked IOH100….IOH700, where the letters denoted the abbreviation of the compound name (iron oxyhydroxide), and the numbers identified the temperature of activation of the sample. The dry material was a mineral deposit. The material consisted of oxides and iron oxyhydroxides of various forms (about 70%) with minor admixtures of oxides of other metals (mainly 13.5% of Al_2O_3 and 7.0% of SiO_2). It was formed as a result of water deferrization (processes of air-oxidation of mineral salts with oxygen) at the water treatment stations of the Tomsk Oblast. Wet mineral deposit was a creamy yellow-brown consistency but it agglomerated when drying at 25 °C to be easily ground to a dust. After thermal activation, iron oxyhydroxide samples were stored in a desiccator.

The phase composition of the samples and structure parameters were investigated using a XRD-6000 X-ray diffractometer (Shimadzu, Japan) in Tomsk Regional Center for Collective Use of Scientific Equipment (CCU) of TSU (Tomsk, Russia). The 2.2 kW diffractometer was equipped with a Cu X-ray tube with a long fine focus (LFF). The diffractometer was equipped with a high-precision vertical goniometer with a maximum rotation speed of 1000° per minute and angular reproduction accuracy of 2Θ ±0.001°, a scan interval of 26…163°, and a minimum step ± 0.002°. The X-ray diffraction patterns were interpreted using ASTM. The phase composition of the tested substance is determined by comparing the experimental set of 2θ, dhkl и I/Io values obtained from X-ray spectra with the tabulated dhkl и I/Io values, which are presented in the ASTM file (American Society for Testing and Materials, http: //www.astm.org/). Calculation of the X-ray amorphous fraction of the samples was performed using standard software supplied with the device.

The specific surface area of iron oxyhydroxide sample activated at different temperatures was determined using the method of thermal nitrogen desorption using the Sorbtometer M unit and the calculation via the multipoint BET method in automatic mode in accordance with GOST RF 23401-90.

Samples of iron oxyhydroxide, activated at different temperatures, were investigated during the removal of SCC in the processes of oxidative desulfurization of fuel oil with hydrogen peroxide. To remove SCC from fuel oil a 10 g fuel oil sample was placed into a 500 ml chemical container (a conical flask with a ground joint and a plug for the ground joint) equipped with a magnetic element and a thermometer and then heated to 45°C under stirring in a MSH-300 magnetic stirrer. Upon reaching the required temperature, a weighed portion of the catalyst (iron oxyhydroxide) was added and thoroughly mixed. The concentration of the added catalyst was 0.25-6 wt.%. Then a solution of hydrogen peroxide (30% solution) was poured, the ratio of the raw material's sulfur to the oxidant was changed from 1:1 to 1:30. The duration of oxidation process was 60…120 min, after which extraction was carried out at a temperature of 35–40 °C, the ratio of the solvent to the raw material was 2:1. The extraction was carried out by keeping the reaction mixture under an extractant layer at a given temperature for 60 min. Aqueous acetonitrile was used as an extractant, the water content was 10 vol.%. After extraction the phases were separated: extract – oxidized sulfur-containing products and raffinate – desulfurized heating oil.

For the extraction, high grade acetonitrile RF manufactured by JSC EKOS-1, Moscow, Russia was used. For the oxidation, an aqueous solution of hydrogen peroxide of high purity with a mass fraction of 30% manufactured by LLC Yugtekhkom (Krasnodar, Russia) was used.

RESULTS AND DISCUSSION

Table 1 shows the values of the degree of removal of sulfur from the fuel oil when changing the molar ratio of the sulfur in heating oil to oxidant (hydrogen peroxide).

TABLE 1. The influence of the ratio of sulfur in heating oil : oxidant on the sulfur removal degree (60 min oxidation at 45°C, catalyst – IOH250, with 2.0 wt.% concentration).

Molar ratio S_0 : [O]	Residual content of the sulfur in heating oil, %	The sulfur removal degree, %
1:1	0.35	66.3
1:2	0.30	71.1
1:3	0.28	73.1
1:5	0.08	92.3
1:10	0.08	92.3
1:15	0.12	88.5
1:30	0.35	66.3

According to the data presented in Table 1, the maximum degree of sulfur removal from heating oil is achieved at a molar ratio of sulfur to oxidant of 1:5, the same value is achieved at a molar ratio of "sulfur : oxidant" 1:10. When varying the ratio, the desulfurization degree changes slightly, reaches a maximum at a ratio of 1:5 and 1:10, and then decreases with increasing amount of added hydrogen peroxide. This is probably due to the competition of the main reaction (oxidation of SCC) and the reaction of peroxide decomposition, with an increase in the amount of hydrogen peroxide in the reaction mixture.

Fig. 1 shows the effect of the amount of added catalyst on the process of oxidative desulfurization of fuel oil. According to the data presented on Fig.1, the maximum desulfurization depth of heating oil is achieved at a catalyst concentration of 2.0 %. Under similar conditions but at a lower catalyst concentration the residual sulfur content is increased, which may be due to the small number of active sites on the catalyst surface. The pattern of the change in the residual sulfur content in fuel oil with an increase in the concentration of the catalyst is uniformly dropping. With an increase in the concentration of the catalyst, an increase in the residual content of total sulfur in the purified feedstock is observed, which may be due to the shielding of the active sites on the catalyst surface by oxidation products. A similar pattern of the dependence of the residual sulfur content in fuel oil on the catalyst concentration is observed when using an iron hydroxide sample thermally activated at 250°C.
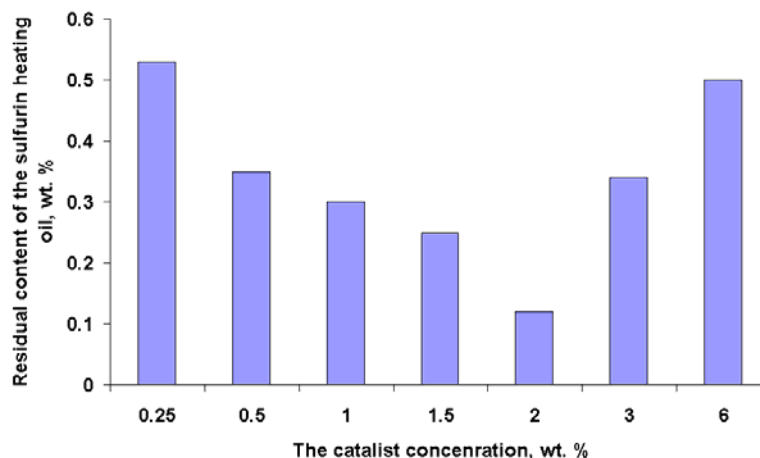

FIGURE 1. Effect of catalyst concentration on residual sulfur content in heating oil: 60 min oxidation at 45°C, molar ratio "sulfur:oxidant" = 1:10, catalyst – IOH200.

A study was conducted of the effect of process duration on the degree of sulfur removal from fuel oil. The dependence of the residual sulfur content in the heating oil after oxidation using hydrogen peroxide in the presence of various forms of iron oxyhydroxide on the time of oxidation is presented in Table 2.

TABLE 2. The effect of the time of the process of fuel oil oxidation in the presence of various forms of iron oxyhydroxide on the sulfur content (oxidation at 45°C; the ratio of sulfur: H_2O_2: catalyst = 1: 4: 0.25).

Catalyst name	Oxidation time, min	Sulfur content in heating oil after the desulfurization process, wt. %	The SSC removal degree, %
IOH100	15	0.83	20
	30	0.65	38
	45	0.45	57
	60	0.32	69
	90	0.31	70
	120	0.31	70
IOH200	15	0.80	21
	30	0.55	47
	45	0.35	66
	60	0.15	86
	90	0.16	85
	120	0.16	85
IOH250	15	0.78	25
	30	0.50	52
	45	0.30	71
	60	0.12	88
	90	0.11	89
	120	0.13	87
IOH350	15	0.90	13
	30	0.70	33
	45	0.55	47
	60	0.45	57
	90	0.44	58
	120	0.43	59
IOH700	15	0.95	9
	30	0.80	21
	45	0.70	33
	60	0.55	47
	90	0.54	48
	120	0.56	46

As can be seen from the Table 2, the optimal process duration is 60 and 90 minutes. The SSC removal degree reaches 69 and 70; 85 and 86; 88 and 89; 57 and 58; 47 and 48% for IOH100, IOH200, IOH250, IOH350, IOH700, respectively. A further increase in the duration leads to some constant or slight change in the degree of removal of oxidized sulfur-containing compounds by 1%.

Figure 2 presents a histogram illustrating the effect of heat treatment of iron oxyhydroxide samples, and hence the composition of the catalyst formed during heat treatment, on the depth of heating oil desulfurization.

According to the data presented in the histogram (Fig. 2), the best results were obtained in the oxidation of fuel oil with hydrogen peroxide in the presence of catalysts OIH200, OIH250, i.e. iron oxyhydroxide activated at 200 or 250°C. It can be assumed that the activity of these catalysts during the oxidation of SCC of fuel oil depends on changes in the phase composition of samples during the heat treatment.

It is necessary to note such a peculiarity in the IOH composition observed when analyzing of diffraction patterns of its thermally activated samples as the presence of the X-ray amorphous phase. Its amount in the IOH100, IOH200, IOH250, IOH350, IOH700 samples was 98, 95, 90, 90, and 25%, respectively. When oxyhydroxide is heated above 250 °C, magnetic phases are observed. Hence, in a IOH sample calcined at 700 °C the main phase is magnetite and ferromagnetic (maghemite and hematite) phases, i.e. oxyhydroxide phases are gradually consumed for the formation of oxide phases during thermal activation of the deposit. Confirmation of this fact can be found in [20], where deposited waste of the water deferrization plants was investigated using the differential thermal analysis. A wide endothermic peak of 50...250°C was observed on all DTA curves of deposit samples. According to the

authors, it suggests the removal of non-structural water, while a decrease in this effect is likely due to the removal of structured water from crystalline hydrates.
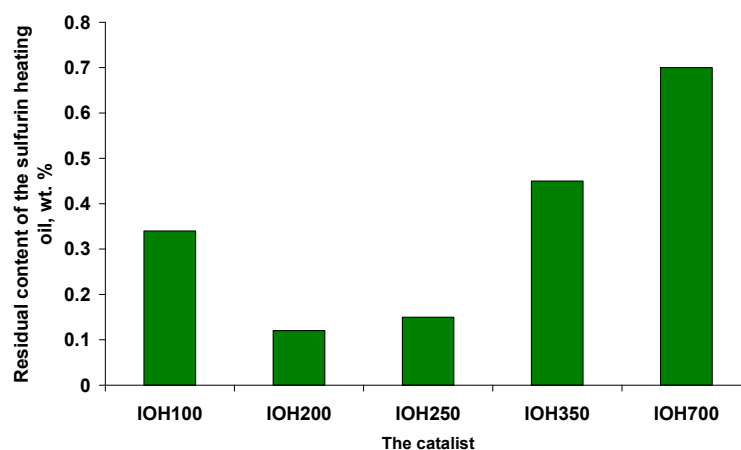

FIGURE 2. Effect of catalyst thermal treatment on the sulfur content in heating oil during the oxidative desulfurization at 45 °C during 60 min.

Table 3 shows the results of X-ray phase analysis of samples after heat treatment in the temperature range of 100…700 °C.

TABLE 3. The phase composition of iron oxyhydroxide, activated at different temperatures.

Sample name	Amorphous phase, %	γ-Fe$_2$O$_3$, maghemite, %	α-Fe$_2$O$_3$, hematite, %	α-FeOOH, goethite, %	β-FeOOH, akaganeite, %	γ-FeOOH, lepidocrocite, %	Fe$_3$O$_4$, magnetite, %
IOH100	98	traces	absent	absent	absent	absent	absent
IOH200	95	traces	traces	absent	2.0	2.5	absent
IOH250	90	traces	traces	absent	5.1	5.2	absent
IOH350	90	4.3	5.5	absent	absent	absent	absent
IOH700	25	16.9	17.3	traces	traces	8.9	31.0

In addition, according to our research, the specific surface area of samples in the series IOH100, IOH200, IOH250, IOH350, and IOH700 decreases from 206 to 110 m^2/g (206, 197, 172, 142, and 110 m^2/g, respectively).

Thus, when samples are heated above 250 °C, crystalline phases of iron oxides (a magnetic component) begin to form in them and the specific surface area decreases, which probably has an adverse effect on the catalytic activity of the samples.

CONCLUSION

In studies, it was shown that water deferrization waste such as iron oxyhydroxide, could serve as catalysts for the removal of sulfur-containing compounds (SCC) from fuel oil during oxidative desulfurization. It has been shown that iron oxyhydroxide was activated by the heat treatment.

In addition, the optimal parameters of the oxidation process were established when removing sulfur-containing compounds (SCC) from fuel oil in the course of oxidative desulfurization. The SCC oxidation occured at 45 °C for 60 minutes with a molar ratio of sulfur:oxidant of 1:3…1:5. Iron oxyhydroxide thermally activated at 200 or 250 °C was used as a catalyst. The content of catalyst in the reaction system was 2.0 wt%. A sample of iron oxyhydroxide, activated at 200 or 250 °C exhibited a high catalytic activity during the oxidation of sulfur compounds of the fuel oil, which was due probably to the beginning of formation of crystalline phases. When carrying out the process of, consisting of successive stages:, Under the above conditions, it is possible to achieve a degree of desulfurization of

fuel oil of 92.3% due to successive removing SCC from fuel oil during the stages of oxidation of SCC and extraction of oxidized SCC from the fuel oil.

The use of iron oxyhydroxide as a catalyst in the course of removal of sulfur-containing compounds from the oil feedstock via oxidative desulfurization could be much in demand for industrial uses, since this easy available low cost catalyst exhibits also a high catalytic activity in oxidation processes.

ACKNOWLEDGMENTS

REFERENCES

1. A.A. Gaile and A.V. Kostenko, Tech. Fuels Oil+ **4,** 3–9 (2005).
2. N.I. Verkhovsky, *Combustion of High-sulfur Fuel Oil in Power Plants* (Energy, Moscow, 1970), p. 447.
3. B.S. Beloselsky and V.N. Pokrovsky, *Sulfur Fuel Oil in the Energy Sector* (Energy, Moscow, 1969), p.420
4. G. F. Bol'shakov, *Organic Sulfur Compounds of Petroleum* (Science, Novosibirsk, 1986), p.247.
5. F. Zannikos, E. Lois and S. Stournas, Fuel Process. Technol. **42**(1), 35–45(1995).
6. M. Asghar, A.S. Mohammad and A.N. Mohammad, Chinese J. Chem. Eng. **17**(5), 869 – 874 (2009).
7. A.V. Anisimov, E.V. Fedorova, A.Z. Lesnugin, V.M. Senyavin, L.A. Aslanov, V.B. Rybakov and A.V. Tarakanova, Catal. Today. **78**, 319–325 (2003).
8. Fam Vinh Tkhai, A.V. Tarakanova, O.V. Kostyuchenko, B.N. Tarasevich, N.S. Kulikov, A.V. Anisimov, Chem. Technol. **8** (12), 534–537 (2007).
9. Y. Wang, G. Li, X. Wang and C. Jin, Energ. Fuel. **21**(3), 1415–1419 (2007).
10. J.L. Garsia-Gutierrez, G.A. Fuentes, M.E. Hernandez-Teran, P. Garsia, F. Murrieta-Guevara and F. Jimenez-Cruz, Appl. Catal. A **334,** 366–373 (2008).
11. L.C. Caero, E. Hernandez, F. Pedraza and F. Murrieta, Catal. Today **107-108**, 564–569 (2005).
12. S. Mondal, Y. Hangun-Balkir, L. Alexandrova, D. Link, B. Howard, P. Zandhuis, A. Cugini, C.P. Horwitz and T.J. Collins, Catal. Today **116**(4), 554-561 (2006).
13. L. Kong, G. Li, X. Wang, Bo Wu, Energ. Fuel. **20**(3), 896–902 (2006).
14. Si. Xiaojuan, C. Shifu , L. Yong , G. Guohua and H. Ming-Yuan, Catal. Lett. **122**(3–4), 321–324 (2008).
15. A. Di Giuseppe, M. Crucianelli, F. De Angelis, C. Crestini and R. Saladino, Appl. Catal. B **89**, 239–245 (2009).
16. Y.Q. Dai Yongchuan, Fuel Process Technol, **89**(10), 927–932 (2008).
17. N.S. Korotaeva, E.E. Sirotkina and T.S. Skorokhodova, Refining and Petrochemicals **12**, 25–29 (2010).
18. L.Yu. Novoselova and E. E. Sirotkina, J. Phys. Chem.-US, **84**(6), 1146–1151 (2010).
19. GOST RF 19121-73 *Petroleum products. Determination of Sulphur Content by Lamp Method*
20. L.Yu. Novoselova and E. E. Sirotkina, J. Phys. Chem.-US, **83**(12), 2330–2335 (2009).