

# The Study of the Desulfurization Process of Oil and Oil Products of “Zhanazhol” Oil Field Using the Approaches of Green Chemistry

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**Abstract**—In this paper we studied sono catalytic oxidative desulfurization of oil and diesel fraction from “Zhanazhol” oil deposits. We have established that the combined effect of the ultrasonic field and oxidant (ozone-air mixture) in the presence of the catalyst on the oil is potentially very effective method of desulfurization of oil and oil products. This method allows increasing the degree of desulfurization of oil by 62%.

**Keywords**—Desulfurization, diesel, oil, oil products, sonication.

## I. INTRODUCTION

At the moment in the refining sector of the world there are some problems related to the rational processing of raw materials of high-sulfur oils, as well as the rational use of secondary distillates. For example, the production of diesel grade Euro 4 from above and sour oil distillates that usually contains aromatic bases require the construction of new plants for hydro refining operating at a pressure of above 5.8 MPa [1], [2]. Efficient process for hydro refining of diesel fractions prevent the formation of thiophenic sulfur compounds and polycyclic aromatic structures in their composition, requiring high pressure and flow rate of hydrogen. In this case, sulfur compounds transform into hydrogen sulfide of which will continue obtaining low-value products: elemental sulfur or sulfuric acid, depending on the technological scheme of the refinery [1], [2].

One of the ways that is largely would reduce flow on the hydro refining of the diesel fuel is a transfer of the given components (sulfur compounds, olefins, polycyclic arenes) to compounds of other classes, such as by pre-ozonation [3], [4]. On the other hand sonication [5], [6] is accompanied by the concentration of energy which is able to change the physical and chemical properties of the fuel (reduction of ash, coking, the amount of solids, density, pour point, and filter coefficient causes depolymerization is increased content of light fractions, cetane number ). When profound structural changes in the molecular composition of hydrocarbons take place, the degree of dispersion of asphaltenes, carbenes increases; Long molecules converted into lighter hydrocarbon compounds. Obtaining diesel fuel conforming to Euro 4 will remove a wide range of environmental problems [7], [8]. Therefore, research in this area is of great interest in the scientific community.

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## II. EXPERIMENTAL PART

### A. Research Objects

The object of investigation was crude oil and diesel fraction of “Zhanazhol” oil field (Kazakhstan).

### B. Methods of Investigation

The studies were conducted at the certified testing laboratory (Certificate №KZ.И.02.1572) of research and comprehensive analysis of fuels and refined products of Research Institute of New Chemical technologies and materials by Al-Farabi Kazakh National University.

The determination of distillation of oil and oil fractions carried out on the experimental unit (AVR-LAB-02), which determines the composition of petroleum fractions, according to GOST 2177-99, ISO 3405 and ASTM D 86.

The determination of the cetane index of diesel fuel carried out by calculation regarding GOST 27768-88, based on the fluid density and boiling point of 50% fraction in accordance with GOST 2177-82.

The determination of cloud point, freezing point and limit point of diesel fuel carried out on the unit (OPLCM “CRYSTAL”) according to the ISO 9001.

Diesel fuel density determination performed using a densitometer. Determination of sulfur in diesel fuel composition was carried out on the unit (“Spectroscan S”) by the GOST R 51947-2002, ASTM D 4294-98.

The determination of certain comparative deviations of analysis results carried out in accordance with GOST. We took the arithmetic mean value for the result of the analysis. This arithmetic mean value calculated to the accuracy of the regulatory two parallel experiments with a proven level of probability between two parallel experiments conducted by 95%, which does not exceed the values specified in state standard.

Investigation of the action of ultrasonic waves on the oil of “Zhanazhol” oil deposit conducted by placing the 0.08 dm<sup>3</sup> of oil in a multifunctional laboratory ultrasonic complex MLUC 3/22 OL at the frequency of 22 kHz (30% power). The process goes during 5 minutes at room temperature in the presence of a catalyst (0.2% of oil) and an oxidant (ozone-air mixture), followed by removal of the purified part of oil.

Ozonation is carried out as follows: The original diesel fraction of oil in a volume of 0.02-0.03 dm<sup>3</sup> is poured into a bubbler made of glass. Then, the air supply unit is connected to the ozonator EUIA 941.711.001 № 143-94 and the output of the ozone is checked. For the uniform output of ozone it is

connected to the gas meter and regulated the rate of release of air from the pump to achieve the necessary speed. After that, the ozone-air mixture with a specific consumption of 8.7; 17; 35 g / kg is passed through a diesel fuel. Ozonation duration is 30 to 90 minutes. Next, the processed ozone-air mixture of diesel fuel is subjected to hydrogenation on skeletal catalyst at 25°C and atmospheric pressure.

### III. RESULTS AND DISCUSSION

Data on physical-chemical characteristics of the crude oil of "Zhanazhol" oil field are given in Table I.

Table I shows that the density of oil from wells №1-4 ranges from 814,5-818,4 kg / m<sup>3</sup> and kinematic viscosity is within 17,9-5,7 cSt, the mass fraction of paraffin is 3.34%, the total sulfur is within 2,630-2,670 wt%, mass fraction of water is 0.09%, mass fraction of solids is within 0,040-0,048%.

TABLE I  
PHYSICAL AND CHEMICAL PARAMETERS OF CRUDE OIL FROM "ZHANAZHOL" OIL FIELD

| Parameters  | Samples of oil from Zhanazhol oil field wells |       |       |       |
|---|---|-------|-------|-------|
|   | 1   | 2     | 3     | 4     |
| Density at 20°C, kg / m <sup>3</sup>              | 814,5   | 819,2 | 816,6 | 818,4 |
| Kinematic viscosity at 20°C, cSt                  | 17,9  | 6,4   | 4,9   | 5,7   |
| Freezing point, °C                                | -38   | -40   | -42   | -44   |
| Mass fraction of water, % not more than           | 0,09  | 0,08  | 0,10  | 0,09  |
| Content of mechanical impurities, % not more than | 0,048   | 0,041 | 0,044 | 0,040 |
| Sulfur, wt%                                       | 2,65  | 2,63  | 2,63  | 2,67  |
| Nitrogen, wt %                                    | 0,13  | -     | -     | -     |
| Silica resin, wt %                                | 9,8   | 7,9   | 4,6   | 2,7   |
| Asphaltenes, wt %                                 | 0,60  | 0,69  | 0,50  | 0,36  |
| Paraffins, wt %                                   | 2,95  | 4,6   | 6,87  | 8,1   |
| Freezing point of paraffin, °C                    | 51  | 46    | 47    | 50    |
| Coking ability, %                                 | 2,12  | 1,9   | 1,4   | 1,3   |
| Ash, %  | 0,22  | 0,21  | 0,23  | 0,30  |
| Acid number, mg KOH / g                           | 0,13  | 0,11  | 0,12  | 0,15  |
| Density at 20°C, kg / m <sup>3</sup>              | 814,5   | 819,2 | 816,6 | 818,4 |
| Fractional composition, % mass                    |   |       |       |       |
| Up to 200°C                                       | 25,8  | 32,6  | 29,4  | 31,4  |
| Up to 350°C                                       | 47,7  | 54,9  | 54,3  | 58,1  |
| >350°C  | 26,6  | 12,5  | 16,3  | 10,5  |

Increasing demands on the quality of crude oil and petroleum products to stimulate new approaches to directional change in their composition and structure. Research in this direction with the use of non-traditional technologies is of great interest in the scientific community.

Among such technologies can be isolated sonication hydrocarbons interest, which has grown significantly over the past 10-15 years, which is due in the first place, the potential of the cracking processes of hydrocarbons at relatively low average temperatures and medium pressures in comparison with the same parameters of traditional technologies refinery.

Based on published data [9] on the stimulating effect of ultrasonic vibrations on the different physical-chemical, especially catalytic processes by accelerating the processes of heat and mass transfer in the cavitation field, an attempt was

made to use ultrasound in the catalytic oxidation of organic sulfur compounds in a hydrocarbon medium. It assumed that in this case be able to increase the effectiveness of the desulfurization of petroleum and petroleum products.

Preliminary experiments showed that a promising way of sulfur oil purification step is periodic processing in the ultrasound field in the presence of a catalyst and an oxidant (ozone-air mixture), followed by removal of part of the purified oil. In the absence of a catalyst, ultrasonic treatment does not significantly reduce the sulfur content in petroleum.

According to [10], the number of cycles should be at least four, and then the removal efficiency of sulfur oil decreases and further purification is necessary to perform the regeneration of the catalyst in an aqueous medium under the influence of ultrasound. During our investigations of the sulfur dropped after two cycles of this treatment in the presence of Ni-skeletal catalyst obtained from the alloy Ni-Al-Fe-Cr-Ti (51.1%, 46.9%, 0.075%, 0.8593%, and 0.914%). In addition, it observed that after the process occurs there is a separation into four layers: an aqueous phase, purified oil, aqueous-hydrocarbon emulsion and catalyst (Fig. 1)

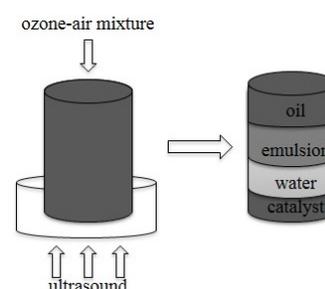


Fig. 1 Schematic representation of the sono catalytic process

Table II shows the results of analyzing the total sulfur content of the oil before and after ultrasonic oxidative desulfurization after two treatment cycles.

TABLE II  
RESULTS OF THE ANALYSIS OF TOTAL SULFUR IN THE OIL

| Sample                       | Mass fraction of phase, wt% | Sulfur content, wt% |
|------------------------------|-----------------------------|---------------------|
| Reference oil                | 100                         | 2.645               |
| Aqueous phase                | 27                          | 0.040               |
| Purified oil                 | 26                          | 1.640               |
| Aqueous-hydrocarbon emulsion | 47                          | 3.970               |

Experimental results show that a significant part of the sulfur compounds proceeds in newly formed aqueous phase, and the sulfur content in the hydrocarbon phase is reduced from 2.645 to 1.640 wt.%.

A byproduct of sono catalytic desulfurization reaction is the inverse emulsion of water in the oil and the water content of this emulsion depends on the intensity of ultrasonic treatment not linearly, it has maximum. In the separation of this emulsion it was found that a significant part of sulfur compounds turns in the formed aqueous-hydrocarbon phase (Fig. 2).

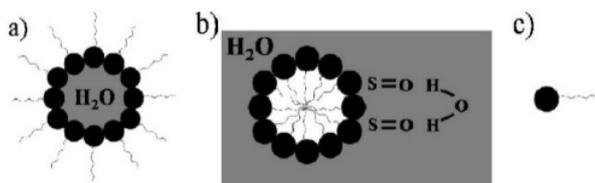


Fig. 2 Schematic representation of the processes of transferring sulfur-containing organic compounds from hydrocarbons in the invert emulsion droplets in an ultrasound exposure: (a) drop of an inverse emulsion with adsorbed interfacial oxidized sulfur-containing organic compounds; (b) micelle consisting of molecules of oxidized organic sulfur compounds; (c) the structure of amphiphilic molecules of oxidized organic sulfur compounds

Fig. 2 illustrates the physical and chemical bases of the process of removing sulfur-containing organic compounds as a result of ultrasonic treatment in the presence of a catalyst and oxidant. It may be assumed, that the amphiphilic molecules of oxidized sulfur-containing organic compounds, which resulting from sono catalytic oxidation, adsorbed on the surface of the water droplets in the emulsion of reverse account solvation polar sulfoxide groups aqueous phase, whereas nonpolar hydrocarbon radicals converted to a hydrocarbon medium. During the separating such inverse emulsion into an aqueous and a hydrocarbon phases the molecules of organic sulfur-containing compounds pass into the aqueous phase, forming micelles. Thus, the content of organic sulfur compounds in the hydrocarbon phase of the emulsion is significantly reduced and compared with the sulfur content in the hydrocarbon phase formed as a result of the ultrasonic treatment. Further, we analyzed the fractional composition of oil and determined the amount of sulfur in gasoline and diesel fraction. As a result, after the ultrasonic treatment the yield of the gasoline fraction increased from 15.6 to 21.9 wt.% and the diesel fraction - from 47.7 to 58.6 wt.%. As well as a decrease in the amount of sulfur in the liquid fraction of oil: gasoline fraction - up to 0.1240 wt.%, diesel fraction - up to 0.614 wt.%.

We held the infrared spectroscopic study of original and processed oil. In IR spectrum revealed that in the test samples of the reference oil has dominated normal and iso-structured paraffins, there are long paraffinic chains (absorption bands 1458, 2854, 2924, 2955  $\text{cm}^{-1}$ ). It is noted the presence of the OH groups (2341  $\text{cm}^{-1}$ ) and hetero (2360  $\text{cm}^{-1}$ ). Also highlighted absorption bands corresponding oxygenated organic (1169  $\text{cm}^{-1}$ ) and aromatics (873  $\text{cm}^{-1}$ ) and alkyl halide (617-693, 726-740  $\text{cm}^{-1}$ ) are contained in much smaller quantities than paraffin.

When interpreting spectrograms oil sonicated can see a change in the absorption bands of 2341-2360  $\text{cm}^{-1}$ , corresponding to OH groups, the intensity peaks are largely decreased. However, it should be noted that, after ultrasonic treatment, new bands are observed in the region of 1606-1660  $\text{cm}^{-1}$  - responsible for the presence of unsaturated paraffins and 1113  $\text{cm}^{-1}$  corresponding esters, and the peaks defining oxygen-containing organic compounds are not observed.

The IR spectra of treated oil ozone-air mixture there is a

significant decrease in the intensity of the absorption bands characteristic for paraffins (2855, 2871, 2924, 2955  $\text{cm}^{-1}$ ), hetero (2359  $\text{cm}^{-1}$ ) and OH groups (2340  $\text{cm}^{-1}$ ). Also, in the spectrogram of the sample oil were found novel low intensity peaks corresponding to the presence of ester (1108  $\text{cm}^{-1}$ ) and aromatics (1035  $\text{cm}^{-1}$ ).

In the sample treated oil and simultaneously ultrasound ozone-air mixture, there is a significant increase in the intensification of the absorption bands, the corresponding alkyl halides (615-697, 725-766, 806-849  $\text{cm}^{-1}$ ) and ester (1107  $\text{cm}^{-1}$ ), aromatic compounds (873  $\text{cm}^{-1}$ ) and paraffins (1459, 2854, 2923  $\text{cm}^{-1}$ ). To observe the formation of new absorption bands of medium and weak intensity, corresponding to the presence of unsaturated paraffins (1605, 1641, 1658  $\text{cm}^{-1}$ ) substituted ethylenes (1302-1376  $\text{cm}^{-1}$ ) and the secondary alcohol (1207  $\text{cm}^{-1}$ ), while absorption band responsible for the presence of heteroatomic compounds decreased significantly. Next, we studied the effect of ozonation on the diesel fraction of oil from "Zhanazhol" oil field.

For comparative analysis were defined physical-chemical parameters of the initial and hydrogenated diesel fraction of oil from "Zhanazhol" oil field without pre-treatment by ozone-air mixture. Cetane index, showing the quality of the initial diesel fuel was - 51.9. The indicator on the complete combustion of diesel fuel, 50% and 90% of sublimation are 220°C and 270°C. Temperatures triggering classification of diesel, crystallization time of paraffins in diesel and characterize the operational duration - the cloud point, pour point and filtration of diesel fuel amounted to -30.3; -36.1; -42.2 respectively. The density of diesel fuel was 0.801  $\text{kg/m}^3$ . The sulfur content of testing diesel fuel was 1 wt.%.

It is marked that after the hydrogenation of initial diesel fuel the sulfur content decreased to 0.0240, the cetane number increased to 52.6; the temperature of 50% and 90% sublimation fractions slightly increased, the initial boiling point increased, cloud point, pour point and filtration temperature reduced.

As follows from the spectral analysis of the investigated diesel fuels are not equal in their hydrocarbon content. IR spectra of diesel fuel that obtained by direct distillation of the oil from "Zhanazhol" oil field, characterized by absorption bands in the frequency range 3000-2800  $\text{cm}^{-1}$  (alkanes), 1460.29  $\text{cm}^{-1}$  (arenes), 1377.63  $\text{cm}^{-1}$  (methylbenzenes), 722.55  $\text{cm}^{-1}$  (cis-dienes).

The intensity of the absorption bands of alkanes in the IR spectra of diesel fractions, after hydrogenation, noted in the absorption frequencies of 2955.93; 2956.06; 2956.04; 2955.96  $\text{cm}^{-1}$ . And the absorption bands of medium intensity are visible in the frequency 2855.07; 2855.11; 2855.05; 2855.10  $\text{cm}^{-1}$ . Also, in the IR spectra seen the absorption bands of high, medium and low intensity corresponding arene groups in the frequency 1460.29; 1460.10; 1460.22; 1460.16  $\text{cm}^{-1}$ . The absorption bands of methylbenzene detected at 1377.63; 1377.68; 1377.65; 1377.6  $\text{cm}^{-1}$ ; cis diene groups occurring as part of the diesel fuel and detected at frequencies 722.55; 722.63; 722.47; 722.56  $\text{cm}^{-1}$ .

After treatment by zone-air mixture diesel fuel is subjected to hydrogenation on skeletal catalyst (alloy composition of Ni - Al - Fe - Cr - Ti) at 25 ° C and atmospheric pressure.

The results of preliminary ozonation influence on diesel fuel are shown in Table III.

TABLE III  
THE INFLUENCE OF OZONE ON THE DIESEL FRACTION OF OIL OF "ZHANAZHOL" OIL FIELD

| Parameters                                       | Samples of oil      |                          |   |  |  |
|--|---------------------|--------------------------|---|--|--|
|  | Initial diesel fuel | Hydrogenated diesel fuel | Ozonation and hydrotreating:                      |  |  |
|  |                     |                          | The specific consumption 8.7 g / kg during 30 min | The specific consumption 17 g / kg during 30 min | The specific consumption 35 g / kg during 90 min |
| Density at 20°C, kg / m <sup>3</sup>             | 801                 | 803                      | 798   | 800  | 798  |
| Iodine Number                                    | 28.7                | 28.0                     | 26.4  | 23.8   | 22.2   |
| Cetane Index                                     | 51.8                | 52.6                     | 54.6  | 54.5   | 55.0   |
| Refractive Index                                 | 1.445               | 1.445                    | 1.445   | 1.445  | 1.447  |
| Cloud Point, °C                                  | -30.3               | -30.5                    | -27.0   | -30.2  | -28.2  |
| Filtration temperature, °C                       | -36.1               | -36.2                    | -34.7   | -35.7  | -35.9  |
| Pour Point, °C                                   | -42.2               | -42.7                    | -40.7   | -41.9  | -42.4  |
| The total amount of sulfur, wt. %                | 0.8426              | 0.5447                   | 0.042   | 0.069  | 0.086  |
| The volume of absorbed hydrogen, dm <sup>3</sup> | -                   | 0.059                    | 0.060   | 0.060  | 0.067  |
| Starting boiling, °C                             | 147                 | 166                      | 167   | 160  | 171  |
| 50% distillation temperature, °C                 | 220                 | 225                      | 235   | 236  | 239  |
| 90% distillation temperature, °C                 | 270                 | 273                      | 273   | 274  | 281  |

TABLE IV  
THE RESULTS OF IR ANALYSIS OF THE HYDROCARBON COMPOSITION OF THE INITIAL, HYDROGENATED, AND THEN HYDROGENATING THE OZONIZED DIESEL OF "ZHANAZHOL" OIL FIELD

| Hydrocarbons according to their absorption frequencies | Initial Diesel fuel (DF) | DF – hydrogenated, ozonized with followed by hydrogenation |   |  |
|--|--------------------------|--|---|--|
|  |                          | Hydrogenated   | Ozonized/ Hydrogenated ( $\nu_{oz.} = 8.7$ g/kg, $\tau_{oz.} = 60$ min) | Ozonized/ Hydrogenated ( $\nu_{oz.} = 17.7$ g/kg, $\tau_{oz.} = 30$ min) |
|  |                          |  |   |  |
| $\nu_{CH_3}^{as}$ , alkanes                            | 2955,93                  | 2956,06  | 2956,04   | 2955,96  |
| $\nu_{CH_2}^s$ , alkanes                               | 2855,07                  | 2855,11  | 2855,05   | 2855,10  |
| $\nu_{C-C(arenes)}$ , arenes                           | 1460,29                  | 1460,10  | 1460,22   | 1460,16  |
| $\delta_{CH_3}^s$ , methylbenzenes                     | 1377,63                  | 1377,68  | 1377,65   | 1377,63  |
| $\delta_{=CH}$ , cis-dienes                            | 722,55                   | 722,63   | 722,47  | 722,56   |

On the basis of the Table III data, it is possible to note the change of the all physical and chemical characteristics of diesel fuel. Identified an increase in the cetane index compared to the original and hydrogenated diesel oil in the pre-ozonated and hydrogenated diesel oil fractions. Moreover, with increasing of the flow rate of ozone-air mixture the cetane index increased in the series: 51.8 < 52.6 < 54.5 < 54.6 < 55.0. A marked decline in the density: 0.803 > 0.801 > 0.800 > 0.798. Accordingly, when the Iodine Number in the initial diesel fuel was 28.7, after the hydrogenation was 28.0 and after ozonation and subsequent hydrogenation decreased even for 26,4 (8.7 g / kg during 30 min) > 23.8 (17 g / kg during 30 min) > 22.2 (35 g / kg during 90 min). In process of increasing the volumetric feed rate of the ozone-air mixture the absorbed total amount of hydrogen increased. If the direct hydrogenation of the total amount of absorbed hydrogen amounted to 0.059 dm<sup>3</sup>, then the hydrogenation after ozonation it rose to 0.060 dm<sup>3</sup> (8.7 g/kg during 30 min); 0.060 dm<sup>3</sup> (17 g/kg during 30 min) and 0.067 dm<sup>3</sup> (35 g/kg during 90 min). Improvement in the fractional composition of diesel fuel depending on the variation of the cetane number has also been marked. There was an increase, "the first drop in temperature," which characterizes the beginning of the boiling

point of the fractions in the process of ozonation, ° C: 147 > 160 > 166 > 167 > 171.

Comparison of the results of spectral analysis of an initial diesel fuel after hydrogenation and ozonation followed by hydrogenation showed the deviation of the absorption bands corresponding to the aliphatic hydrocarbons composition CHx. This can be explained to a change in physical-chemical parameters of ozonated followed by hydrogenation of diesel fuel (Table IV).

As follows from the results of the studies with increasing of the flow rate of the ozone-air mixture, ozonation process goes more deeply, leading to a noticeable change in the physical-chemical properties of diesel fractions. The ozonation of diesel fuel in the range of test velocities, the maximum amount of hydrogen is absorbed at a rate of 8.7 g/kg and 60 min time. Diesel fuel ozonized under these conditions showed higher results than with hydrogenated diesel oil without ozonation

There is a decrease of refractive index in the increase of the cetane index from 51.90 to 55.05. After ozonation hydrogenated diesel oil decreased significantly the pour point, cloud point and filtration temperature. Depending on conditions of ozonation, it is noted a significant change of iodine numbers and density of diesel fuels.

#### IV. CONCLUSION

The studies we can conclude that the use of batch processing speed in the ultrasonic field in the presence of catalyst (Ni-skeletal catalyst obtained from the alloy Ni-Al-Fe-Cr-Ti) and oxidant (ozone-air mixture) is potentially very effective method improving the quality of petroleum products, allowing purposefully modify their chemical composition by reducing the content of organic sulfur compounds, since the sulfur content in the oil is reduced from 2.645 to 1.640 wt.%. In addition, there has been increase in the yield of liquid products: the gasoline fraction – from 15.6 to 21.9 wt.% and the diesel fraction -.from 47.7 to 58.6 wt.%. As well as a decrease in the amount of sulfur in the liquid fractions of oil: gasoline fraction – up to 0.1240 wt.%, diesel fraction – up to 0.6140 w.%. Thus, we can resume that it is the combined effect of the catalyst and ultrasonic treatment results in the most efficient removal of organosulfur compounds from hydrocarbons. By IR spectroscopy to study the composition of reference, treated with ultrasound, ozone-air mixture, at the same time ultrasound and ozone-air mixture of oil, in the latter case, the absorption band responsible for the presence of heteroatomic compounds decreased significantly. Thus, pretreatment of diesel fuel by ozonation process allows its deeper hydrogenation. Treatment of the of diesel fuel by ozone-air mixture is achieved lowering the amount of sulfur compared to the initial to 46%.

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