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Advantages of Combining Different Processes for Diesel Fuel Desulfurization

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Abstract

The integration of oxidative desulfurization and hydrotreating allows, involving heavy oil fractions and fractions of secondary processes, obtaining motor fuels that comply with the regulations of the Russian Federation. For fuel samples with different sulfur content, we performed experiments to determine sulfur content, hydrocarbon-type, sulfur- and nitrogen-containing composition of compounds. The research shows that preliminary oxidative desulfurization decreases the content of heteroatomic and polyaromatic compounds. Thus, it is reasonable to combine these processes for fractions with an initial sulfur content of more than 0.200 mass%.

Keywords*: Desulfurization; Diesel fuel; Hydrotreating; Oxidative desulfurization.*

1. Introduction

Diesel fuel (DF) is one of the most demanded petroleum products in the world market. According to OPEC forecasts, vehicles using a diesel engine will reach 45% by 2021. DF production is growing, in 2010-2017 its consumption reached 76.831 million tons in the Russian Federation [1]. DF demand is high in the European and Asian markets. However, the discrepancy between the DF quality and environmental requirements in these regions hinders the export.

The content of aromatic hydrocarbons (HC) in DF is tightly controlled [2]. This group of compounds is responsible for most of the non-combustible and solid particles in the exhaust gases of diesel engines [3]. The content of sulfur and nitrogen, as undesirable components, is declared for compliance with the Technical Regulations of the Customs Union (TRCU 013/2011 of 18.10.2011 No. 826).

The content of sulfur compounds (SC) in diesel fraction (DFr) is from 0.02 to 2.00 mass%. There is a conventional graduation into active and inactive (neutral) SC. Active SC are represented by free sulfur, mercaptans, and hydrogen sulfide, and upon contact with metal, they cause corrosion; their presence in petroleum products is not allowed. Inactive SC do not cause corrosion; they are sulfides, disulfides, thiophene, and their derivatives, forming 70–80% of the total mass of SC. It has been established that any SC in DF when it enters internal combustion engines (ICE) becomes active and, as a consequence, causes corrosion of the cylinder-piston group [4]. SC poison the catalysts during the processing of diesel fuel, form sulfur dioxide during the oxidation of DF and poison the environment.

In addition to SC, the diesel fraction contains nitrogen-containing compounds (NCC) [5], which have a toxic effect on HT catalysts. That is why the NCC preliminary reduction has a positive effect on the catalyst life cycle and the degree of DF desulfurization [6].

To achieve a sulfur content of less than 10 ppm, we need to reconstruct the traditional HT to increase the SC conversion degree. It requires more resident time, the increase in hydrogen consumption, and the use of expensive catalysts [3]. Spent HT catalyst is a solid waste, its disposal results in carbon dioxide emissions. The listed factors indicate the need to develop a more stable technology for upgrading DF, capable of increasing the efficiency of HT [7].

The oxidative desulfurization (OD), as an addition to the existing HT units, is a promising technology that can reduce the cost of producing diesel fuel with a low sulfur content [8]. The economic feasibility of using OD depends on the feedstock composition and the process parameters [9]. As an alternative to traditional hydrodesulfurization technology, OD technology does not involve hydrogen, so it decreases capital costs. During OD the separation of the hydrocarbon part from the oxidation products of the SC occurs with relative ease. The method is promising due to the high level of desulfurization and the commercially valuable resulting products – sulfoxides and sulfones. Hydrogen peroxide is the most popular oxidizing agent because it is a cheap, commercially available, non-polluting agent. OD is superior to HT as difficultly desulfurized DBT is easily oxidized at atmospheric pressure and a temperature of no higher than 100°C to sulfones, sulfones can be easily extracted or adsorbed from DFr.

Most papers on unconventional desulfurization methods present the results of the model mixtures oxidation with various oxidizing agents [10-20]. So, we cannot fully study the change in the group and component composition of DFr. Currently, some papers prove the effectiveness of the OD on real oil samples [20- 22]. Some papers on the OD of fuels and catalytic cracking products study the influence of the main parameters on the completeness and rate of oxidation for DBT derivatives [23] and its model mixtures with hydrocarbons [23-25]. In addition, the studies were performed on hydrotreating fuels which makes it difficult to assess the comparative efficiency of these processes.

The combination of oxidation in the presence of transition metal salts and absorption/extraction was also studied [26]. The studies were carried out for straight-run non-hydrotreated DFr, the maximum sulfur recovery was 60 mass%, however, the authors did not give the group composition of sulfur compounds before and after the experiments, which does not allow judging the effect of oxidizing and extracting agents on various types of compounds. A promising technology is a preliminary OD followed by HT, as, for example, proposed in the paper [27]. Such a sequence of processes makes it possible to provide a high degree of conversion [21], to get rid of SCes that are difficult to extract during HT, and to reduce the content of NCC to extend the service life of the HT catalyst. This sequence of processing requires higher consumption of the oxidizing mixture, but the consumption of hydrogen-containing gas (HCG) for hydrotreating reduces; therefore, this processing procedure is economically feasible.

The paper aims to study the total efficiency of the sequential combination of OD and HT processes in terms of such parameters as the conversion of sulfur and nitrogen compounds; change in the group composition of sulfur compounds and the content of polyaromatic compounds.

2. Experimental

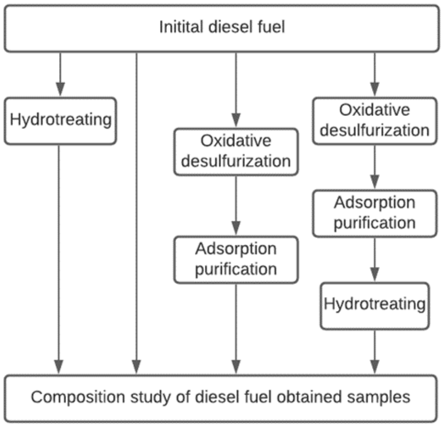


Fig. 1. Experimental research flowchart

Figure 1 shows our experimental research flowchart. DF samples after the study were separately subjected to both HT with subsequent analysis and OD with adsorption purification and analysis. In parallel, we combined the processes: the samples were subjected to OD followed by adsorption purification, and then to HT, after which we made the analysis.

The OD unit is a temperature-controlled batch reactor equipped with a stirrer for homogenizing the mixture. We performed experimental studies under the conditions proposed in the paper [28]. Table I shows OD parameters. The method involves two-phase oxidation of the distillate with 30% hydrogen peroxide based on an aqueous solution of 80% formic acid to convert thiophene sulfur into the corresponding sulfones. It was found [25] that formic acid gives a greater oxidative effect than stronger or weaker acids. The yield of oxidation products was 95–97 mass%. The samples obtained after oxidation were subjected to adsorption purification. The adsorption was carried out on a glass column at room temperature. Polar compounds, such as sulfoxides and sulfones, during the adsorption purification, were sufficiently firmly adhered to the silica gel surface. This made it possible to easily separate them from the hydrocarbon part of the samples [21].

Table 1. Oxidative desulfurization parameters

Parameter	Value
Molar ratio $S_{\text{общ}}:H_2O_2$	1:15
Molar ratio $H_2O_2:HCOOH$	3:4
Temperature, °C	35
Oxidation time, h	0.5–8
Stirrer rotation speed in the reactor, rpm	2100
Fraction mass for analysis, g	10

The HT process was on a laboratory catalytic unit under increased pressure for the initial fractions and fractions that after oxidative desulfurization under conditions close to the industrial (Figure 2).

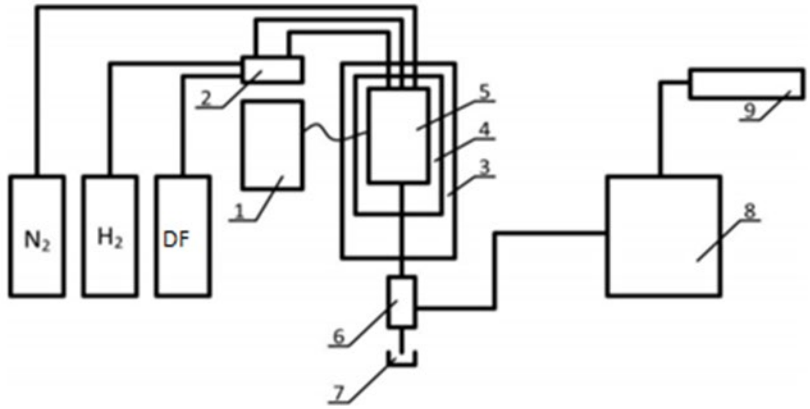


Fig. 2. Process flow diagram of a laboratory catalytic hydrodesulfurization unit:
1 – temperature regulator; 2 – gas dosing package; 3 – heating chamber; 4 – reactor jacket; 5 – reactor; 6 – separator; 7 – receiver; 8 – chromatographical unit; 9 – drawing.

The HT of the initial DFr and DFr after OD was out under conditions close to the industrial process: the volumetric flow rate of the liquid feed was 0.05 ml/min, the pressure was 3.3 MPa, the hydrogen/feed ratio was 300/1, and the temperature was 350 °C. HT was on an industrial GKD-202 aluminum-nickel-molybdenum catalyst based on CoO (12 mass%), NiO (2.2 mass%), MoO_3 (no less than 13 mass%) and Na_2O (no less than 0.4 mass%); catalyst mass m_{kat}= 5.0153 g, granule size 0.5–2 mm; reactor volume 10 cm^3. Before the DFr HT, the catalyst was subjected to sulfidation directly in the reactor using straight-run DP containing 0.814 mass% sulfide sulfur. We performed sulfidation according to the method presented in the paper by G.K. Boreskov [14]. The process went until a sharp increase in the concentration of hydrogen sulfide in gaseous products. It was a sign for the metal phase saturation of the catalyst with sulfur [14]. The sulfided catalyst has a high activity and less tendency to coke formation and a twice as long cycle length [14].

Feedstock and hydrogen entered the reactor from top to bottom: liquid metering pump fed the DFr; an automatic dispenser controlled the hydrogen supply. A single-area electric furnace provided the reactor heating; it also made it possible to maintain the temperature over the catalyst bed with an error of less than 1.5%.

The reaction products entered a direct flow cooler. After product separation in a high-pressure separator, we collected liquid reaction products for analysis by pouring them into a receiver. Gaseous products were discharged into the atmosphere through a side connection, a shut-off valve, a back-pressure reducer and an exhaust ventilation. After the completion of the HT process, the obtained hydrogenated product goes under further study.

When studying the composition of the obtained DFr samples, it was determined: the content of total sulfur according to GOST R 51947-2002; content of SC groups by GLC method; group hydrocarbon composition by LAC method; total nitrogen content using the VarioELCube elemental analyzer. Liquid adsorption chromatography on activated alumina of II degree of Brockmann activity established the hydrocarbon-type composition. GLC determined the content of groups of sulfur compounds.

The group composition of the SC was determined using GLC on a sulfurselective flame photometric detector (FPD) in accordance with ASTM D 5623-94 (2009) on a “Kristall-2000M” chromatograph on a quartz capillary column (diameter 0.530 mm, length 1000 mm, adsorbent - HYSER -S). Chromatographic conditions: linear temperature rise from 50 to 290 °C, column heating rate is 4 deg/min; the sample injection is by using an automatic dosing device. The qualitative composition of sulfur compounds was determined by comparing the retention times of individual compounds (di-n-hexyl sulfide, benzothiophene, dibenzothiophene) and the analyzed components. We also used the data given in the papers [29-31]. The chromatograms determine and calculate the number of SC groups, which are markers of DF. The samples contain DBT and its homologues, as well as a wide range of benzothiophene homologues. According to the data obtained, most of the sulfur in all samples is contained in thiophene compounds; the content of benzothiophene homologues is greater than the number of DBT homologues. Table II shows group composition of DFr sulfur compounds

We selected three DF samples for the experiment. Samples contain the following amount of total sulfur W_S in the form of sulfides and thiophenes, mass%: 1.730 (sample №1), 0.243 (sample №2), and 0.074 (sample №3).

Table 2. Group composition of diesel fractions sulfur compounds, mass %

Sulfur compounds	W_S in sample № 1	W_S in sample № 2	W_S in sample № 3
Sulphides	0.410	0.043	0.014
Thiophenes	1.319	0.200	0.060
including:			
benzothiophene homologues	0.675	0.121	0.037
dibenzothiophene and its homologues	0.643	0.079	0.023

3. Results and discussion

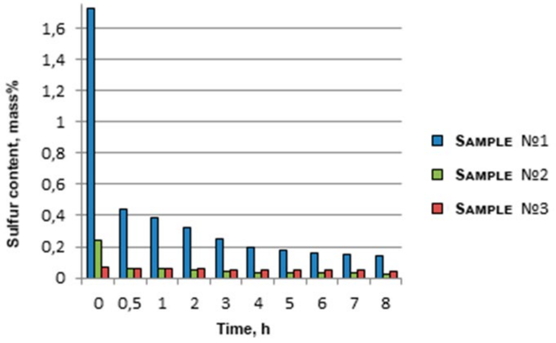
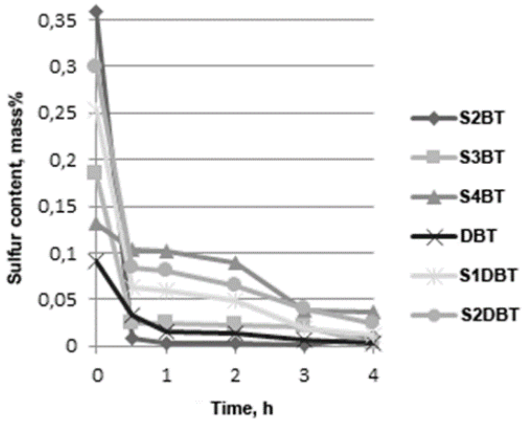


Fig. 3. Change in total sulfur content depending on the sample oxidation time

Sample №1 oxidation for 30 min followed by adsorption purification results in the removal of up to 75.0 rel. % (Figure 3), for sample №2 – 74.1 rel. % sulfur. A further increase in the duration of the oxidation process (up to 8 h) makes it possible to remove additionally more than 17.0 mass% sulfur in samples №1 and 14.8 mass% in №2. The highest conversion rate for samples №1 and №2 is when the experiment goes for 30 minutes.

With OD for 30 min of sample №3, the degree of total sulfur conversion is 13.5, during 8-hour oxidation is 37.8 mass%. Alkyl-substituted, sterically closed benzo- and dibenzothiophenes, which have a lower reactivity, are more difficult to extract than others [21]. A large number of polycyclic aromatic SC, which are mainly represented by alkyl-substituted compounds, significantly slow down the rate of desulfurization in sample No. 3.

Figures 4–6 show graphs of changes in the content of various SC groups. The tendencies are similar for samples №1 and №2. There is a sharp decrease in the content of almost all SC groups in 30 minutes of oxidation. The initial low sulfur content in sample No. 3 and the content of alkyl-substituted benzo- and dibenzothiophenes is 6% higher than in the rest of the samples reduce the rate of SC conversion.



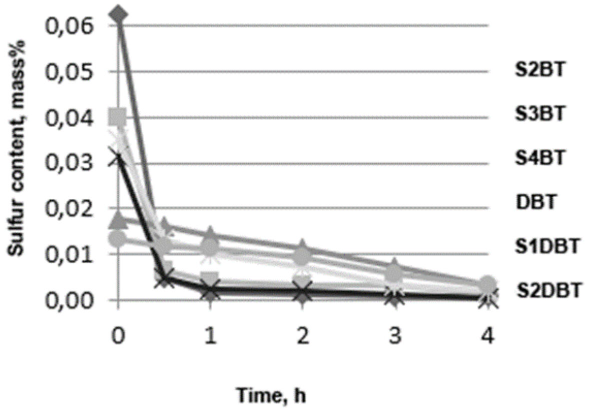


Fig. 4. Change in the content of SC groups depending on the sample № 1 oxidation time.

Fig. 5. Change in the content of SC groups depending on the sample № 2 oxidation time.

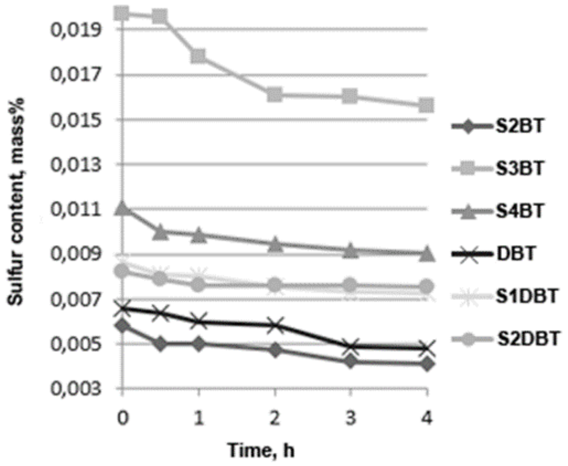


Fig. 6. Change in the content of SC groups depending on the sample № 3 oxidation time.

Table 3 shows the results of measuring the SC in the DF after the HT. The content of S2DBT compounds after HT is higher than after the OD (on average by 37.3%).

Table 3. The content of sulfur compounds in diesel fuel after hydrotreating, mass%

DF sample	Sulfur content in sulfur compounds, mass%					
	S$_2$BT	S$_3$BT	S$_4$BT	DBT	S$_1$DBT	S$_2$DBT
1	0.0095	0.0017	0.0321	0.0017	0.0099	0.0312
2	0.0004	0.0009	0.0017	0.0004	0.0012	0.0058
3	0.0005	0.0010	0.0019	0.0004	0.0015	0.0080

The results of changes in the nitrogen content are presented in Table 4, total sulfur in the Table 5, hydrocarbon-type composition in Table 6.

Total nitrogen content decreases during the OD (Table 4). The highest initial nitrogen content in sample №1, the degree of nitrogen conversion during oxidation for this sample is also higher is 30.4 mass%. For samples №2 and №3, the degree of extraction is equal to 21.8 mass% and 16.7 mass%, respectively. Because nitrogen poisons the active sites of the HT catalyst, a decrease in its content in the preceding processes will increase the catalyst life.

Table V shows that the degree of sulfur conversion for sample №1 is the highest – during HT it is 88.8%, when combining OD with HT it is 95.7%. For samples № 2 and № 3, the degree of conversion after HT is 71.1% and 82.4%, after combining OD with HT – 92.2% and 87.8%, respectively. For all samples, when the HT and OD are combined, the degree of conversion is higher, which indicates the efficiency of combining these processes. The degree of conversion for sample №3 is lower than for other samples. It is because this sample has a low initial content of SC, represented by thiophene and its homologues in high concentration. For sample №3, the sulfur content after OD followed by HT reached the value corresponding to the standards.

For all samples, there is a tendency to an increase in the number of saturated HC (by 3–5 mass%) and a decrease in the total amount of aromatic hydrocarbons (Table VI), as reactions of polyaromatic compounds and hydrogenation of HC destructuring go during the OD. Aromatic compounds are precursors of coke formation and their reduction in the processes of DFr-s purification will increase the cycle run of the HT catalyst.

Table 4. Nitrogen content in feedstock and refining products, mass%

DF sample	Initial nitrogen content	OD (4 h)	HT	OD (4 h)+HT
1	0.5427	0.3911	0.3996	0.2057
2	0.5612	0.3908	0.2121	0.1798
3	0.5525	0.4321	0.3746	0.2271

Table 5. Sulfur content in feedstock and refining products, mass%

DF sample	Initial sulfur content	OD (4 h)	HT	OD (4 h)+HT
1	1.730	0.200	0.193	0.074
2	0.243	0.035	0.070	0.019
3	0.074	0.051	0.013	0.009

Table 6. Results of determining the group composition of aromatic hydrocarbons in the diesel fraction

DF sample	Content, mass%		
	Monocyclic aromatic hydrocarbons	Naphthalene and its derivatives	Anthracene and polynuclear aromatic hydrocarbons
№ 1	1.28	3.18	10.60
№ 1 after OD (4 h)	1.05	1.41	9.60
№ 1 after HT	1.18	1.40	10.12
№1 after OD (4 h)+HT	1.14	1.23	9.46
№2	5.18	2.13	37.43
№ 2 after OD (4 h)	3.94	1.95	34.69
№2 after HT	3.28	1.99	30.67
№2 after OD (4 h)+HT	2.69	1.82	29.96
№3	8.11	5.82	31.85
№ 3 after OD (4 h)	3.45	4.54	30.98
№ 3 after HT	6.45	4.49	27.32
№ 3 after OD (4 h)+HT	2.14	2.01	27.29

4. Conclusion

As a result of the study of the content of total sulfur and nitrogen, the group hydrocarbon composition of DFr during OD, HT, and when these processes are combined, it was found that the combination of OD and HT processes is more effective. The study shows that our solution will increase the cycle length, reduce the amount of consumed hydrogen, soften the conditions for the HT process, due to the preliminary decrease in the content of SC and NCC, polyaromatic HC. It is more expedient to carry out the OD process for DFr with an initial sulfur content of more than 0.20 mass%, as it will reduce the amount of hydrogen consumed for the hydrogenolysis of the residual content of SC in the HT reactor, and will reduce the toxic effect on the HT catalyst due to the preliminary decrease in the content of NCC and polyaromatic hydrocarbons.

Symbols and abbreviations:

HT – hydrotreating;
DF – diesel fuel;
DFr– diesel fraction;
OD – oxidative desulfurization;
SC – sulphur compounds;
NCC– nitrogen-containing compounds;
HC – hydrocarbons;
S2BT – dimethylbenzothiophene;
S3BT – trimethylbenzothiophene;
S4BT – tetramethylbenzothiophene;
DBT – dibenzothiophene;
S1DBT – methyldibenzothiophene;
S2DBT– dimethyldibenzothiophene;
ICE – internal combustion engine;
GLC – gas liquid chromatography.

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Declarations of interest: *none.*

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