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APPLICATION OF NON-CATALYTIC OXIDATIVE DESULPHURIZATION PROCESS FOR OBTAINING DIESEL FUELS WITH IMPROVED LUBRICITY

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Abstract. The fractions of diesel oil have been desulphurized *via* air oxidation without the catalysts in the presence of water. The products of sulphuric compounds oxidation were extracted by adsorption or joint adsorption and rectification. The samples of desulphurized diesel oil have been analyzed in accordance with reference documents after their treatment by alkali. The lubricity of the raw materials (straight-run diesel oil and hydrogenised fuel), desulphurized straight-run diesel oil (DSDO), hydrogenised fuel with DSDO additives and two samples of the fraction 553–623 K purified in the presence of water and without it has been determined.

Keywords: sulphur, diesel fuel, oxidative desulphurization, lubricity.

1. Introduction

It is well known, that the sulphur content in diesel fuels, as well as in other transportation fuels, is a very serious environmental problem because during combustion sulphur compounds are converted mainly to sulphur dioxide (SO₂), which is a major cause of air pollution and acid rains [1, 2].

Diesel fuels sulphur also significantly contribute to fine particulate matter emissions through the formation of sulphates both in the exhaust stream and, later, in the atmosphere. Furthermore the efficiency of some exhaust after-treatment systems is reduced as fuel sulphur content increases, while others are rendered permanently ineffective through sulphur poisoning [3].

To prevent air pollution caused by exhaust gases, governments of many countries all over the world have mandated sulphur removal from transportation fuels since the last decade. For example, from 2009 in the USA the sulphur maximal content in on-road fuels has to be

10 ppm [4, 5]. Identical or even stronger demands were made for the fuels produced in the European Union [6]. Many other countries [7-12] have also started to produce and consume “clean” automotive fuels.

Demands for diesel fuels in Ukraine are soft. However, since 2006 the sulphur content for the commercial diesel fuel produced in accordance with standards must not exceed the following values: 500, 1000 and 2000 ppm. In accordance with standards the fuel with the maximum sulphur content of 10 or 50 ppm is produced.

Up to date the only one industrial technology aiming at the sulphur content reduction is a catalytic hydrofining (hydrodesulphurization (HDS)). There are no HDS plants in three oil refineries in Ukraine (Open Joint Stock Company NPK-Halychyna (Drohobych), Open Joint Stock Company Naftokhimik Prykarpattya (Nadvirna), Open Joint Stock Company Khersonnaftopererobka (Kherson)). These oil refineries were designed for the refining of Ukrainian light oil with a very low sulphur content but now they have to use mainly Russian heavy oil with the high sulphur content. They are not able to meet requirements of the standards and to produce diesel fuels with sulphur content less than 2000 ppm. Existing hydrofining plants also cannot produce standards fuels meeting the demands.

At the same time HDS is the only one widely used industrial technology, which has a number of shortcomings:

- application of complicated equipment and purified hydrogen which is in short supply;
- removal of heteroatomic compounds and the “desirable” part of aromatic hydrocarbons together with sulphuric compounds, resulting in the amount decrease of the products capable of sorption over metal surfaces and lubricate them;
- impossibility of some thiophene derivatives removal.

Alternative technologies of diesel fractions desulphurization including extraction, selective adsorption, biodesulphurization, and oxidative desulphurization (ODS) [13, 14] have been investigated extensively in the past few decades. Among these processes, ODS is considered to be one of the promising new methods and is currently receiving growing attention. In comparison with the conventional HDS process, the greatest advantages of ODS are that it may be carried out in the liquid phase, under mild conditions, without expensive hydrogen, and allows to remove condensed sulphuric compounds [13, 14].

All ODS methods have two stages: oxidation of sulphur-containing organic compounds to sulphoxides and sulphones directly in the fuel, and then, removal of sulphoxides and sulphones from the oxidation-treated fuel, thereby obtaining desulphurized fuel.

There are few problems with the currently used ODS processes. One of them is the insufficient selectivity of the used oxidants. Insufficient selectivity causes partial oxidation of the hydrocarbons resulting in the decrease of the quality and the yield of desulphurized fuels and the by-products formation. For improving the ODS process selectivity (to minimize the degree of the hydrocarbon oxidation and the by-product yield) many authors propose to use different oxidants and catalysts [13, 14] which are expensive and in many cases inaccessible. As a result the ODS processes become more expensive and complicated.

We have developed the technological principles of the ODS process for diesel fractions. The essence of the proposed process is a non-catalytic oxidation by air of sulphuric compounds present in diesel fractions to the corresponding sulphoxides and sulphones with their

further removal by such known methods as rectification or adsorption. The oxidation is carried out at 453–493 K and 3.0 MPa with water because it is capable to display an inhibitory effect during the liquid-phase hydrocarbon oxidation. Obviously, under aforementioned conditions more products of oxidation will be produced compared with the processes using catalysts and expensive oxidants. We only minimized the oxidation of hydrocarbon due to the application of water and carried out desulphurization under the conditions providing industrial application of the refined fuel and the oxidation products.

The aim of this work was to establish the possibility:

- to obtain refined fuel with the sulphur content of 2000 ppm *via* oxidative desulphurization of straight-run diesel fractions (SRDF) with high sulphur content and fuel with 50 ppm of sulphur using hydrofined diesel fuel (HDF);
- to apply refined fuels as components for commercial diesel fuel improving its lubricity.

2. Experimental

The oxidation was carried out at an enlarged laboratory plant [15]. It consists of a reactor block; air compression and purification system; gaseous reaction products cooling and recovery system; temperature, pressure, and consumption control and measuring instruments. The main apparatus is a bubble reactor with the volume of 0.7 l. The reactor construction allows to keep the pressure up to 15 MPa at 623 K.

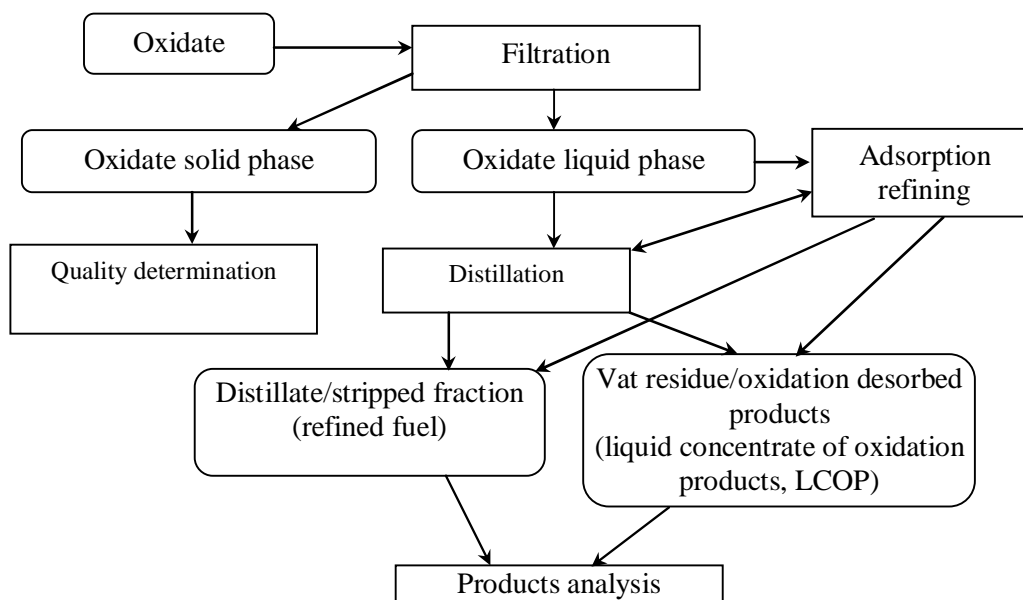


Fig. 1. Scheme of oxidate division and investigation

Table 1

Characteristics of initial diesel fractions

Index	Straight-run diesel fraction from JSC "Naftokhimik Prykarpattya"	Hydrofined diesel fuel from JSC "Ukratnafta"
Cetane number	50	–
Distillation characteristics, 50 % (V/V) recovered at temperature, K	539	554
90 % (V/V) recovered at temperature, K	638	631
Kinematic viscosity at 293 K, mm ² /s	4.7	–
Pour point, K	-3	-9
Flash point in closed crucible, K	64	–
Content of total sulphur, mas % (ppm)	0.671 (6710)	0.055 (550)
Content of mercaptan sulphur, mas % (ppm)	0.009 (90)	0.001 (10)
Content of H ₂ S	absent	absent
Test on copper plate	stand the test	stand the test
Concentration of actual gums, mg/100 cm ³	25	12
Acidity, mg KOH/100 cm ³	1.8	0.0
Iodine number, g iodine /100 g	1.13	–
Ash, mas %	0.004	–
Coking ability of 10 vol % residue, %	0.05	0,01
Filtration coefficient	1.24	–
Content of mechanical impurities	absent	absent
Content of water	absent	absent
Density at 293 K, kg/m ³	844	839

Table 2

Characteristics of narrow fractions obtained by distillation of straight-run diesel fraction

Index	438–553 K fraction	553–623 K fraction	438–623 K fraction
Content of total sulphur, mas % (ppm)	0.323 (3230)	0.869 (8690)	0.572 (5720)
Concentration of actual gums, mg/100 cm ³	7.5	15.0	11.9
Acidity, mg KOH/100 cm ³	1.6	5.9	3.5

In the case of diesel fraction oxidation with water, we separated the water phase and then divided and analyzed SRDF or HDF (oxidate) according to the scheme that was shown in Fig. 1.

Distillation was carried out by the Engler's method. Adsorption was performed by the developed method with silica gel as adsorbents. Benzene was used for the refined fuel desorption. The mixture of alcohol and benzene was applied for desorption of LCOP.

Lubricity was assessed by the high-frequency reciprocating ring (HFRR) in accordance with ISO 12156-1:2006.

The characteristics of the initial materials are presented in Table 1. Our previous investigations [16] showed that desulphurization results for the raw material with high sulphur content were the worst. The use of nar-

row diesel fractions allows to increase the sulphur removal degree. Therefore, the straight-run diesel fraction was distilled by two narrow fractions, which are characterized in Table 2.

Obtained results demonstrate that the main part of sulphur and compounds capable of condensation is located in heavy fractions: the increase of the boiling point increases the content of total sulphur and actual gums content.

3. Results and Discussion

The experimental results of desulphurization of 438–553 K and 553–623 K fractions in the presence of water under optimum conditions are shown in Table 3.

Table 3

Characteristics of desulphurized 438–553 K and 553–623 K fractions

Index	438–553 K fraction	553–623 K fraction
Content of total sulphur, mas % (ppm)	0.069 (690)	0.246 (2460)
Concentration of actual gums, mg/100 cm ³	3.5	9.2
Acidity, mg KOH/100 cm ³	1.5	5.4

Table 4

Characteristics of desulphurized 438–623 K fraction

Index	Values according to DSTU 3868-99	Actual values
Cetane number	≥ 45	46
Distillation characteristics, 50 % (V/V) recovered at temperature, K	≤ 548	545
90 % (V/V) recovered at temperature, K	≤ 643	620
Kinematic viscosity at 293 K, mm ² /s	3,0-5,5	3,2
Pour point, K	≤ - 283	- 283
Flash point in closed crucible, K	≥ 318	354
Content of total sulphur, mas % (ppm)	≤ 0,2 (2000)	0,138 (1380)
Content of mercaptan sulphur, mas % (ppm)	≤ 0,010 (100)	0,001 (10)
Content of H ₂ S	absent	absent
Test on copper plate	stand the test	stand the test
Concentration of actual gums, mg/100 cm ³	≤ 30	5,5
Acidity, mg KOH/100 cm ³	≤ 5,0	2,2
Iodine number, g iodine /100 g	≤ 5,0	1,1
Ash, mas %	≤ 0,010	0,003
Coking ability of 10 vol-% residue, %	≤ 0,25	0,002
Filtration coefficient	≤ 3,00	2,40
Content of mechanical impurities	absent	absent
Content of water	absent	absent
Density at 293 K, kg/m ³	≤ 850	827

Table 5

Characteristics of desulphurized hydrofined diesel fuel

Index	Values according to DSTU 4840:2007	Actual values
Content of total sulphur, mas % (ppm)	≤ 0.005 (50)	0.004 (40)
Concentration of actual gums, mg/100 cm ³	–	8.3
Acidity, mg KOH/100 cm ³	–	3.0

Table 6

Characteristics of desulphurized 553–623 K fraction

Index	Without water	In the presence of water
Content of total sulphur, mas % (ppm)	0.654 (6540)	0.618 (6180)
Concentration of actual gums, mg/100 cm ³	41.0	27.0
Acidity, mg KOH/100 cm ³	10.5	5.1

Table 7

**Characteristics (obtaining methods) of the samples used
to assay the lubricity of initial materials and obtained products**

Sample No.	Characteristics
1	HDF (Table 1)
2	438–623 K straight-run diesel fraction (Table 2)
3	438–623 K desulphurized fraction after alkali treatment; the alkali amount is 1000 mg KOH per 100 cm ³ of the product, 20 mass-% aqueous solution
4	438–623 K desulphurized fraction after alkali treatment; the alkali amount is 100 mg KOH per 100 cm ³ of the product, 2 mass-% aqueous solution (Table 4)
5	Mixture of sample No.1 (90 mas %) and No.3 (10 mas %)
6	Mixture of sample No.1 (97 mas %) and No.3 (3 mas %)
7	Refined fuel (distillate) obtained <i>via</i> desulphurization without water (Table 6)
8	Refined fuel (distillate) obtained <i>via</i> desulphurization in the presence of water (Table 6)

Table 8

Tribological test results of investigated samples

Sample No.	Corrected wear scar diameter, μm	Friction coefficient	Lubricating film thickness, %
1	530	0.388	12
2	569	0.242	7
3	552	0.245	28
4	386	0.204	55
5	520	0.320	6
6	506	0.344	12
7	393	0.200	48
8	400	0.197	46

Adsorption was used for the division of oxidate liquid phase obtained at the desulphurization of 438–553 K fraction; adsorption and double distillation as distillation-adsorption-distillation were applied for the separation of oxidate liquid phase got at the desulphurization of 553–623 K fraction. One can see from Table 3 that desulphurized products with the sulphur content of 0.069 mas % (the degree of sulphur removal is 78.63 %) and 0.246 mas % (the degree of sulphur removal is 71.69 %) are obtained, correspondingly.

Excluding acidity and sulphur content in 553-623 K fraction all indexes correspond to standards requirements. After alkali treatment (alkali amount is equal to 100 mg KOH per 100 cm³ of the product, 2 mas % aqueous solution) and mixing of both fractions we received the fuel completely meeting standards requirements (Table 4).

The increase of alkali amount (1000 mg KOH per 100 cm³ of the product, 20) does not change the acidity of obtained products.

The oxidative desulphurization of HDF allows to obtain the fuel fulfilling standards' requirements (Table 5). In this case adsorption was used for the division of oxidate liquid phase.

To determine the influence of water, which is used for the reduction of hydrocarbon oxidation intensity, on the lubricity of obtained fuel, the 553–623 K fraction was desulphurized without water and in the presence of it. In the last case the ratio (v/v) water : raw material was equal to 1 : 5. Distillation was used for the division of oxidate liquid phase. The results are presented in Table 6. Unsatisfactory results of desulphurization shown in Table 6, are probably caused by the non-optimal process conditions and the application of distillation alone.

To assay the lubricity of initial materials and obtained products, tribological tests were carried out for 8 samples which are described in Table 7.

The results of tribological tests performed for the samples are given in Table 8.

The results of tribological tests for the samples No. 1, 2 and 4 confirm that 438-623 K fraction after oxidative desulphurization and "moderate" alkalization (the sample No.4) has higher lubricity compared with hydrofined diesel fuel (the sample No.1) and initial straight-run diesel fraction (the sample No.2); the corrected wear scar diameter and friction coefficient are lower and the lubricating films thickness is higher. The corrected wear scar diameter of the sample No. 4 is less than the limit value for the diesel fuels (460 micrometers) in accordance with ISO 12156-2:2077 and Ukrainian standards. The improvement in the lubricity of 438-623 K SRDF after oxidative desulphurization and "moderate" alkalization is probably caused by the oxygen-containing compounds remaining in this sample.

The straight-run diesel fraction 438-623 K after oxidative desulphurization and "deep" (sample No.3) has unsatisfactory tribological properties compared with the sample No.4. Probably, the reason is that the alkali excess neutralizes acids and also influences other oxygen-containing compounds. At the same time salts of organic acids, the saponification compounds or alkali may remain in these products. The synergetic effect of the mixture of the samples No.1 and No.3 confirms this fact. The samples No.5 and No.6 have less diameter of wear compared with the initial substances. Moreover, the decrease in amount of "deeply" alkalized desulphurized SRDF (the sample No.3) decreases the corrected wear scar diameter. Obviously the dilution of the sample No.3 aligns the negative effect of alkali treatment residuals because of their concentration decrease in the mixture. The positive effect of surfactants introduced into hydrogenate with the sample No.3 is constant because even the small amount of them improves the lubricity. Residuals of sulphones, sulphoxides or oxygen-containing compounds may be as surfactants. Also, the friction coefficient of the sample No. 5 and the sample No. 6 is lower than the friction coefficient of the sample No. 1 due to the presence of the sample No. 3 with far better antifriction properties than the sample No. 1.

The desulphurization process performed in the presence of water (the sample No.8) and the process carried out without water (the sample No.7) allows to obtain the fuels with a comparable lubricity.

4. Conclusions

1. The developed non-catalytic oxidative desulphurization process allows to obtain the diesel fuel with the sulphur content of 1400 ppm meeting the requirements of Ukrainian standards using the straight-run diesel fuel fraction with the sulphur content of 5700 ppm as the initial material. The hydrofined diesel fuel with the sulphur content of 550 ppm may be desulphurized by aforementioned method to produce the diesel fuel with 40 ppm of sulphur which fulfil the standards' demands.

2. Fuels after the oxidative treatment have a higher lubricity compared with the initial straight-run diesel fuel fraction and the initial hydrofined diesel fuel. The suggested method allows to obtain the products, which may be used as components or additives for hydrofined fuels improving their lubricity.

3. In the alkali treatment of refined products the moderate amount of alkali should be used. The amount is a little greater than the acidity value of refined products.

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ЗАСТОСУВАННЯ НЕКАТАЛІТИЧНОЇ ОКСИДАЦІЙНОЇ ДЕСУЛЬФУРИЗАЦІЇ ДЛЯ ОДЕРЖАННЯ ДИЗЕЛЬНИХ ПАЛИВ З ПОКРАЩЕНИМИ МАСТИЛЬНИМИ ВЛАСТИВОСТЯМИ

Анотація. Здійснено знесірчування дизельних фракцій внаслідок їх окиснення повітрям без каталізаторів за присут-

ності води. Продукти окиснення сірчистих сполук з оксидату вилучали адсорбцією або комбінацією адсорбції та перегонки. Зразки знесірчених дизельних фракцій після оброблення їх лугом аналізували у відповідності до нормативних документів. Порівняно мастильні властивості вихідної сировини (прямогонна дизельна фракція і гідрогенізатор), знесірченої прямогонної дизельної фракції (ЗПДФ), гідрогенізатору з додатками ЗПДФ, а також двох зразків фр. 553–623 К, очищених за присутності води та без неї.

Ключові слова: сірка, дизельне паливо, окисдаційне знесірчування, мастильні властивості.