

## STUDY ON HYDRODYNAMIC PARAMETERS OF THE OXIDATIVE DESULFURIZATION OF HIGH SULFUR STRAIGHT-RUN OIL FRACTIONS

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**Abstract.** The article deals with the determination of hydrodynamic parameters necessary to conduct the desulfurization process of straight-run kerosene (SRKF) and straight-run diesel fractions (SRDF) *via* oxidation of sulfuric organic compounds, followed by the removal of oxidation products. The established parameters which are characterized by the linear rate of the oxidant (air) movement and the dummy contact time between the oxidant and the feedstock allow the process to be carried out without stirring. The proposed technology can be used for the purification of petroleum fuels produced by a small scale, when hydrotreating is economically unprofitable or technologically impossible. This process can also be used for the aftertreatment of hydrogenates and partial desulfurization of straight-run fractions to produce fuel components with improved lubricating properties.

**Keywords:** sulfur, jet fuel, diesel fuel, oxidative desulfurization, hydrodynamic parameters, lubricity.

### 1. Introduction

Over the last years, the emissions of SO<sub>x</sub> from combustion fuels have become a serious environmental problem. Strict environmental policies were implemented worldwide limiting the sulfur level in fuels to 10 ppm [1]. Diesel fuel (DF) became a major transportation fuel and also became a big source of pollution. To prevent air pollution caused by exhaust gases the governments of many countries around the world have mandated the sulfur removal from transportation fuels since the past decade. For example, according to the USA specifications the mandatory sulfur content in diesel fuel had to be restricted up to 15 ppm (since July, 2006) [2, 3]. From 2009 the sulfur maximal content in these fuels has to be 10 ppm [3]. The Parliament of the European Union (EU) passed (January 30<sup>th</sup>, 2003) a resolution on diesel and gasoline quality (P5\_TA-PROV(2003)0029). According

to this regulation, sulfur content in “sulfur-free” fuels has to be no more than 10 ppm. In general, all developed countries and many of developing countries had an average value of the sulfur content in transportation fuels about 10 ppm from 2003–2010 [2–4].

In Ukraine, the requirements are not so strict, but the permissible content of sulfur compounds has been significantly reduced in recent years. According to standards of Ukraine it is allowed to produce DF with the sulfur content of 10 ppm and 500–2000 ppm (DSTU 8705:2017); 10, 50 and 350 ppm (DSTU 7688:2015); 10 and 50 ppm (DSTU 4840:2007).

The requirements for the environmental properties of jet fuels (JF) are less strict both in the world and in Ukraine. Therefore, the contribution of aviation to environmental pollution is becoming increasingly noticeable because the sulfur content of JF is 0.1–0.4 wt % (1000–4000 ppm); for special kinds of JF the sulfur content up to 1.0 wt % (10,000 ppm) is allowed. This is related to the problems of flight safety, power consumption of jet fuel and its stability during transportation and storage. This approach is also caused by the fact that the major emissions of JF combustion products occur at high altitudes [5–9].

Hydrotreating (HDS), which to date is the main technology for the fuels purification from sulfur compounds, has several disadvantages:

– along with sulfur compounds all other heteroatomic substances are removed and some part of the aromatics is hydrated, which automatically reduces the amount of substances capable of adsorbing on metal surfaces and worsens the lubricating properties of fuels;

– thiophene compounds and other condensed sulfur compounds that may be present in the feedstock are not hydrotreated due to the spatial difficulties occurred during their contact with the catalysts.

In addition, for economic reasons, hydrotreating cannot be organized for small scale production of DF or JF (for example, at plastics and rubber recycling facilities).

Alternative technologies of the straight-run fractions desulfurization have been investigated extensively in the past few decades, including extraction, selective adsorption, biodesulfurization, and oxidative desulfuri-

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zation (ODS). Among these new processes, ODS is considered to be one of the promising new methods and is currently receiving growing attention. The greatest advantage of ODS compared with the conventional HDS process is that it can be carried out in the liquid phase, under very mild conditions, and does not need expensive hydrogen [1, 10].

Existing industrial oxidation purification processes are aimed only at the extraction of sour sulfur or at the increase of JF thermo-oxidative stability after hydrotreating. Most ODS processes, which have been developed and improved over the last 20 years, are designed to reduce sulfur content to 10–15 ppm and even less in hydrotreated fuels. These processes, as well as HDS, are relatively complex and require the use of expensive catalysts and oxidizers [11–15].

We are studying the oxidation desulfurization of straight-run kerosene diesel fractions with the high sulfur content, as well as hydrogenates due to their air treatment without the use of expensive catalysts and strong oxidizers. Previously we determined the process main conditions (pressure, fractional composition of feedstocks, the method of sulfur oxidation products separation) and proved that oxidation is desirable to be carried out in the liquid phase in the presence of water [16–18]. We established the effect of temperature and water:feedstock ratio [19] and showed the possibility of obtaining commercial jet fuels [20] and components of diesel fuels with good lubricating properties [21].

It is well known that mixing the reaction medium can affect the delivery rate of the gaseous reagent, its dispersion, *etc.* On the other hand, the mechanical stirring dramatically increases the energy costs of the process and complicates the equipment design. Therefore, the next stage

of experiments and the aim of this work is the choice of optimal hydrodynamic parameters of the process.

## 2. Experimental

### 2.1. Experimental Methods and Analyses

The oxidation was carried out at an enlarged laboratory plant [22]. It consists of a reactor block; air compression and purification systems; gaseous reaction products cooling and recovery system; temperature, pressure, and consumption control and measuring instruments. The main apparatus is a bubble reactor by the volume of 0.7 l. The reactor provides the pressure up to 15 MPa at 623 K.

The vertical movement of the reaction mixture in the reactor is achieved by installing a cylindrical tube in the reactor vessel. When the mixer is in operation, the reaction mixture is circulated upwards through the inner space of the pipe and down into the space between the reactor vessel and the pipe.

In the case of feedstock oxidation with water, we separated the water phase and then divided and analyzed oxidate phase according to the scheme 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.

Feedstock and products were analyzed using standard methods. Lubricity was evaluated by the high-frequency reciprocating rig (HFRR) in accordance with ISO 12156-1:2006.

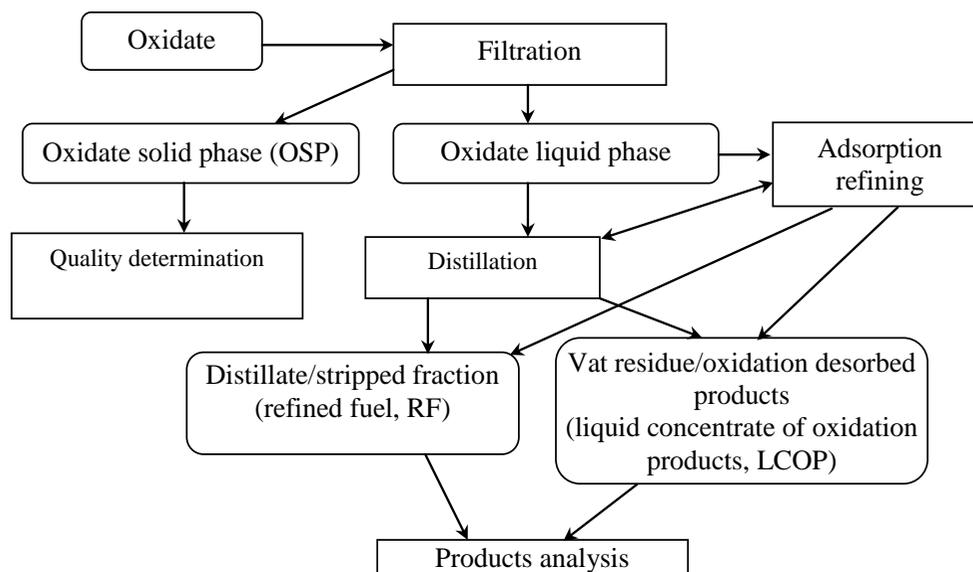


Fig. 1. Scheme of oxidate division and investigation

Table 1

**Characteristics of initial straight-run kerosene fraction**

Index	Straight-run kerosene fuel from OJSC "Galychyna" (SRKF)
Density at 293 K, kg/m <sup>3</sup>	788
Distillation characteristics	
Initial boiling point, K	411
10 % (v/v) distilled at temperature, K	434
50 % (v/v) distilled at temperature, K	456
90 % (v/v) distilled at temperature, K	493
98 % (v/v) distilled at temperature, K	565
Kinematic viscosity at 293 K, mm <sup>2</sup> /s	1.45
Low heat value, kJ/kg	43209
Smoke point, mm	13
Acidity, mg KOH/100 cm <sup>3</sup>	0.7
Iodine number, g I <sub>2</sub> per 100 g	0.41
Closed flash point, K	307
Wax appearance point, K	209
Thermooxidative stability under static mode at 423 K, mg per 100 cm <sup>3</sup>	33.3
Content of aromatic hydrocarbons, wt %	27
Content of actual gums, mg/100 cm <sup>3</sup>	9.0
Content of total sulfur, wt % (ppm)	0.151 (1510)
Content of sour sulfur, wt % (ppm)	0.0063 (63)
Content of H <sub>2</sub> S	absent
Copper strip corrosion test	stands the test
Ash content, wt %	0.0014
Content of mechanical impurities	absent
Content of water	absent
Reacting with water, points	1
Electric conductivity at 293 K, pS/m	12

Table 2

**Characteristics of initial diesel fraction**

Index	Straight-run diesel fuel from OJSC "Galychyna" (SRDF)	>593 K fraction from SRDF (>593 K fr)	Hydrofined diesel fuel from OJSC "Ukratnafta" (HDF)
Cetane number	45	–	–
Distillation characteristics			
50 % (V/V) recovered at temperature, K	548	–	554
90 % (V/V) recovered at temperature, K	619	–	631
Kinematic viscosity at 293 K, mm <sup>2</sup> /s	5.2	–	–
Pour point, K	257	–	-9
Flash point in closed crucible, K	351	–	–
Content of total sulfur, wt % (ppm)	0.250 (2500)	0.671 (6710)	0.055 (550)
Content of sour sulfur, wt % (ppm)	0.013 (130)	–	0.001 (10)
Content of H <sub>2</sub> S	absent	–	absent
Copper strip corrosion test	stands the test	–	stands the test
Concentration of actual gums, mg/100 cm <sup>3</sup>	28	49	12
Acidity, mg KOH/100 cm <sup>3</sup>	2.8	11.5	0.0
Iodine number, g iodine /100 g	3.74	–	–
Ash content, wt %	0.030	–	–
Coking ability of 10 vol % residue, %	0.23	–	0.01
Filtration coefficient	0.15	–	–
Content of mechanical impurities	absent	–	absent
Content of water	absent	–	absent
Density at 293 K, kg/m <sup>3</sup>	838	869	839

## 2.2. Initial Materials

The gas and diesel fractions were withdrawn at OJSC “Galychyna” (Drogobych, Ukraine) and OJSC “Ukratnafta” (Kremenchuk, Ukraine) and used for studying the hydrodynamic parameters.

The characteristics of the initial kerosene fraction are presented in Table 1.

The characteristics of the initial diesel fraction are presented in Table 2. To increase the concentration of sulfur compounds in the initial diesel, a residual fraction (>593 K) was distilled from it. This made it possible to compare the effect of hydrodynamic parameters on the desulfurization process of feedstock with a significantly different sulfur content.

## 2.3. Processing of Results

The sulfur removal degree (RDS, %) was calculated in accordance with the formula (1):

$$RDS = \frac{S_{t0} - S_t}{S_{t0}} \cdot 100. \quad (1)$$

where  $S_{t0}$  is the content of total sulfur in the initial feedstock, wt %;  $S_t$  is the content of total sulfur in refined fuel, wt %.

The yield of oxidate phase (OF, solid phase + liquid phase), oxidate solid phase (OSP), refined fuel (RF), and liquid concentrate of oxidation products (LCOP) were calculated in accordance with Fig. 1.

To characterize the hydrodynamic parameters of the oxidant motion and to calculate the basic dimensions of the reactor during its simulation (reproduction), linear rate of the oxidant (LRO) and time of contact between the feedstock and oxidant (hereinafter referred to as a dummy contact time) were calculated.

LRO was calculated as the ratio between volumetric flow rate of oxidant ( $\text{m}^3/\text{s}$ ) and the cross-sectional area of the reactor ( $\text{m}^2$ ). To simplify the model description LRO was determined under normal conditions. The dummy contact time ( $\tau_f$ , s), was calculated as the ratio of the feedstock layer height (m) to LRO (m/s).

To describe the air : feedstock ratio, time and contact area between them we used the term “volumetric oxidant flow rate” (VOFR,  $\text{min}^{-1}$ ), which is numerically equal to the ratio of oxidant consumption ( $\text{m}^3/\text{min}$ ) to the feedstock volume ( $\text{m}^3$ ).

A modified Reynolds criterion was calculated to characterize the stirring intensity of reaction medium:

$$Re_m = \frac{nd_x}{\nu_w} \quad (2)$$

where  $n$  is the stirrer speed, rpm;  $d_x = \frac{D_r \cdot d_s}{d_c^2}$  is a modified characteristic parameter of the reactor equal to

1.725;  $D_r$ ,  $d_s$  and  $d_c$  are the diameters of a reactor, stirrer and circulating tube, respectively, m;  $\nu_w$  is a viscosity of water at 293 K.

The reactor, stirrer and circulation pipe had the following geometric parameters:  $D_r/d_c = 2.27$ ;  $d_s/d_c = 0.76$ ; reactor height / circulation pipe height  $H/h = 2.47$ ; inclination of the stirrer blades is 35–45°; the number of holes for air supply is 225 per  $1 \text{ m}^2$ .

## 3. Results and Discussion

The process of oxidation desulfurization (OD) under study is a heterophase one. There are four phases in contact: air (gas), feedstock (liquid), water (liquid), solid oxidation products (solid phase). There is no information in the literature about the hydrodynamics of such a system in a vertical stirred reactor. The study of hydrodynamics is also complicated by changes in medium characteristics over time, high temperatures and pressures.

Gun and Levich [23, 24] found the residence time of the gaseous reagent in the liquid medium and the surface of the interfacial contact to be the main factors of the process that determine the rate of gas reaction components transition (in this case, oxygen) to liquid reagents in a two-phase reaction system liquid : gas. Direct determination of these parameters during the OD process for liquid fuels is practically impossible. In turn, they depend on a number of process factors, the main of which are gas flow velocity, liquid to gas ratio, reactor design, liquid characteristics (first of all, density and viscosity). So, in order to simplify the description of the hydrodynamics, the following parameters were used for all experiments carried out without stirring the reaction medium: the air : feedstock ratio (VOFR,  $\text{min}^{-1}$ ); linear rate of the oxidant (LRO, m/s); dummy contact time between the liquid and gaseous phases ( $\tau_f$ , s). The calculation procedures for these parameters are given in Subsection 2.3. To characterize the process under stirring, the reactor geometric parameters and the value of stirrer speed were used. Section 2.3 describes the relationship between the stirrer speed and the modified Reynolds criterion. The above indices and criteria are not true values characterizing the hydrodynamic regime of the system, the area and the contact time of feedstock with the oxidizer in the presence of water. However, knowing these parameters makes it easy to reproduce (simulate) the process in another reactor.

The studies were carried out at different values of VOFR and constant temperature, pressure and water feedstock ratios. Distillation was used to extract the LCOP (OLP obtained from SRDF was distilled to 553 K; the > 593 K fr – to 623 K). The results obtained are presented in Tables 3-4.

Table 3

Effect of LRO and  $\tau_f$  on the main products yield

Entry	LRO, m/s	$\tau_f$ , s	Yield relative to the feedstock, wt %			
			OF	OSP	RF	LCOP
VOFR = 1.080 min <sup>-1</sup> (feedstock is SRDF)						
1	0.0013	56	98.61	0.03	95.03	3.55
2	0.0026	56	98.65	0.08	94.89	3.68
3	0.0031	56	98.81	0.09	94.8	3.92
VOFR = 2.160 min <sup>-1</sup> (feedstock is SRDF)						
4	0.0026	28	97.99	0.08	94.12	3.79
VOFR = 2.160 min <sup>-1</sup> (feedstock is SRDF)						
5	0.0091	28	98.29	0.15	94.02	4.12
6	0.0104	28	98.20	0.20	93.79	4.21
7	0.0143	28	97.99	0.16	93.75	4.08
8	0.0208	28	98.01	0.22	93.68	4.11
VOFR = 1.650 min <sup>-1</sup> (feedstock is >593 K fr)						
9	0.0015	35	97.56	0.18	85.61	11.77
10	0.0030	35	97.34	0.29	85.40	11.65
11	0.0056	36	96.90	0.47	85.09	11.34
VOFR = 0.825 min <sup>-1</sup> (feedstock is >593 K fr)						
12	0.0015	69	97.66	0.25	85.42	11.99
VOFR = 1.212 min <sup>-1</sup> (feedstock is >593 K fr)						
13	0.0045	23	96.95	0.80	84.98	11.17

Table 4

Effect of LRO and  $\tau_f$  on the RF characteristics

Entry	LRO, m/s	$\tau_f$ , s	Index			
			Content of total sulfur, wt %	Concentration of actual gums, mg/100 cm <sup>3</sup>	Acidity, mg KOH/100 cm <sup>3</sup>	RDS, %
VOFR = 1.080 min <sup>-1</sup> (feedstock is SRDF)						
1	0.0013	56	0.086	0.8	17.6	43.05
2	0.0026	56	0.061	1.2	22.4	59.60
3	0.0031	56	0.059	2.0	27.61	60.93
VOFR = 2.160 min <sup>-1</sup> (feedstock is SRDF)						
4	0.0026	28	0.064	1.6	28.5	57.62
VOFR = 2.160 min <sup>-1</sup> (feedstock is SRDF)						
5	0.0091	28	0.062	2.1	31.8	58.94
6	0.0104	28	0.064	2.2	32.2	57.62
7	0.0143	28	0.060	2.2	31.9	60.26
8	0.0208	28	0.061	2.3	32.1	59.60
VOFR = 1.650 min <sup>-1</sup> (feedstock is >593 K fr)						
9	0.0015	35	0.422	25	16.9	37.11
10	0.0030	35	0.383	39	22.8	42.92
11	0.0056	36	0.381	43	24.8	43.22
VOFR = 0.825 min <sup>-1</sup> (feedstock is >593 K fr)						
12	0.0015	69	0.382	19	15.8	43.07
VOFR = 1.212 min <sup>-1</sup> (feedstock is >593 K fr)						
13	0.0045	23	0.490	59	25.7	26.97

The increase in LRO value from 0.0013–0.0015 to 0.0026–0.0030 m/s intensifies the oxidation of sulfur compounds and the hydrocarbon medium as well, resulting in the increase of RDS, OSP yield, acidity and concentra-

tion of actual gums in the final products (especially when using diesel fraction). Further increase in LRO value to 0.0091 m/s has minor or no effect on the oxidation intensity and sulfur removal and insignificantly increases

the intensity of the hydrocarbon medium oxidation. The increase in LRO value from 0.0091 to 0.0208 m/s has no effect on the main characteristics of the process (entries 4–8, Tables 3–4).

The increase in dummy contact time from 28–35 to 56–69 s slightly affects the amount of removed sulfur. This could be explained by the lack of oxygen (70–80 % was used) to accomplish the process. During SRDF desulfurization, the amount of oxygen exceeded the theoretically required value by 4–8 times to oxidize all sulfur compounds to sulfones. When the diesel fraction > 593 K was desulfurized, the amount of oxygen exceeded the theoretically required value by only 1.25 times at VOFR = 0.825 min<sup>-1</sup>, and by 2.5 times at VOFR = 1.650 min<sup>-1</sup>.

When the fraction >593 K fr was oxidized by oxygen-enriched air at VOFR = 0.825 min<sup>-1</sup> and O<sub>2</sub> content of 45 vol % (the amount of oxygen was 2.5 times greater than theoretically required for the oxidation of all sulfur compounds to sulfones) under other identical conditions (entry 11, Tables 3–4), the sulfur content in distillate (refined fuel) was 0.350 wt % (the sulfur removal degree 47.76 wt %). It means that with the same amount of oxygen, an increase in the dummy contact time from 36 to 69 s results in the increase of RDS value by less than 4.5 %.

Thus, we can assert that the minimum allowable values of LRO and  $\tau_f$  are 0.0015–0.0030 m/s and 28–35 s respectively. For the geometric dimensions of the reactor, given in Subsection 2.3, the determined parameters will provide the required modes of motion and the surface of

oxygen contact with the reaction medium, and therefore, sufficient RDS.

To study the dependence of the process characteristics on the stirring intensity we also used >593 K fr and SRDF. The effect of stirring intensity on the OD process was studied for 5 min (for comparison, SRDF was oxidized for 20 min). This period of time was chosen to exclude the possibility of oxidation due to the dissolved oxygen. The results obtained are presented in Tables 5–6.

In all cases, the presence and increase of the stirring intensity contributes to some decrease in the distillate yield, an increase in the LCOP amount and almost tenfold increase of the OSP yield (Table 5). At the process time of 5 minutes the distillate yield is higher and the amount of the solid phase is lower compared with those at 20 minutes, which is a consequence of the lower oxidation depth of the feedstock components. At the same time, the increase in stirring intensity has no noticeable effect on the total amount of oxidate. The possible reason is the increase in the oxidation rate of the fuel hydrocarbon part and formation of greater amount of both soluble (LCOP) and insoluble (OSP) products occurred due to the better contact of oxygen and the feedstock with increased stirring intensity, regardless of the process time. The effect of the stirring intensity on the oxidation of the feedstock hydrocarbon part is confirmed by the data presented in Table 6. With the increase in stirring intensity at 5 min and at 20 min the concentration of actual gum in the distillate increases by 2–10 times and distillate acidity by 2–3 times.

Table 5

Effect of stirring intensity on the main products yield

Re <sub>m</sub>	Yield relative to the feedstock, wt %			
	OF	OSP	RF	LCOP
5 min (feedstock is SRDF)				
0	99.57	0.02	96.04	3.51
8.59·10 <sup>8</sup>	99.28	0.15	95.59	3.54
3.44·10 <sup>9</sup>	99.04	0.24	95.18	3.62
6.87·10 <sup>9</sup>	98.86	0.29	94.86	3.71
20 min (feedstock is SRDF)				
0	97.51	0.09	93.76	3.66
8.59·10 <sup>8</sup>	97.32	0.64	93.02	3.66
3.44·10 <sup>9</sup>	97.24	0.83	92.44	3.97
6.87·10 <sup>9</sup>	96.74	0.89	91.85	4.00
5 min (feedstock is >593 K fr)				
0	98.96	0	87.91	11.05
8.59·10 <sup>8</sup>	98.73	0.32	87.02	11.39
3.44·10 <sup>9</sup>	98.86	0.87	86.58	11.41

Table 6

## Effect of stirring intensity on the RF characteristics

Re <sub>m</sub>	Index			
	Content of total sulfur, wt %	Concentration of actual gums, mg/100 cm <sup>3</sup>	Acidity, mg KOH/100 cm <sup>3</sup>	RDS, %
5 min (feedstock is SRDF)				
0	0.106	1.0	6.7	29.80
8.59·10 <sup>8</sup>	0.104	1.6	8.4	31.13
3.44·10 <sup>9</sup>	0.101	2.5	10.5	33.11
6.87·10 <sup>9</sup>	0.099	3.5	12.3	34.44
20 min (feedstock is SRDF)				
0	0.052	1.70	24.3	65.56
8.59·10 <sup>8</sup>	0.051	4.00	37.4	66.23
3.44·10 <sup>9</sup>	0.052	5.80	39.5	65.56
6.87·10 <sup>9</sup>	0.060	11	40.2	60.26
5 min (feedstock is >593 K fr)				
0	0.376	39	22.8	43.96
8.59·10 <sup>8</sup>	0.354	54	29.7	47.24
3.44·10 <sup>9</sup>	0.339	71	63.4	49.48

On the other hand, the oxidation depth of the sulfur compounds is slightly affected by the stirring intensity: RDS value increases by 1.10-1.15 times maximum. At the process time of 20 min with the increase in Re<sub>m</sub> value this index even tends to decrease. This is due to the fact that the intensification of the hydrocarbons oxidation reduces the selectivity of sulfur compounds removal. In addition, the sulfur compounds remaining in the RF are distributed in a smaller volume as the distillate yield decreases. Instead, at the process time of 5 min, the value of RDS tends to increase slightly, because for short process time the oxidation rate of sulfur compounds may depend on the contact phase surface, *i.e.*, on the stirring intensity of the reaction medium.

Thus, for LRO values less than 0.0015–0.0030 m/s and process time greater than 5 min, the oxidation rate of sulfur compounds is practically independent of the stirring intensity and, consequently, the contact area air–feedstock (the contact area of the reacting phases). It means that the process proceeds in the kinetic region. In this case,  $\tau_f$  should exceed 28–35 s. Oxidation of the fuel hydrocarbon part occurs in the diffusion region, so the stirring intensifies the hydrocarbons oxidation, and negatively

affects the process characteristics. Therefore, when carrying out the oxidation process without stirring the reaction medium selectivity will increase.

As can be seen from the data obtained, it is possible to reduce the sulfur content in SRDF (meets the requirements of both European and Ukrainian standards). It is impossible for the fraction >593 K fr. The reasons are the high sulfur content in the feedstock, other non-optimal process factors, and application of distillation for the separation of liquid products instead of its combination with adsorption. On the other hand, with stricter requirements for the sulfur content in diesel fuel (0.05–0.035 wt % or 500–350 ppm) the resulting products will not be able to be obtained by the described method. In this case, it is suggested to use an oxidation plant for the aftertreatment of the hydrotreated diesel fractions.

So the next step was to study the oxidation desulfurization of hydrogenate under optimum hydrodynamic parameters. The hydrogenate from the wide diesel fraction was withdrawn at OJSC Ukratnafta (Kremenchuk, Ukraine) and contained 0.055 wt % of sulfur. Distillation or adsorption was used to separate RF and LCOP. The experimental results are presented in Tables 7-8.

Table 7

## Main products yield

Entry	Feedstock	Yield relative to the feedstock, wt %			
		OF	OSP	RF	LCOP
1	HDF	98.42	0.43	95.24 <sup>1</sup>	3.18
2	HDF	98.42	0.43	95.93 <sup>2</sup>	2.49

Notes: <sup>1</sup> distillation was used to separate RF and LCOP; <sup>2</sup> adsorption was used to separate RF and LCOP/

Table 8

**RF characteristics**

Entry	Product	Index			
		Content of total sulfur, wt %	Concentration of actual gums, mg/100 cm <sup>3</sup>	Acidity, mg KOH/100 cm <sup>3</sup>	RDS, %
1	RF <sup>1</sup>	0.008	11	2.1 <sup>3</sup>	85.45
2	RF <sup>2</sup>	0.004	8.3	3.0	92.73

Notes: <sup>1</sup> distillation was used to separate RF and LCOP; <sup>2</sup> adsorption was used to separate RF and LCOP; <sup>3</sup> RF was alkali treated, the yield of the products after treatment was 0.71 wt % relative to distillate, the sulfur content of the non-alkaline distillate was 0.008 wt %.

Table 9

**Characteristics 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 from OJSC “Naftokhimik Prykarpattya”. Content of total sulfur was 0.671 wt % (6710 ppm)
3	438–623 K desulfurized fraction from OJSC “Naftokhimik Prykarpattya”. Content of total sulfur was 0.138 wt % (1380 ppm)

Table 10

**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	386	0.204	55

As can be seen from the obtained results, by means of the developed process it is possible to remove at least 80 % of sulfur remaining after hydrotreating, even when only distillation is used for the separation.

Since one of the main drawbacks of the hydrotreating is the reduction of fuels lubricating properties, an effect of the developed process on this index was studied. The characteristics of the analyzed samples are presented in Table 9, and tribological test results – in Table 10. To obtain the sample No.3 (Table 9) the OD was used under conditions close to the optimum ones using the determined hydrodynamic parameters. A combination of adsorption and distillation was used to separate RF and LCOP. To reduce the acidity of the refined fuel the alkali treatment was applied after the process; the alkali amount was 100 mg KOH per 100 cm<sup>3</sup> of the product, 2 % (wt/wt) aqueous solution.

The results of tribological tests performed for the samples are given in Table 10.

The results of tribological tests confirm that the fraction 438–623 K after oxidative desulfurization and “mild” alkali treatment (the sample No.3) has a higher lubricity compared with the hydrotreated 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.3 is less than the limit value for the diesel fuels (460 μm) in accordance with ISO 12156-2:2077. The improvement in the lubricity of the sample is probably caused by the oxygen-containing compounds remaining in it.

**4. Conclusions**

In order the sulfur compounds oxidation reactions proceed in the kinetic region without mechanical stirring of the reaction medium, it is sufficient to provide the LRO higher than 0.0015–0.0026 m/s. The minimum allowable dummy contact time between the oxidizer and the feedstock should be 28–35 s.

Due to the developed non-catalytic oxidative desulfurization process it is possible to use the straight-run diesel fuel fraction with the sulfur content of 6710 ppm as the raw material to obtain the diesel fuel with the sulfur content of 1380 ppm that meets the standard of Ukraine (DSTU 8705:2017).

The hydrotreated diesel fuel with the sulfur content of 550 ppm may be desulfurized by the developed method to obtain the diesel fuel with 40 ppm of sulfur that meets

the standards of Ukraine (DSTU 4840:2007 and DSTU 7688:2015).

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

## References

- [1] Ismagilov Z., Yashnik S., Kerzhentsev M. *et al.*: *Cat. Rev. Sci. Eng.*, 2011, **53**, 199. <https://doi.org/10.1080/01614940.2011.596426>
- [2] Regulatory Impact Analysis: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements. United States Environmental Protection Agency, Air and Radiation, EPA420-R-00-026, December 2000.
- [3] United States Environmental Protection Agency, February, 2001. <https://www.epa.gov>
- [4] Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control). <http://data.europa.eu/eli/dir/2010/75/oj>
- [5] Link D., Baltrus J., Rothenberger K. *et al.*: *Energ. Fuel.*, 2003, **17**, 1292. <https://doi.org/10.1021/ef0300747>
- [6] World jet fuel specifications. 2008. <http://large.stanford.edu/courses/2017/ph240/chhoal/docs/exxon-2008.pdf>
- [7] Boichenko S., Vovk O., Iakovlieva, A.: *Chem. Chem. Technol.*, 2013, **7**, 305. <https://doi.org/10.23939/chcht07.03.305>
- [8] Yakovleva A., Boichenko S., Lejda K. *et al.*: *Chem. Technolog. Fuels Oils*, 2017, **53**, 1. <https://doi.org/10.1007/s10553-017-0774-x>
- [9] Iakovlieva A., Boichenko S., Gay A.: *Chem. Chem. Technol.*, 2014, **8**, 107. <https://doi.org/10.23939/chcht08.01.107>
- [10] Banisharif F., Dehghani M., Capel-Sánchez M., Campos-Martin J.: *Ind. Eng. Chem. Res.*, 2017, **56**, 3839. <https://doi.org/10.1021/acs.iecr.7b00089>
- [11] Babich I., Moulijn J.: *Fuel*, 2003, **82**, 607. [https://doi.org/10.1016/S0016-2361\(02\)00324-1](https://doi.org/10.1016/S0016-2361(02)00324-1)
- [12] Wang B., Dai B., Kang L., Zhu M.: *Fuel*, 2020, **265**, 117029.
- [13] Liu W., Li T., Yu G. *et al.*: *Fuel*, 2020, **265**, 116967. <https://doi.org/10.1016/j.fuel.2019.116967>
- [14] Mirante F., Alves A. *et al.*: *Fuel*, 2020, **259**, 116213. <https://doi.org/10.1016/j.fuel.2019.116213>
- [15] Julião D., Mirante F. *et al.*: *Fuel*, 2019, **241**, 616. <https://doi.org/10.1016/j.fuel.2018.11.095>
- [16] Pysh'yev S., Bratychak M., Lazorko O., Shyshchak O.: *Pol. J. Environ. Stud.*, 2005, **14**, 123.
- [17] Lazorko O., Pysh'yev S., Bratychak M.: *Chem. Chem. Technol.*, 2008, **2**, 309.
- [18] Pysh'yev S., Lazorko O., Bratychak M.: *Chem. Chem. Technol.*, 2009, **3**, 77.
- [19] Pysh'yev S., Lazorko O., Bratychak M.: *Chem. Chem. Technol.*, 2009, **3**, 163.
- [20] Paniv P., Pysh'yev S., Haivanovych V., Lazorko O.: *Khimia i Technologia Topлива i Masel*, 2006, **3**, 7.
- [21] Pysh'yev S.: *Chem. Chem. Technol.*, 2012, **6**, 229. <https://doi.org/10.23939/chcht06.02.229>
- [22] Antonyshyn V., Humenetsky V.: *Visnyk Nats. Univ. Lvivska Polytechnika*, 1974, **82**, 94.
- [23] Gun R.: *Neftianye Bitumy. Lhimia, Moskva* 1973.
- [24] Levych V.: *Physico-Khimicheskaya Hydrodynamika. Izd-vo AN SSSR, Moskva* 1952.

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## ДОСЛІДЖЕННЯ ГІДРОДИНАМІЧНИХ ПАРАМЕТРІВ ОКСИДАЦІЙНОГО ЗНЕСІРЧЕННЯ ПРЯМОГОННИХ НАФТОВИХ ФРАКЦІЙ З ВИСОКИМ ВМІСТОМ СІРКИ

**Анотація.** Встановлено необхідні гідродинамічні параметри процесу знесірчення прямогонних газових (SRKF) і дизельних фракцій (SRDF) внаслідок окиснення сірчистих органічних сполук з наступним вилученням продуктів окиснення. Гідродинамічні параметри, які характеризуються лінійною швидкістю руху оксиданту (повітря) та фіктивним часом контакту між оксидантом і сировиною, дають можливість здійснювати процес без перемішування. Запропонована технологія може використовуватися для очищення нафтових палив малотонажних виробництв, коли економічно невигідно або технологічно неможливо використовувати гідроочищення. Показано, що даний процес можна застосовувати для доочищення гідрогенізаторів та часткового знесірчення прямогонних фракцій з метою виробництва компонентів палив з покращеними мастильними властивостями.

**Ключові слова:** сірка, реактивне паливо, дизельне паливо, оксидаційне знесірчення, гідродинамічні параметри, мастильна здатність.