Serhiy PYSHYEV^{1*}, Michael BRATYCHAK¹, Vasyi HAYVANOVYCH¹, Pavlo PANIV¹ and Witold WACŁAWEK²

WATER EFFECT ON OXIDATIVE DESULPHURIZATION PROCESS OF STRAIGHT-RUN KEROSENE FRACTION

WPŁYW WODY NA UTLENIAJĄCY PROCES ODSIARCZANIA FRAKCJI NAFTY

Abstract: Sulphur dioxide obtained during fuels burning in combustion engines is one of the main pollutants. In diesel oils and gasolines the sulphur content must be 5-10 ppm and in jet fuels - 300-3000 ppm. However the production of hydrofined jet fuel is problematic. The reason is deterioration of fuel stability and antioxygenic properties. The oxidative desulphurization of straight-run kerosene was investigated. This method combines oxidation by atmospheric oxygen of sulphur compounds under increased temperature and pressure in the presence of water in the reaction medium, and removal of oxidized sulphur compounds from the oxidation-treated fuel via rectification. It was showed that water partially extracts from the hydrocarbon medium acidic compounds, formed in the beginning stage of oxidation, dissociation of which leads to the formation in water acidic medium. As a result, a pathway of the hydroperoxides decomposition partially changes from the formation of carbonic acids and oxyacids to the formation of alcohols, phenols and alkylphenols, which displayed an inhibitory effect in hydrocarbon oxidation. It was assumed that an inhibitory effect of water, in addition to the creation reverse micelles with peroxides and complexes with free radicals, caused by oxidation products created in the beginning stage of oxidation. The effect of water/kerosene ratio on the oxidative desulphurization of straight-run kerosene fraction has been examined. It was found that water improves process selectivity with insignificant influence on the degree of sulphur recovery. The optimum value of water/kerosene ratio for the fuel containing 0.15% mass of sulphuric compounds has been determined.

Keywords: jet fuel, oxidative desulphurization, sulphur, sulphoxides, sulphones

The process of deep desulphurization of liquid hydrocarbon fuels has increasingly received attention among world scientists during the last few decades. The reason is acceptance of restrictions in pollutant-contained emissions for car exhaust results in a change in fuel quality specifications [1-8]. The most severe restrictions concern sulphur content in automotive fuels. From 2009 the sulphur maximal content in gasoline and in diesel fuels was up to 10 ppm [4, 7]. Many countries of Eastern Europe [9-11], Asia [12-15], South America [16-19], South Africa [20] and Australia [21, 22] have started to produce and consume “clean” automotive fuels along with the developed countries of Western Europe and North America.

¹ Lviv Polytecnic National University, Bandery 12, 79013 Lviv, Ukraine

² Opole University, ul. Oleska 48, 45-591 Opole, Poland, email: wacławek@uni.opole.pl

*Corresponding author: gajva@polynet.lviv.ua

There is considerable discussion about changing *jet fuels* (JF) used in aviation to fuels with ultra-low sulphur content. On the one side, it is obvious that aviation considerably pollutes the environment because the production of JF is sizable and will increase in the nearest decade from 8 to 10% in the total amount of all fuels [23]. Moreover, today the sulphur content in JF is 300-3000 ppm [24]. Investigations in the USA show that aviation is a large source for air pollution by sulphur oxides and solid products of incomplete combustion (soot), especially around airports [25, 26]. It is well-known, also, that at higher temperatures solid deposits are formed from sulphuric compounds in the feed system of jet engines [27]. Consequently, the usage of JF with low-sulphur content would help to improve the existing ecological situation around airports [28], as well as improve the thermal-oxidative stability of fuels themselves.

On the other side, usage of low-sulphur JF creates some usage problems: flight safety, low JF energy intensity, and fuel stability during transportation and storage [25, 26]. The problem with ultra-low sulphur content JF resulting from deep catalytic *hydro-desulphurization* (HDS) of kerosene oil distillates is their very low lubricity. As a result of the HDS process, almost all surface-active compounds which provide reliable lubricity are hydrogenated. Also such fuels have low aromatics content, which considerably decreases the environmental pollution with solid products of incomplete combustion and allows the creation called “invisible airplanes” (planes without trails). At the same time the possibility of fuel bleeding from elastomeric seals in fuel lines grows sharply. The seals are normally in contact with aromatic hydrocarbons present in the fuel, which causes them to swell. All these facts, of course, degrade flight safety. Moreover, removal of aromatic and sulphuric compounds from JF decreases fuel energy intensity which results in decreased flight distances. Modern JF (especially for civil aviation) has no additives, therefore deep removal of sulphur-, nitrogen- and oxygen-containing compounds, which are natural antioxidants, worsens fuel stability during transportation and storage [29].

It is obvious that the requirements of the ecological properties of JF soon will become stronger [24]. Hence different laboratories have tried to develop new types of JF with ultra-low sulphur content which meet the demands concerning flight safety and stability. In our mind, the *oxidative desulphurization* (ODS) method is one of the alternative methods of obtaining low-sulphuric fuels, which guarantees flight safety. There are many different methods of ODS of oil distillates, which allow the production of fuels with sulphur content of a few ppm [30].

All ODS methods have two stages: oxidation of sulphuric-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. ODS has a number of advantages over HDS. First of all, it is possible to fully recover sulphuric compounds, including those, which cannot be extracted by HDS (alkyl-substituted benzo- and dibenzothiophenes), and it is also possible to perform ODS processes in a less severe environment in the absence of expensive hydrogen [30].

There are few problems with the currently used processes of ODS development. One of them is not enough selectivity of the used oxidants and, as result, partial oxidation of the hydrocarbon takes place which causes a decrease in the quality and yield of the desulphurized fuels, as well as by-products formation. For improving the process selectivity of ODS (minimizing the degree of the hydrocarbon oxidation and by-product yield) many authors propose to use different oxidants and catalysts [30] which are expensive and in

many cases not available. As result it makes the processes of ODS more costly and more complicated.

We have developed the technological principles of the process of ODS for straight-run kerosene fractions. The essence of the proposed process is non-catalytic oxidation by air of sulphuric compounds present in kerosene fractions to the corresponding sulphoxides and sulphones with their further removal by such known methods as rectification, extraction or adsorption. The aim of the investigation was to determine the possible principles of kerosene non-catalytic oxidative desulphurization and minimize an influence of the undesirable hydrocarbon oxidation on the ODS process. In our opinion, this issue can be resolved via a combination of the two ways: first, directing the hydrocarbon oxidation reactions toward the formation of oxidation products having non-acid properties (alcohols, ketenes, esters, lactones and epoxides); second, to propose a practical use of the obtained by-products.

We propose to perform the ODS process of kerosene using atmospheric oxygen without a catalyst under increased pressure and temperatures in the presence of water. The reason why we propose to perform the ODS process in the presence of water is its ability to display an inhibitory effect during the liquid-phase hydrocarbon oxidation, which has been reported by many authors [31-39].

On the other hand, it was observed in our previous study [40] that during the oxidation of oil residuals the presence of a definite amount of water, which selectively dissolves atmospheric oxygen and forms hydrophilic emulsions with a large contact area "water/petroleum product", is able to increase a rate of the oxidation process. Also, it has to be noted that the presence of water in the reactor increases process safety.

Because of the opposing findings regarding effect of water's in hydrocarbons oxidation reactions, detailed above, it is important to know how large influence water has over non-catalytic oxidation of kerosene. The present paper is dedicated to the experimental study of the influence of water over non-catalytic ODS of kerosene.

Experimental

A sample of kerosene (the main characteristics of which are represented in Table 1) was received from JSC "NPK-Galychyna" and was obtained via the processing of an oil mixture from West-Siberia and Ukrainian.

Oxidation of the initial kerosene was carried out in an enlarged laboratory unit. The unit's main apparatus was a reactor of the bubble type with mechanical stirring. Oxidation was carried out under increased temperatures (to meet a satisfactory level of the oxidation of sulphur compounds without a catalyst) and pressure (3 MPa), which allowed the holding reagents to remain in the liquid state. The temperature and duration of the process, as well as the oxidant flow rate were held constant. Previous investigations [41] established the temperature (180-190°C) at which the process will proceed in the kinetic area without stirring. The amount of water used was characterized as water/kerosene volumetric ratio.

Oxidation-treated fuel was segregated from the water phase, filtered for the removal of solid products and then rectification (as a simplest method) was used to remove the oxidized sulphur compounds (sulphoxides and sulphones) from distillates. Desulphurized kerosene (so-called distillate) and vat residue, which is the concentrate of liquid oxidation products such as sulphones and sulphoxides, was obtained in the process.

Table 1

Main characteristics of raw material

Characteristics	Kerosene	Test method
Boiling characteristics [°C]:		GOST 2177-82
Initial boiling point	138	
10%	161	
50%	183	
90%	220	
98%	292	
Sulphur content [% mass]:		
total	0.15	GOST 19121-73
mercaptan	0.0063	GOST 17323-71
Concentration of actual gums [mg/100 cm ³]	9.0	GOST 8489-85
Thermal-oxidative stability (TOS) under static conditions at 150°C, mg/100 cm ³	33.3	GOST 9144-79
Acidity, mg KOH/100 cm ³	0.7	GOST 5985-79

The following characteristics were determined for the distillate by standard methods: the content of total and mercaptan sulphurs, the content of actual gums, the acidity, and the *thermal-oxidative stability* (TOS) under static conditions. The presence of oxygen-containing groups in the distillate was determined by IR-spectroscopy. Only one value was determined for the vat residue and the solid phase - the total sulphur content.

Gaseous products were analyzed by gas chromatography using a model LHM chromatograph that was equipped with a detector to measure the heat conductivity. Since gaseous products included polar and non-polar components, the separation of gases was performed on two chromatographic columns. In the first column, which was filled with a non-polar sorbent (Polisorb-1), gas was separated into the following components: $N_2 + O_2 + CH_4 + CO$; CO_2 ; C_2H_2 ; C_2H_6 ; $C_3H_8 + C_3H_6$; and SO_2 . In the second column, which was filled with a zeolite CaX sorbent, components that were not separated in first column were separated in the following order: N_2 , O_2 , CH_4 , CO .

The conditions of chromatography were as follows: the transporting gas - H_2 ; the temperature of the first column - 343 K; the temperature of the second column - 293 K; the temperature of detector - 373 K; the detector current - 160 mA; and the H_2 usage - 40 cm³/min.

It should be noted that the gaseous products consisted mainly of oxygen and nitrogen. Therefore, the oxygen conversion degree (ratio of the difference between the oxygen concentrations in the air and gaseous products to its concentration in the air) was calculated on the basis of the data of chromatographic analysis.

The IR-spectra of the initial kerosene and the obtained distillates were obtained using the IR-spectrometry SPECORD M80. For the analysis, the special KBr cells were used with absorbing layer thicknesses 0.1 and 1.0 mm.

Results and discussion

The results obtained show that oxidative refinement without water is accompanied by the formation of a considerable amount of insoluble solid phase and a relatively low product yield (see Table 2). The introduction of even a small amount of water into the reaction medium considerably increases the product yield in general and the distillate yield in

particular. Moreover, the presence of water sharply decreases the amount of formed solid phase. All these facts can only be explained by inhibiting influence of water on the oxidation of the hydrocarbons.

The obtained results correspond very well with previously mentioned publications by many authors about the inhibition by water the hydrocarbons oxidation reactions [31-39]. It is known that in keeping with the theory of liquid-phase oxidation the oxidation of hydrocarbons with molecular oxygen occurs by the chain free-radical mechanism and proceeds via a stage of hydroperoxides or peroxides formation, which should participate in a chain branching processes [31-34]. The rate of the chain reaction can be decreased either by three ways:

- reducing the initiation rate (reducing the peroxides formation);
- diminishing the chain branching rate (diminishing the peroxides decomposition rate into free radicals);
- decreasing the chain propagation rate (deactivation of the free radicals or reducing their reactivity).

A number of authors showed that, in the presence of natural surfactants (sulphur, oxygen and nitrogen compounds) in the hydrocarbons medium, hydroperoxides, as amphiphilic compounds possessing surface activity, create H-bonds with the water and, as result of that, absorb on the hydrocarbons/water emulsion boundary with the formation of reverse micelles. Peroxides involved into micelles become more stable and the rate of their decomposition with free radicals formation decreases and as result of that the total reaction rate decreases as well [36-39]. Csanyi et al reported that in the presence of high water concentrations an overall rate of oxidation decreases, because of the competing formation of the cyclic hydro-peroxide dimers which are kinetically less active [42].

Table 2

The effect of water/ kerosene ratio on the product yield

Water/kerosene ratio X : Y	Yield [% mass] on raw materials			
	by oxidation- treated fuel	distillate	solid products	vat residue
0 : 1	96.64	92.77	0.42	3.45
1 : 10	98.27	94.24	0.10	3.93
1 : 5	98.96	94.84	0.10	4.02
1 : 3	99.03	94.94	0.10	3.99
1 : 2	98.13	94.23	0.09	3.81
1 : 1.5	97.51	93.76	0.09	3.66
1 : 1	96.87	93.29	0.02	3.56
1.5 : 1	96.27	92.75	0.02	3.50

In analogy to Denisov, who showed that alcohols can form H-bonds with the peroxy radicals and decrease their reactivity [43], Crytko and Bub showed that the influence of water on the oxidation of toluene by atmospheric oxygen can be explained by the formation of free radical/water complexes ($\text{PhCH}_2\cdots\text{H}_2\text{O}$), which must be treated as an additional component and leads to the alteration of their kinetic behaviour [34].

In other words, it has been reported by many authors that water displays an inhibitory effect on the hydrocarbon liquid phase oxidation process via creation of the reverse micelles with peroxides on the chain branching stage (decomposition of peroxides into free radicals)

and complexes creation with free radicals on the chain propagation stage (chain termination by deactivation of free radicals).

In addition to that, in our opinion, there is one more reason for the hydrocarbons oxidation degree decreasing under influence of water. In the presence of water intermediate products of oxidation (low-molecular keto-acids, oxy-acids, as well as sulpho-acids) and the products of their condensation obtained at the beginning of the oxidative refinement (sources of solid phase formation) are partially removed from the hydrocarbon medium into the water phase. It leads to decrease of solid phase formation (see Table 2) and increasing acidity of the water phase. This fact is confirmed by experimental results: the water phase obtained at a water/kerosene ratio equal to 1:5 has pronounced acidity 330 mg KOH/100 cm³, which corresponds to a pH value equal to 2 (pH of the initial distilled water was equal to 6).

It is known that depending on the pH of the reaction medium decomposition pathway of hydroperoxide can be different and oxidation products will be different as well [44, 45]. Study of the oxidation of individual hydrocarbons [44-46] showed that in this case decomposition of the primary hydroperoxides basically leads to the acid formation; secondary - to alcohols, ketenes, acids and hydrocarbons formation; tertiary - alcohols (phenols) and acetone. It was observed in [46] that in the neutral medium under mild temperatures the oxidation process occurs by the chain free-radical mechanism with mostly primary peroxides formation. In the acidic medium the oxidation reaction can occur by ion mechanism with regrouping intermediate products and formation of the tertiary peroxides, decomposition of which leads to the alcohols and phenols formation. Studies of the oxidation mechanism of isopropylbenzene (see scheme below) showed that in the acidic medium decomposition of the tertiary peroxides leads to the phenol and acetone formation [47].

It was assumed that during oxidation without water, the formation of primary and secondary peroxides mostly takes place. Decomposition of primary and secondary peroxides leads to the acids and olefins formation, which are sources of undesirable condensation products (solid phase, gums).

It should be noted that according to [47] only strong acids show an influence on the reaction pathway. In our case we do not use any strong (inorganic) acids and it is known that in hydrocarbon medium organic acids practically do not dissociate. In the alcohol, acids or aldehydes medium organic acids dissociate very little, but in the aqueous medium a dissociation degree increases. For example, for benzoic acid a constant of dissociation (pKa) is equal 4.18; in the alcohol solution of cyclohexane - 10.24; in the metacresol - 10.29; in the acetophenone - 9.76 [48]. It also should be noted that pKa of the sulphur-contented organic acids (products of the sulphur compounds oxidation) in water solution are very close to the pKa of the inorganic acids. For example, for phenolsulpho (HOC₆H₄SO₃H) acid pKa = 0.39, for nitric (HNO₃) acid pKa = -1.64 [48].

Thus, an addition of water into the reaction medium leads to the dissociation ("increases" the force) of organic acids which were created at the beginning stage of

oxidation. As result of that, some oxidation reactions can proceed according to the scheme showed above with phenols and tertiary alcohols formation, which displayed an inhibitory effect in hydrocarbon oxidation even in small (0.0005-0.1%) amounts [49, 50].

In order to confirm the formation of compounds with phenol or tertiary-alcohol groups in the presence of water, we analyzed IR-spectra of the distillates in the absorption area of $4000\text{--}3200\text{ cm}^{-1}$ corresponding to these groups. The sample amount was increased 10 times. The IR-spectrum of the distillate obtained in the presence of water confirms the presence of phenol, its derivatives or tertiary-alcohols: 4030, 3910, 3860, 3720, 3660 and about 3550 cm^{-1} (see Fig. 1). The relative peak heights of distillates obtained without water are considerably less.

Fig. 1. **IR-spectra** of distillates in the absorption area $4000\text{--}3200\text{ cm}^{-1}$: 1 - distillates obtained in the presence of water with water/kerosene ratio = 1:10; 2 - distillate obtained in a non-aqueous medium

Decreasing of the velocity of hydrocarbon oxidation reactions to the acidic compounds in the presence of water confirms by decrease distillates acidity and content diminution of the intermediate oxidation products dissolved in the oxidation-treated fuel. The distillates obtained from the oxidation of kerosene in a non-aqueous medium have the highest acidity. In the presence of water, the acidity of the distillates decreases because the oxidations of hydrocarbons are inhibited by the created phenols. Moreover, a decreasing of the distillates acidity can be resulted by partial dissolution of the already formed acid components in the water phase. The increase in the water/kerosene ratio decreases the distillates acidity (Table 3).

As seen in Table 3, the increase in the water/kerosene ratio decreases the content of actual gums in the distillate and improves its TOS. Since both values characterize the

degree of oxidation of the hydrocarbon medium, in other words the presence of intermediate oxidation products which are sources of soluble gums and insoluble solid powdery deposits, improvement in the above-mentioned values directly reflects a reduction in the amount of partial oxidation products in the distillate.

Table 3

The dependence of obtained product quality on water/ kerosene ratio

Water/ kerosene ratio X:Y	Total sulphur content [% mass]		Content in the distillate			Distillate's TOS [mg/100 cm ³]	Distillate's Acidity [mg KOH/ 100 cm ³]
	solid product	vat residue	total sulphur [% mass]	mercaptan sulphur [% mass]	actual gums [mg/100 cm ³]		
0 : 1	4.50	0.82	0.059	0.0012	3.8	19.6	75.2
1 : 10	3.28	0.79	0.058	0.0017	2.0	13.4	33.8
1 : 5	2.96	0.80	0.057	0.0017	2.0	11.5	29.5
1 : 3	3.18	0.81	0.055	0.0017	1.9	11.4	27.8
1 : 2	3.45	0.83	0.053	0.0016	1.8	11.3	26.1
1 : 1.5	3.70	0.88	0.052	0.0015	1.7	11.3	24.3
1 : 1	3.84	0.97	0.051	0.0015	1.5	11.2	22.4
1.5 : 1	3.98	0.98	0.050	0.0015	1.0	11.0	20.9

Also, it should be noted that TOS of distillates obtained by oxidative refinement without water decreased considerably for a few days and the content of actual gums increased 2-3 times. This fact can be explained by condensation processes caused by the slow gradual decomposition of hydroperoxides, which are still present in the distillate after oxidative refinement. At the same time, such phenomena was absent in distillates obtained in the presence of water because in the presence of water the decomposition time of peroxides is commensurate with the oxidation time.

Decreasing of the intermediate products content (acidic compounds in first) is in good agreement with the result of IR-spectroscopy. An IR-spectra of the initial kerosene, distillate obtained after oxidation without water and distillate obtained at oxidation with water/kerosene ratio = 1:10 are presented in Figure 2.

We can see from Figure 2 that in all three cases IR-spectra confirm the presence of the following bonds typical for the JF: C-H - arenes (primary and secondary), C-H - aliphatic, C=C - arenes, =CH₂, =C=CH, (CH₃)₂=C-, -CH₃, etc. However, the IR-spectrum of the distillate obtained following oxidation without water has a peak at 1725 cm⁻¹, which is typical for carbonyl or carboxyl groups. The presence of these groups confirms the intensive oxidation of the hydrocarbon medium of the kerosene with acid compound formation. The peak height in the same absorption area of the IR-spectrum obtained for the oxidation of kerosene in the presence of water with a water/kerosene ratio = 1:10 is 2-2.5 times less than in the previous case. This fact indicates a sharp decrease in acid, aldehyde and ketene compounds in the distillate.

All these experimentally obtained results give us an opportunity to state that water displays an inhibitory effect not just because of the H-bonds formation with peroxides and free radicals, as was observed by many authors, but also because of the water's ability to change a pathway of the hydro-peroxides decomposition from the acidic compounds (acids and oxy-acids) formation to the formation of the non-acidic (alcohols, phenols and alkyl-phenols) compounds, which have inhibitory properties. It should be noted that, this

conclusion has to be confirmed by additional experimental study with direct and more precise analysis of the content of intermediate products (oxygen-contained: hydroxyl, carboxyl, carbonyl, and ether groups, peroxides and free radicals) in the distillates.

Fig. 2. **IR-spectra** of the initial kerosene and the samples of the obtained distillates: 1 - initial kerosene; 2 - distillate obtained in a non-aqueous medium; 3 - distillate obtained in the presence of water with water/kerosene ratio = 1:10

Obviously, the inhibiting ability of water does not affect the oxidation and condensation reactions of sulphuric compounds because by their nature they have a tendency toward the completion of the mentioned reactions. Hence, sulphuric compounds react with atmospheric oxygen faster than a sufficient amount of phenol created for inhibition.

Moreover, if non-viscous raw material is used and the process takes place without forced mixing, water does not practically affect the rate of oxygen transfer through the phase interface, as it was observed during the oxidation of the high viscosity oil products [40]. Also, the amount of oxygen dissolved in the kerosene under pressure in the reactor is enough for oxidation of all sulphuric compounds to sulphones.

Since an increase in the amount of water breaks the oxidation process of the hydrocarbon medium, the degree of oxygen conversion decreases (see Fig. 3).

Fig. 3. The dependence of oxygen conversion degree upon water/kerosene ratio ratio

It should be noted that increasing the water/kerosene ratio to values higher than 1:3 decreases distillate yield. We explain this fact by partial dissolution of the products of the hydrocarbon oxidation in water. On the other hand, the change of the above-mentioned ratio for all practical proposes does not affect both total and mercaptan sulphur content in the distillate (Table 3) nor the degree of recovery of total and mercaptan sulphur (Figs. 1 and 2) and, in addition, will lead to decreasing reactor capacity.

Fig. 4. The dependence of recovery degree of total sulphur upon water/ kerosene ratio

Fig. 5. The dependence of the mercaptan sulphur removal degree upon water/kerosene

Obtained results give us an opportunity to affirm that via the proposed ODS process (oxidation-treatment in the presence of water in reaction medium) a product can be obtained which meets requirements of the Ukrainian specification (content of total sulphur - 0.1-0.25% mass, content of mercaptan sulphur - 0.003% mass) to the jet fuels [GOST 10227-86*].

As it was noted at the beginning, to make ODS processes more economically acceptable a practical use of the obtained by-products has to be proposed. The main by-product of the studied process is a vat residue with a yield of about 3.5% mass. The vat residue is a concentrate of the sulfoxides, sulphones and products of hydrocarbon oxidation (compounds with high amount of the oxygen-contained groups). A study of the vat residue properties and possible ways of his practical use was not the purpose of the present paper and will be a subject of separate scientific research. But previous, our study showed that vat residue has very good surface-active properties and can be used as a component of the “Cutting Fluids” for metalworking and machining processes.

Conclusions

Performed research and obtained results showed that water *displays* an inhibitory effect on the hydrocarbon oxidation reactions in the processes of the oxidative desulphurization of the strait-run kerosene cuts. The main results obtained can be summarized as follows:

- An inhibitory effect of water caused by its ability to changes a mechanism of the hydrocarbon oxidation via directing a hydroperoxides decomposition pathway from the formation of acids and oxy-acids to the formation of alcohols, phenols and alkyl-phenols, which inhibits oxidation reactions of hydrocarbons, in addition to the H-bonds formation with peroxides and free radicals, as was observed by many authors.
- The presence of water in the reaction medium and the increase of water/kerosene ratio essentially increase the process selectivity, resulting in an improvement of the quality (operational characteristics) of the desulphurized fuel.
- An increase in the water/kerosene ratio up to 1:3 promotes an increased of the desulphurized fuel yield. Further increase in the water amount in the reaction medium decreases the distillate yield.
- The degree of sulphur removal practically does not depend on the water/kerosene ratio;
- The optimal water/kerosene ratio is in the range of 1:5 and 1:10. Such values provide maximum yield of the desulphurized fuel and high level of the sulphur recovery degree using minimum water amount in order to reduce energy costs.
- A non-catalytic oxidative desulphurization method yields the possibility of obtaining of desulphurized fuel which will meet requirements concerning sulphur content in the jet fuels of the Ukraine.
- A non-catalytic ODS can obtain more alluring economical prospects if a practical usage for the obtained vat residue, as a main liquid by-product of oxidation, will be proposed.

Acknowledgments

The authors are deeply grateful to Dr. Mark Goldman for assistance in preparation of this article.

References

- [1] EPA-Gasoline RIA, Regulatory Impact Analysis-Control of Air Pollution from New Motor Vehicles: Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulphur Control Requirements. US Environmental Protection Agency, Air and Radiation, EPA420-R-99-023. December 1999.
- [2] EPA-RFG-II, Phase II RFG Report on Performance Testing. US Environmental Protection Agency, Air and Radiation, EPA420-R-99-025. April 1999.
- [3] Directive of the European Parliament and of the Council, Brussels COM. 2001, 11.05.
- [4] EPA, Control of Air Pollution from New Motor Vehicles Amendment to the Tier-2/Gasoline Sulphur Regulations, US Environmental Protection Agency. April 2001.
- [5] Dixon-Decleve S. World Refining Houston. 2004;14:19.
- [6] EPA-Diesel RIA, Regulatory Impact Analysis: Heavy-duty Engine and Vehicle Standards and Highway Diesel Fuel Sulphur Control Requirements, United States Environmental Protection Agency, Air and Radiation, EPA420-R-00-026. December 2000.
- [7] EPA, EPA Gives the Green Light on Diesel Sulphur Rule, Press Release, United States Environmental Protection Agency. February 2001.
- [8] Sayles R. Hydrocarbon processing. 2005;84:39-43.
- [9] Anonymous. World Refining Houston. 2005;15:17.
- [10] Anonymous. World Refining Houston. 2005;15:14.
- [11] Anonymous. World Refining Houston. 2005;15:14.
- [12] Murata S, Murata K, Kidena K, Nomur M. Energy Fuels. 2004;18:116-121.
- [13] Anonymous. World Refining Houston. 2004;14:20.
- [14] Anonymous. World Refining Houston. 2004;14:21.
- [15] Glunt J. World Refining Houston. 2004;14:46-49.
- [16] Peckham J. World Refining Houston. 2004;14:26.
- [17] Anonymous. World Refining Houston. 2005;15:11.
- [18] Anonymous. World Refining Houston. 2005;15:9.
- [19] Anonymous. World Refining Houston. 2005;15:10.
- [20] Anonymous. World Refining Houston. 2004;14:18.
- [21] Anonymous. World Refining Houston. 2005;15:13.
- [22] Anonymous. World Refining Houston. 2005;15:14.
- [23] Higgins T. Jet World Refining Houston. 2005;15:4.
- [24] Link DD, Baltrus JP, Rothenberger KS. Energy & Fuels. 2003;17:1292-1302. DOI: 10.1039/B416929H.
- [25] Peckham J. Gas-to-Liquids News. 2000;3:1.
- [26] Peckham J. Diesel Fuel News. 2001;5:1.
- [27] Kauffman RE. Eng. Gas Turb. Power. 1997;119:322-327.
- [28] Controlling Airport-Related Air Pollution. NESCAUM Report. Northeast States for Coordinated Air Use Management. Boston: MA; 2003.
- [29] Mushrush GW, Beal EJ, Slone E, Hardy DR. Energy&Fuels. 1996;10:504-508.
- [30] Babich IV, Moulijn JA. Fuel. 2003;82:607-631.
- [31] Denisov ET, Afanas'ev IB. Oxidation and Antioxidants in Organic Chemistry and Biology. Boca Raton: CRC Press; 2005.
- [32] Frankel EN. Lipid Oxidation, 2nd Ed. Glasgow: The Oily Press; 2005.
- [33] Kamal-Eldin A. Lipid Oxidation Pathways. Champaign, Illinois: AOCS PRESS; 2003. DOI: 10.1002/ejlt.200600090.
- [34] Crytko MP, Bub GK. Ind Eng Chem Prod Res Dev. 1981; 20:481-486.
- [35] Shiraishi Y, Naito T, Hirai T, Komasaawa I. Chem Commun. 2001;14:1256-1257.
- [36] Csanyi LJ, Jaky K. Phys. Chem Chem Phys. 2001;3:2018-2024.
- [37] Kasaikina OT, Kartasheva ZS, Pisarenko LM. Russ J of General Chem. 2008;78:1533-154.
- [38] Kellerby SS, McClements DJ, J. Decker EA. Agric. Food Chem. 2006;54:7879.
- [39] Burlakovoi EB, Kasaikinoi OT, Kartashovoi ZS, Maksimovoi TV. Okislenie, okislitel'nyi stress i antioksidanty (in Russian). Moskva: RUDN; 2006.
- [40] Hayvanovych VI. Issledovaniye okisleniya vysokomolekulyarnykh soyedinyeniy nefti kyslorodom vozduha v vodno-emulsiionnoy sredy i v benzol'nom rastvorye (in Russian) [PhD Thesis]. Lviv: LPI; 1980.
- [41] Hayvanovych VI, Paniv PM, Pysh'yev SV, Antonyshyn VI. Naftova i gazova promyslovist (in Ukrainian). 2001;5:47.
- [42] Csanyi LJ, Jaky K, Kiss JT. J of Mol Cat. 1993;80:353-364.

- [43] Denisov ET, Mitskevich NI, Agabekov VE. Liquid Phase Oxidation of Oxygen-Containing Compounds. New York: Plenum Press; 1977.
- [44] Moscher H, Warster CJ. Am Chem Soc. 1955;77:545.
- [45] Hiatt RR, Visser T. Canad Chem Soc. 1964;42:1243.
- [46] Rao TSS, Awasthi S. E-J of Chem Jan. 2007; 4:1-13.
- [47] Kruzhalov BD, Golovanenko BI. Sovmesnoye polucensye fenola i acetona (in Russian). Moskva: Gosudarstvennoye nauchno-tehnicheskoye izdatelstvo himicheskoy literatury; 1963.
- [48] Spravochnik khimika. V. 1-4 (in Russian). Moskva: Himiya; 1965.
- [49] Michalak A. Polish J of Environ Stud. 2006; 15:523.
- [50] Safonov AS, Ushakov AI, Hrishyn VV. Khimotolohiya GSM (in Russian). SPb: NPIKC; 2007.

WPŁYW WODY NA UTLENIAJĄCY PROCES ODSIARCZANIA FRAKCJI NAFTY

Abstrakt: Dیتlenek siarki powstający podczas spalania paliw w silnikach spalinowych jest jednym z głównych zanieczyszczeń. W olejach napędowych i benzynie zawartość siarki powinna mieścić się w granicach 5-10 ppm, a w paliwach do silników odrzutowych - 300-3000 ppm. Jednak wykorzystanie paliwa lotniczego modyfikowanego metodą hydrotorafinacji jest problematyczne ze względu na pogorszenie stabilności i właściwości utleniających takich paliw. Badano odsiarczanie frakcji naftowej metodą utleniania. Metoda ta łączy utlenianie tlenem atmosferycznym związków siarki przy podwyższonej temperaturze i ciśnieniu, w obecności wody w środowisku reakcji, oraz usunięcie utlenionych związków siarki z paliwa na drodze rektyfikacji. Wykazano, że woda częściowo wyodrębnia ze środowiska węglowodorowego kwaśne związki utworzone w początkowym etapie utleniania. Szlak rozkładu hydronadtlenków zmienia się częściowo z tworzenia kwasów karboksylowych i kwasów tlenowych na powstawanie alkoholi, fenoli i alkilofenoli, które okazały się inhibitorem utleniania węglowodorów. Założono, że hamujący wpływ wody, oprócz tworzenia miceli odwróconej z nadtlenkami i kompleksów z wolnymi rodnikami, spowodowany był produktami utleniania utworzonymi w początkowym etapie reakcji. Badano wpływ proporcji wody i frakcji naftowej na odsiarczanie oksydacyjne. Stwierdzono, że woda poprawia selektywność procesu i ma niewielki wpływ na stopień odzysku siarki. Ustalono optymalną wartość stosunku woda/frakcja naftowa dla paliwa zawierającego 0,15% masowych związków siarki.

Słowa kluczowe: paliwa do silników odrzutowych, odsiarczanie utleniające, siarka, sulfotlenki, sulfony