

Desulfurization and Demetalization of Used Engine Oil in Laboratory Scale

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ABSTRACT

This paper describes a laboratory method for treatment of used engine oil FENIX SUPERIOR SAE 15W-40 with the intention of decreasing sulfur and selected metal content at an acceptable level. FENIX SUPERIOR SAE 15W-40, produced by manufacturer Joint Stock Company FAM Krusevac, is used for lubrication of the most modern four-stroke diesel and gas engines of passenger and commercial vehicles, engine construction, mining and agricultural machinery, as well as stationary power aggregates, including highly overloaded engines working in harsh environmental conditions. Exhausted oil samples were obtained from the three sources: diesel and gas engines of passenger cars and agricultural machines-tractors were treated according to a novel two-step technology. In the first step, physical operations, such as centrifugation, filtration, and separation, were applied in order to remove mechanical impurities (sludge), condensed material and water. In the second step, chemical oxidation using three agents, i.e., hydrogen peroxide, sodium hypochlorite, and potassium persulfate, was applied to achieve the removal of the sulfur containing compounds. Based on the obtained results at a laboratory level, a technology at a semi-industrial level for the treatment of waste oil was proposed. A new ecologically friendly technology developed for treatment of waste oil offers appropriate advantages in comparison to commercially available technologies.

1. Introduction

The current legislation, related to the quality of engine lubricating oil, defines some very strict limits on sulfur concentration which ranges from 5 to 50 ppm [1-3]. In contrast to

lighter oil products, the sulfur in the base oil can be found as elemental sulfur, H₂S, or as thiophene and its derivatives. If the heavy oil fractions are used for energy production during the combustion process, the sulfur

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contained in the fuel is converted into sulfur oxides, which will be a source of acid rain and air pollution. There are two types of oxides, i.e., SO_2 and SO_3 , which can spread into the atmosphere causing respiratory disorder and major environmental damage. Moreover, hydrogen sulfide and mercaptans can lead to corrosion, occurring during the production and transportation of the fuel [4]. In order to achieve a certain sulfur level, prescribed by law, desulfurization processes of petroleum derivatives are an important part of the post-treatment process of oil before entering the market. Following oil exploitation, its parameter changes, and contamination by sulfur containing degradation products and metal ions occurs at different extents depending on the quality of used oil and exploitation conditions. Many technologies have been developed in order to design/develop efficient technologies for treatment of exhausted oils. Two main directions for the waste oil treatment could be recognized:

(1) If the waste oil has to be incinerated, this can be done in a cement factory; however, the extraction of large quantities of soot and toxic gases, such as SO_2 and SO_3 , during combustion presents danger for the environment. However, in case when the waste oil is used for burning in steam-boilers, it is necessary that oil be removed from sulfur and be mixed with the heavy oil in a given weight percentage according to design technology. During oil burning, a large amount of soot is released due to high content of long alkane series.

(2) The second option concerns the development of appropriate technologies and applying them to processes of waste oils recycling in order to improve the final products parameters, i.e., to achieve oil

properties close to ones prescribed by law. Many extraction and desulfurization processes, for removing sulfur-containing compounds, have been patented. Extraction with polyethylene methylether decreases the sulfur content by 30 % in petrol, diesel fuel, gas oil, and other raw oil fractions [5,6]. An extraction process combined with hydrotreating or oxidation can be effective. Patented extractive agents used in combination with hydrotreating include the following items: methanol, acetonitrile, *N*-methylformamide, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, furfural, dimethylsulfoxide [7], and polyethylene glycols [8]. The extraction of raw petrol using these extractive agents and application of mild hydrotreating will give almost complete removal of mercaptanes and thiophenes and result in 94 % removal of the overall sulfur content [8]. Efficient desulfurization was performed by hydrotreating after an extraction step [9]. Extraction with heterocyclic nitrogen compounds (pyrrolidones, etc.) followed by hydrotreating provided sulfur content which reduced below 0.01 wt % [10].

Oxidation of sulfur containing compounds with peroxides, in the presence of a Ni-V based catalyst, followed by the removal of the oxidized sulfur compounds by thermal decomposition at 300–400 °C in the presence of ferric oxide liberates sulfur dioxide. The next step in the desulfurization process is performed by hydrogenation in the presence of Co/Mo catalyst. From petroleum fraction boiling above 250 °C, 40 % sulfur was removed by oxidation and 45 % by hydrogenation [11,12]. Arabian crude oil, containing 2.6 wt % of sulfur, was dissolved in petroleum-ether and treated with butyl hydro-peroxide in the presence of

molybdenum catalyst at 90 °C for 60 h. Sulfur content, after oil separation and cooling, was found to be decreasing from 2.6 to 1.6 wt % [13].

In another research, tert-butyl hydroperoxide was used for oxidation of crude oil in the presence of vanadium acetylacetonate at 90 °C. Conversion rate to oxidation products, of up to 74 %, was obtained for sulfur containing compounds [14]. Similar results were obtained by oxidation with peroxides at 400–415 °C and 60–65 atm [15]. Some relatively cheap oxidants, such as nitrogen oxides and nitric acid, were studied; however, the tests produced inadequate results [16]. The most promising result for reducing sulfur content in diesel fuel, such as light oil, was obtained by peroxyacid oxidation, i.e., mixture of formic acid/hydrogen peroxide (HCOOH/H₂O₂). Removal of sulfones and sulfoxides, created during oxidation, was carried out by extraction followed by adsorption with silica gel to reach sulfur content of 7.0 ppm [17]. Another effective process was suggested by Mei et al. [18, 19] in which phosphotungstic acid, tetraoctyl ammonium bromide and ultrasound were used at 75 °C to complete the oxidation. The oxidized product was then extracted with acetonitrile. Under these conditions dibenzothiophene and its derivatives were removed from diesel fuel at a rate of more than 99 %. In recent years, many desulfurization processes with peroxides have been patented; in most cases, invention results have shown that, in the final product, fuel had a total sulfur content between 100 and 15 ppm [20] and from gas oil to 82 % [21]. In 2004, a submitted patent application described that oxidation of crude oil was carried out by hydrogen peroxide in the presence of transition metal catalysts,

such as tungsten or tungstates (tungstic acid, metal tungstates, etc.) for diesel-containing systems and Fenton-type catalysts (ferrous salts) for crude oil, surface-active agent, and radiation with ultrasonic energy at 125 °C and 3 atm. The resulting sulfur content was reduced from 2.5 % to 0.7 % [22].

The literature describes the procedures of desulfurization of liquid fuels [4, 23-26], while oxidative desulfurization of waste engine oil was present in the available literature. Nowadays, the conventional industrial process used in hydrodesulfurization processes of oil distillate in refineries is well known. The process for gasoil hydrodesulfurization is carried out at high temperatures up to 400 °C and at pressure of 7×10^3 kN/m² using Co/Mo and Ni/Mo as catalysts. By hydrodesulfurization, the sulfur is removed from mercaptans, thioethers, sulfides, disulfides and thiophenes; however, it was shown that this process has certain limitations in the treatment of alkylated aromatic sulfur compounds; besides, it is an applicable process in refineries for treatment of gasoil /naphtha on a commercial scale. Oxidative desulfurization of heavy oil [27], which contained high level of sulfur, was carried out by the use of hydrogen peroxide, acetic and formic acid as the catalyst. The experimental tests showed that sulfur amount was decreased from 2.75 to 1.14 %, and chemical mixing of H₂O₂/acetic acid has better effect in comparison with chemical mixing of H₂O₂/formic acid for desulfurization of heavy oil. The oxidation process enables milder reaction conditions: a lower temperature of about 60 °C, operation at atmospheric pressure, and simple manufacture of the reactor. In doing so, sulfur, containing aromatic compounds thiophene, benzo-thiophene, and dibenzo-

thiophene sulfone, and others, was transformed into sulfoxides and sulfones which could be extracted by using an appropriate solvent.

In this study, the waste oil, obtained after consumption in gas and diesel cars and tractors, has been treated in order to remove sulfur. Desulfurization has been carried out with hydrogen peroxide (H_2O_2), sodium hypochlorite ($NaOCl$), and potassium peroxodisulfate ($K_2S_2O_8$) oxidants. These oxidizing agents have been previously used in reactions of synthesis of tioncarbmates [28], where a high degree of conversion of reactants to the products was obtained. Prior to the oxidation step, simple waste oil treatment was performed by applying centrifugation or filtration in order to remove mechanical impurities, water and condensed carbonaceous materials. Optimization of the process of oxidative desulfurization was carried out with respect to the reaction time, temperature, and molar ratio of the sulfur in the oil and oxidizing agent.

2. Experimental

2.1. Materials

All the chemicals used in this study were of analytical grade or commercial product, and they were used as received. The commercial oil product FENIX SUPERIOR SAE 15W-40 and used oils were supplied by Joint Stock Company FAM Krusevac; hydrogen peroxide, H_2O_2 , (35.50 %), PubChem; sodium hypochlorite - solution, $NaOCl$, (161.6 g of active $Cl_2/1000\text{ cm}^3$ solution); H.I. Župa, KRUŠEVAC; potassium persulfate-white crystalline solid, $K_2S_2O_8$, $\geq 99.0\%$ SIGMA-ALDRICH, Acetonitrile, CH_3CN , HPLC grade $\geq 99.3\%$ and sulfuric acid, 93-98.5 % RTB Bor Grupa TIR d.o.o.

2.2. General laboratory procedure of the preparation of waste oil sample

Fifty g of sample of used (waste) oil was placed in a 100 cm^3 beaker which were following by stirring and heating at $60\text{ }^\circ\text{C}$ for 5 min. Then, the oil was subjected to centrifugation in order to separate oil phase from the sludge (a precipitate consisting of form solid particles and condensed organic materials dispersed in water phase). The separated dark colored oily phase was analyzed for sulfur content by ASTM D4294 standard method [29] and used as a feeding material for the removal of the present chemical contaminants. Characteristics of industrial oil product FENIX SUPERIOR SAE 15W-40 were analyzed by standard methods ASTM D1500, ASTM E1252, ISO3675 and ASTM D6481 for color, IC-spectrum, density, and metal content, respectively. Removal of selected containnats was performed according to designed technology, and the obtained material was subjected to characterization according to standard test methds. The bottom phase was set aside in order to charaterize and, according to the obtained result, to perform appropriate treatment. Atomic apsrption spectrophotometry was used to determine contents of metals: zinc, calcium, and magnesium.

2.3. General procedure for the treatment of waste oil sample by oxidation with hydrogen peroxide

50.0 g (432 ppm S) of the prepared sample oil was added to a 250 cm^3 three-necked flask equipped with reflux condenser, thermometer, and dropping funnel and followed by the stirring and heating at $75\text{ }^\circ\text{C}$, by using magnetic stirrer applied. From a dropping funnel, 6.5 mL of 15 % aqueous hydrogen

peroxide (0.0677 mol), was slowly added for 15 min with vigorous stirring and maintaining the temperature at 75 °C. During 30 min. of the reaction, the mixture was observed. When the foaming was terminated, the reaction mixture was additionally stirred for 5 min and poured into a separate funnel where the upper organic oil phase was separated from water fraction. The organic oily layer was washed two times with warm distilled water and acetonitrile was comparatively used and, then, placed into a vacuum evaporator, heated at 80 °C, and vacuumed (at 35 mmHg vacuum) for 30 min to remove residual water, or alternatively by using granular silica gel. The resulting product was analyzed for sulfur content according to ASTM D4294 method [29], whereas atomic absorption spectrophotometry was used to determine zinc, calcium, and magnesium contents.

2.4. General procedure for the treatment of waste oil sample by oxidation with sodium hypochlorite

50.0 g (432 ppm S) of the prepared sample oil was added to a 250 cm³ three-necked flask equipped with reflux condenser, thermometer and dropping funnel followed by the stirring and heating at 50 °C, by using magnetic stirrer applied. From a dropping funnel, 29.8 cm³ (0.0677 mol) of sodium hypochlorite solution (161.6 g of active Cl₂/1000 cm³ solution) was gradually added during 1 h, and the temperature of the reaction mixture was maintained in the range of 50 to 55 °C. At the beginning of the reaction, an increase in temperature of reaction mixture was observed during the addition of a sodium hypochlorite solution; consequently, after the addition of one-third of the required amount of solution, it was necessary to maintain temperature at 55 °C by applying external heating. At the end of

the reaction, pH value of the reaction mixture was 11. To reach pH 7, an appropriate volume of 10 % mass of sulfuric acid solution was added to the reaction mixture. After completion of the reaction, the reaction mixture was transferred to a separation funnel where the organic oily phase was separated from the aqueous fraction. The upper organic oily layer was washed two times with warm distilled water and acetonitrile was comparatively used and, then, placed into a vacuum evaporator, heated at 80 °C, and evacuated under vacuum (at 35 mmHg vacuum) for 30 min to remove residual water, or using granular silica gel.

2.5. General procedure for the treatment of waste oil sample by oxidation with potassium peroxodisulfate

50.0 g (432 ppm) of the prepared sample oil was added to a 250 cm³ three-necked flask equipped with reflux condenser, thermometer, and dropping funnel followed by the stirring and heating at 80 °C, by using magnetic stirrer applied. From a dropping funnel, 29.8 cm³ (0.0677 mol) solution of potassium peroxodisulfate (18.5 g (0.0677 mol) of 98 % potassium peroxodisulfate dissolved in 30 cm³ of water was gradually added during 1 h, and the temperature of the reaction mixture was maintained in the range of 80 to 100 °C. At the end of the reaction, pH 6 was obtained. After completion of the reaction, the reaction mixture was transferred to a separate funnel, and the organic oily phase was separated from the aqueous fraction. The upper organic oily layer was washed two times with warm distilled water and acetonitrile was comparatively used, dried with anhydrous sodium sulfate, then placed into a vacuum evaporator, heated at 80 °C, and evacuated under vacuum (at 35 mmHg) for 30 min to

remove residual water, or using granular silica gel.

2.6. Analyzing method of sulfur/metals in oil

Analysis of the total content of sulfur in the prepared sample of motor oil was performed according to ASTM D4294 standard testing method. This test method provides rapid and precise measurement of total sulfur in the range of 0.01 wt % (100 ppm) to 3 wt % [29] in petroleum and petroleum products with a minimum of sample preparation. Calibration and standardization of the apparatus was done via 4 standard samples of petroleum and oil cuts. The existing total sulfur in fuel oil, liquid or solid at room temperature would be melted/dissolved by this method and via applying external thermal heating in hydrocarbon solvents; in addition, this provides an accurate measurement of the content of total sulfur. These materials could include diesel fuel, jet fuel, kerosene or the other petroleum compounds produced from distillation like naphtha, residual oil, fuel oil and gas. Samples, like gas, (with high vapor pressure or light hydrocarbons) could not be measured accurately by applying this method because of evaporation of the materials during the analysis.

Metal content in FENIX SUPERIOR SAE 15W-40 oil was determined by manufacturer Joint Stock Company FAM Kruševac and atomic absorption spectrometer Perkin Elmer AAnalyst 200 (MA, USA) was used. Standard optimization procedures and criteria are specified in the manufacturer's manual instruction.

3. Results and discussuon

Following an expolitation period of engine oil, management of the exhausted oil is an

important issue including collection, monitoring, and warehousing performed by a waste generator. The next step is related to adequate processing or disposal in a proper way, conforming to the actual law/regulation. The waste oil may be subjected to combustion (energy production) or as fluid for lubrication of plankings in the building industry, and recycling which offers the possibility to be eventually used in reformulation products for engine lubrication. In doing so, it is necessary, prior to the use of raw materials, to adjust its physico-chemical parameters in accordance to legislations. The main concern of the present study was devoted to the removal of transformed/degraded sulfur containing compounds, inorganic or organic, which mostly originate from the chemical components/additives incorporated in the intial formulation of the oil. Amount of sulfur in the tested oil was found to be around 1 % and comes from the base oil and additives introduced at the appropriate level in the course of the implemented production technology. The base oil, as a raw material used in the production process, contains about 0.6 % of sulfur, while the additional amount of about 0.3 % originates from the additive. Moreover, in the final product as well as in the waste oil, phosphorus and metal salts of zinc, calcium, and magnesium are the elements of interest to be monitored and removed/adjusted to the level prescribed by regulation. Monitoring these contaminant in a waste oil and recycled material is necessary from two aspects: design/optimization of appropriate purification technology and determination of compliance with actual legislation; in other words, evaluating the success of applied purification technology.

In that sense, in the experimental part of the work, both preparation of the sample and

laboratory analysis of waste oil were carried out in order to select appropriate purification technologies. Characteristics of industrial

product of oil FENIX SUPERIOR SAE 15W-40 from manufacturer Joint Stock Company FAM Kruševac are given in Table 1.

Table 1

Characteristics of industrial oil product FENIX SUPERIOR SAE 15W-40.

No.	Characteristics	App.	Freqv.	Unit	Method	Designation	Tolerance
1.	Appearance at 20 °C	+	SS	-	Visual	FAM MI-1	Clear liquid
2.	Color	+	10	-	ASTM D 1500	FAM MI-64	2.5-3.5
3.	IC – spectrum	+	30	-	ASTM E 1252	FAM MI-3	Etalon
4.	Density at 15 °C	+	SS	g/cm ³	ISO3675	FAM MI-61	0.870-0.890
Metal content			10				
Zinc		☑		%			0.13-0.16
Calcium		☑		%			0.22-0.26
5.	Magnesium	☑		%	ASTM D 6481	FAM MI-91	0.01-0.04
	Nitrogen	☑		%			0.08-0.12
	Phosphorus	☑		%			0.12-0.16
	Sulfur	+	H	%			ASTM D4294
6.	Sulphate ash	+	H/PZ	%	ASTM D 874	FAM MI-70	<2.0
7.	Kinematic viscosity at 100 °C	☑	SS	mm ² /s	ASTM D 445	FAM MI-48	12.5-16.3
8.	Kinematic viscosity at 40 °C	-	SS	mm ² /s	ASTM D 445	FAM MI-48	Cited
9.	Viscosity index	☑	SS		ISO 2909	FAM MI-49	min 130
10.	Ignition point	+	30	°C	ASTM D 92	FAM MI-59	min 200
11.	Softening point	+	10	°C	ASTM D 97	FAM MI-58	max -30
12.	Dynamic viscosity at -20 °C	☑	10	mPas	DIN 53018/1	FAM MI-26	<7000
13.	Viscosity after 30 cycles, 100 °C	☑	30	mm ² /s	CEC L-14-A-88		>12,0
14.	HTHS viscosity, 150 °C, 10 ⁶ /s	☑	H	mPas	CEC-CL-23		min 3.5
15.	TBN	☑	SS	mg KOH/g	ASTM D 2896	FAM MI-31	min 9.0
Foaming tendency-stability							
16.	Sequence I	☑				FAM MI-52	max 10/0
	Sequence II	☑	30	ml/ml	ASTM D 892		max 50/0
	Sequence III	☑					max 10/0
	Sequence IV, 150 °C, ASTM D 6082	+					max 100/0
17.	Loss by evaporation, 1h/250 °C	+	30	%	ASTM D 5800		≤13

Legend frequency: SS - each batch; 10 - every tenth; 30 - every thirty; H - approval; PZ - special requirements.

The FENIX SUPERIOR SAE 15W-40 oil, with physico-chemical characteristics shown in Table 1, was used for the lubrication of gasoline and diesel engines and tractor. The

composition of the waste oil samples, obtained from these three sources, is shown in Table 2.

Table 2

Composition of the samples of waste oil from motor engine.

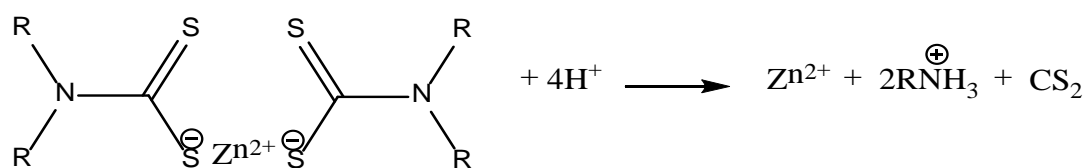
Sample	Mass of oil phase		Mass of sludge		Amount of contents in oil phase							
					Zn		Ca		Mg		S	
	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)
1.	48.18	96.36	1.82	3.64	0.0486	0.101	0.0592	0.123	0.0101	0.021	0.4336	0.900
2.	48.09	96.18	1.91	3.82	0.0451	0.100	0.0577	0.120	0.0096	0.020	0.4717	0.981
3.	47.90	95.80	2.10	4.20	0.0526	0.110	0.0527	0.110	0.0072	0.015	0.4406	0.920

* 50 g of waste engine oil was treated:

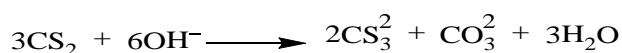
1. waste oil from the car gas engine, 2. waste oil from the car diesel engine, 3. waste oil from tractor.

After use, the waste oil could be treated by performing appropriate technology, or it could be landfilled/transported to institution authorized for further processing. Based on the results of analysis of the samples of waste oil, shown in Table 2, it can be seen that there is an appropriate amount of zinc, calcium, and magnesium, as well as elemental/organic sulfur. This occurs during the use of oil as a result of thermal/chemical degradation/transformation of compounds/additives present in oil used as a lubricant [30]. The extent of particulate contamination is inversely proportional to oil alkalinity, which is a measure of the quantity/transformation of the alkaline buffers initially blended into the oil in order to neutralize acidic component. Once the buffers have been fully neutralized/exhausted by the acidic oil degradation products (created during ordinary operation of any combustion engine), contamination with cations increases

very rapidly. Due to acidic environment, erosion of oil containing compartment and additives increases at higher oil acidity. In the oil phase, sulfur is present in the range of 0.900 to 0.920 %, while its starting amount in the commercial product is 1.10 %. The density of the obtained oil ranges from 0.870 to 0.880 g/cm³ at 20 °C, which is a lower value in comparison with the commercial product. This indicates that there has been a partial degradation of additive and oil constituent, whose products are removed to the mud during centrifugation. Partial oxidation of sulfur during engine operation results in SO₂ formation which reacts with moisture producing sulfuric acid. Sulfuric acid causes decomposition of dithiocarbamates, used as additives [31], to the carbon disulfide, the amine sulphate, and zinc sulphate according to the following equation:



Alkaline environment leads to reactions that produce the metal salts of carbonic and tritiocarbonic acids:



According to the results of waste oil analysis, the developed technology has to provide transformation of the generated contaminants obtained by different processes to produce non-hazardous material that can be safely landfilled or recycled, i.e., used as raw materials in an appropriate production processes. For instance, in this work, selected technologies were developed in order to obtain oil which, after formulation, could be used either for construction or blending with fresh oil possibly used for lubrication of the engine. Two-step technologies were applied: the first step includes the removal of mechanical impurities, in particular the moisture and the sludge. In this way, the oil was separated from the slurry, by centrifugation or filtration. In the second step, an appropriate oxidation procedure was applied to remove sulfur containing compounds. Three oxidizing agents, i.e., hydrogen peroxide, sodium hypochlorite, and potassium persulfate, were used to study effectiveness of sulfur removal. Optimization of the procedure for the treatment of exhausted oil was carried out with respect to the reaction time, temperature and molar ratio of the oxidizing agent, and the amount of the sulfur in the oil. The oil was heated and the oxidation took place at elevated temperature in the presence of the excess of an oxidizing agent, followed by centrifugation and separation of the aqueous and oily phase. The separated aqueous phase was neutralized with the dilute sulfuric acid at pH 7, subjected to

purification (flocculation), filtrated and, then, discharged into water courses.

In that context, study on the use of hydrogen peroxide (H_2O_2) for the treatment of the prepared oil sample, the influence of the mole ratio of reactants, time of reaction and temperature in order to optimize the reaction conditions has been investigated. The results are presented in Table 3 (exps. 1-5).

Based on the results of analysis of the samples of waste oil, shown in Table 3, it can be seen that there is low amount of metal zinc, calcium, and magnesium in the oil phase in relation to the amount present in the non-treated waste oil (Table 2).

According to the results presented in Table 3, it can be concluded that the optimal molar ratio of reactants, i.e., sulfur present in the sample and the hydrogen peroxide solution, is 1:5 (weight ratio is 1 : 5.3). If the amount of oxidizing agent is reduced and the molar ratio of 1:3 (weight ratio is 1 : 3.18) is established, the partial elimination of metal is a result, although lower amount of sulfur is obtained. In the purpose of easier monitoring of results, the influence of reaction time and quantity of oxidants on the amount of residual sulfur is presented in Figure 1. Extending the reaction time to more than 35 min has no significant effect on the oxidation process (Figure 1a). Moreover, increasing the reaction temperature over 75 °C does not provide higher conversion of sulfur or metal removal. According to the presented results in Table 3 (exps. 1-5), the optimal oxidizing condition for sulfur and metal ions removal is the molar ratio of reactants as 1:5 (weight ratio was 1:5.3), reaction time as 30 min, and temperature applied for oil treatment as 75 °C.

Table 3

The effect of the molar ratio of reactants, reaction time, and temperature on the removal of sulfur and metals from the treated oil sample 1 by using H₂O₂, NaOCl, and K₂S₂O₈.

Oxidant H ₂ O ₂								
No. of exp.*	Sulfur (mol/g)	H ₂ O ₂ (mol/g)	Time of reaction (h)	Temperature of reaction (°C)	Amount of S %	Amount of metal elements (%)		
						Zn	Ca	Mg
1.	0,0135/ 0.4328	0,0677/ 2.302	0.60	75.0	0.510	0.000	0.000	0.000
2.	0,0135/ 0.4328	0,0405/ 1.377	1.00	85.0	0.680	0.032	0.029	0.008
3.	0,0135/ 0.4328	0,0677/ 2.302	0.70	75.0	0.510	0.000	0.000	0.000
4.	0,0135/ 0.4328	0,0677/ 2.302	0.80	75.0	0.502	0.000	0.000	0.000
5.	0,0135/ 0.4328	0,0677/ 2.302	1.20	75.0	0.508	0.000	0.000	0.000
Oxidant NaOCl								
No of exp.*	Sulfur (mol/g)	NaOCl (mol/g)	Time of reaction (h)	Temperature of reaction (°C)	Amount of S %	Amount of metal elements (%)		
						Zn	Ca	Mg
6.	0,0135/ 0.4328	0,0677/ 5.044	1.00	55.0	0.550	0.000	0.000	0.000
7.	0,0135/ 0.4328	0,0405/ 3.017	1.00	55.0	0.710	0.022	0.023	0.007
8.	0,0135/ 0.4328	0,0677/ 5.044	1.00	80.0	0.645	0.020	0.026	0.008
9.	0,0135/ 0.4328	0,0677/ 5.044	1.50	55.0	0.525	0.000	0.000	0.000
10.	0,0135/ 0.4328	0,0677/ 5.044	1.50	65.0	0.568	0.000	0.000	0.000
Oxidant K ₂ S ₂ O ₈								
No. of exp.*	Sulfur (mol/g)	K ₂ S ₂ O ₈ (mol/g)	Time of reaction (h)	Temperature of reaction (°C)	Amount of S %	Amount of metal elements (%)		
						Zn	Ca	Mg
11.	0,0135/ 0.4328	0,0677/ 18.279	1.00	80.0	0.530	0.010	0.010	0.008
12.	0,0135/ 0.4328	0,0405/ 10.935	1.00	80.0	0.610	0.020	0.016	0.007
13.	0,0135/ 0.4328	0,0677/ 18.279	1.00	95.0	0.500	0.000	0.008	0.000
14.	0,0135/ 0.4328	0,0677/ 18.279	1.50	95.0	0.501	0.000	0.000	0.000
15.	0,0135/ 0.4328	0,0677/ 18.279	2.00	95.0	0.490	0.000	0.000	0.000

* Prepared and treated oil sample 1 from Table 2.

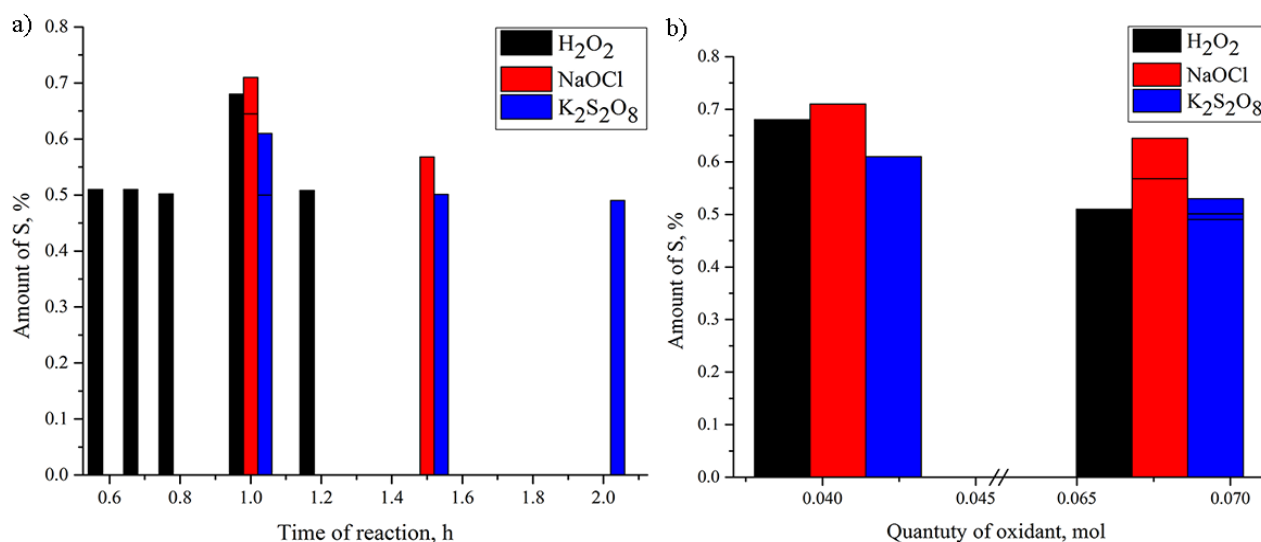


Figure 1. The influence of (a) reaction time and (b) quantity of oxidant on the amount of residual sulfur.

The continuation of this study was related to the process of the sulfur removal from the oil sample 1 using sodium hypochlorite (NaOCl) as an oxidant. The influence of the molar ratio of reactants, reaction time, and temperature on the removal of sulfur and metals was examined, and the results are presented in Table 3 (exps. 6-10).

Based on the results shown in Figure 2, the optimal molar ratio of reactants, i.e., sulfur present in the sample and the sodium hypochlorite, was 1:5 (weight ratio was 1:11.56). If the amount of oxidizing agent is reduced and the ratio of 1:3 (weight ratio is 1:6.96) is established, the partial elimination of metal from oil will not occur, but a lower amount of sulfur will be removed (Figure 1b). Extension of the reaction time to 1.5 h facilitates better elimination of sulfur (Figure 1a) and metals present in the test sample. Increasing the temperature of the reaction at 80 °C gives lower conversion of sulfur present in the treated sample and metals removal. It is probably due to the decomposition of sodium hypochlorite at elevated temperature, resulting in a loss of oxidizing power of this agent. An optimal

oxidizing condition for sulfur and metal ions removal was selected: the molar ratio of reactants-1:5 (weight ratio was 1:11.56), reaction time-90 min, and temperature applied for oil treatment - 55 °C (Table 3; exps. 6-10).

The results of the removal of sulfur and metals present in the oil test sample obtained under optimum conditions defined according by potassium peroxodisulfate ($K_2S_2O_8$) treatment are shown in Table 3 (exps. 11-15).

Optimal amount of the used potassium peroxodisulfate in relation to the sulfur is 5:1 (weight ratio is 42.28:1). Extending the reaction time to 1.5 h affected no significant improvement in sulfur removal (Figure 1a), while temperature of 95 °C contributed to higher extent of oil purification.

In an analogous manner, treatment of oil samples 2 and 3 (Table 2) was performed, and the obtained results are presented in Table 4. The general conclusion obtained from Tables 3 and 4 indicated that the used three oxidizing agents could be efficiently applied to the treatment of all three exhausted oil samples independently on the oil sources, diesel, and gas engines of passenger cars and agricultural machines-tractors.

Table 4

The results of the sulfur and metals removal from the treated oil samples 2 and 3 using H₂O₂, NaOCl, and K₂S₂O₈ according to the optimal procedure.

Oxidant H ₂ O ₂									
No. of exp.	Sulfur (g)	H ₂ O ₂ (g)	Weight ratio S/H ₂ O ₂	Time of reaction (h)	Temperature of reaction (°C)	Amount of metal elements (%)			
						S	Zn	Ca	Mg
16.*	0.432	2.302	0.188	0.60	75.0	0.532	0.011	0.012	0.009
17.**	0.432	1.377	0.314	0.60	75.0	0.520	0.019	0.028	0.014
Oxidant NaOCl									
No of exp.	Sulfur (g)	NaOCl (g)	Weight ratio S/NaOCl	Time of reaction (h)	Temperature of reaction (°C)	Amount of metal elements (%)			
						S	Zn	Ca	Mg
18.*	0.432	5.044	0.086	1.50	55.0	0.572	0.005	0.026	0.005
19.**	0.432	3.017	0.143	1.50	55.0	0.526	0.018	0.017	0.011
Oxidant K ₂ S ₂ O ₈									
No. of exp.	Sulfur (g)	K ₂ S ₂ O ₈ (g)	Weight ratio S/K ₂ S ₂ O ₈	Time of reaction (h)	Temperature of reaction (°C)	Amount of metal elements (%)			
						S	Zn	Ca	Mg
20.*	0.432	18.279	0.024	1.50	95.0	0.518	0.000	0.009	0.011
21.**	0.432	10.935	0.040	1.50	95.0	0.506	0.017	0.011	0.010

* Treated oil sample 2 from Table 2;

** Treated oil sample 3 from Table 2.

Two types of extraction solvents were used, namely warm distilled water and comparatively in a few experiments acetonitrile. Extraction of warm distilled water led to the optimal results by two extraction steps. The additional extraction with acetonitrile contributed to an appropriate increase of extraction (~20 do 35 %), probably because the sulfur compounds were oxidized at lower extent into their corresponding sulfones and sulfoxides [27] which have higher polarity and higher affinity towards polar solvents. For example, following the oxidation of waste oil with hydrogen peroxide (experiment No. 4; Table 3), a subsequent extraction with acetonitrile contributes to a sulfur decrease from 0.502 to 0.331 % (34 % sulfur content decrease). In general, results of oxidative sulfur and cations removal (Table 3) indicate that all investigated oxidizing agents are effective in the purification of the waste motor oil.

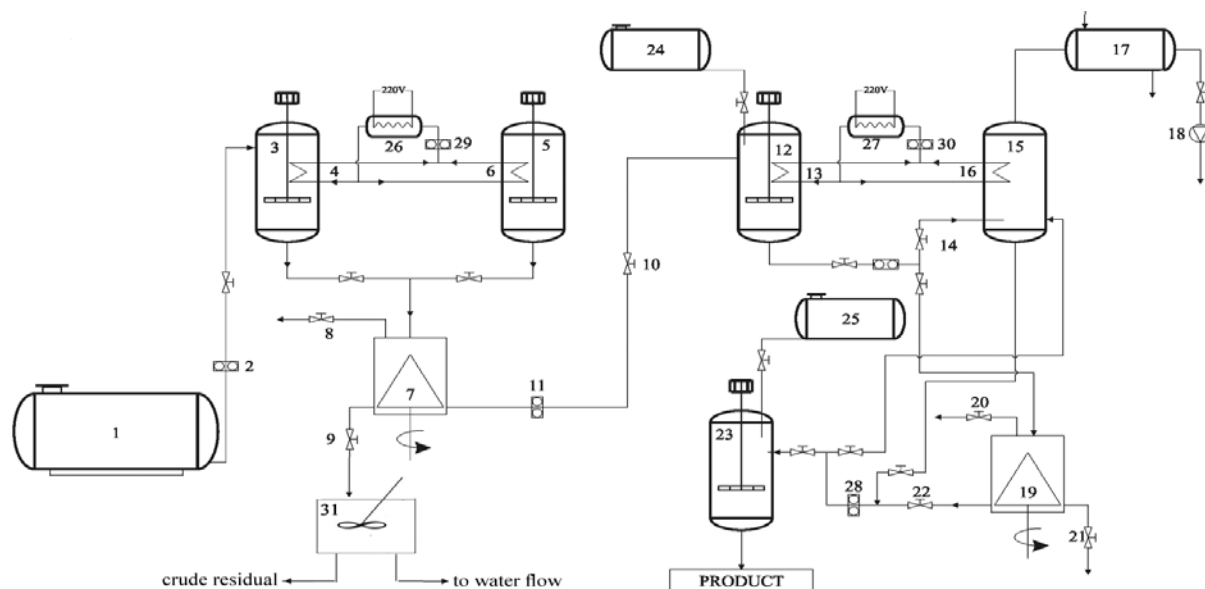
Within the presented oxidant, for the first time, the applied oxidant potassium persulfate

provides the highest level of conversion/removal of sulfur and metals present in the test sample. Also, benefits of potassium persulfate use are related to an easy manipulation of raw materials; thus, transportation cost is the lowest, compared to lower concentration of active component in hydrogen peroxide and sodium hypochlorite solution. On the other hand, its availability and cost are not favorable facts in a consideration of potential applicability. Sulfur present in the additive and oil constituents are oxidized with sulfate, which in the presence of cations, i.e., Zn, Ca and Mg, gave heavily soluble metal sulfates easily separable by centrifugation or filtration at a semi-industrial level. All of the presented solutions/operations included in designed technology are practically feasible to be implemented at a semi-industrial scale. A high degree of the sulfur conversion to sulphates with high reproducibility of the obtained results was obtained under mild operational conditions using relatively cheap,

sodium hypochlorite, and readily available raw materials, sodium hypochlorite, and hydrogen peroxide. Applying operations, such as centrifugation and separation, mud and moisture present in oil, were successfully removed.

Results of the additional experiments, performed with higher quantity of waste oil

(1-2 L) and using mechanical stirrer, showed reproducibility of the obtained results and possible scaling up to a semi-industrial level of production. Therefore, based on optimized laboratory procedures of treatment of waste oil, a process flow diagram of the semi-industrial process is presented in Figure 2.



Legend:

- 1 - Receiving tank for waste oil
- 2, 11, 14, 28 - Oil gear pumps
- 3, 5 - Mixers for heating up to 100 °C, V = 5 m³
- 4, 6, 13, 16 - Thermo-oil heaters
- 7, 19 - Centrifuges Q = 3m³/h
- 8, 20 - Valves for water drain
- 9, 21 - Valves for sludge drain
- 10, 22 - Valves for centrifugation
- 18 - Vacuum pump
- 17 - Cooler
- 12 - Reactor with mixer V = 12 m³
- 15 - Reactor for oil vacuum treatment V = 10 m³
- 23 - Mixer V = 10 m³
- 24, 25 - Dozers for additives I and II V = 2 x 2 m³
- 26, 27 - Thermo-oil heaters
- 29, 30 - Thermo-pumps
- 31 - Unit for waste treatment

Figure 2. Process flow diagram of sulfur/metals removing waste motor oil by chemical oxidants.

Decision-making on the applicability of developed technologies is a critical point at which special care must be exercised for feasibility, operational simplicity, and profitability. The cost analyses of the developed technology are key criteria that must be considered at a decisive point before continuation of the study at pilot and full-scale levels of application. The techno-economic analysis is a complex procedure and generally

includes two categories: capital and maintenance/operational (MO) cost. Design of technology provides data necessary for calculation of the values of capital investment (equipment, construction, installation, etc.). MO cost elements, such as raw materials, chemicals, labor and energy costs, are of different significance to techno-economic analysis. Moreover, the selection of the treatment technology should be based on the

following factors: complexity/feasibility and material/maintenance cost of the facility, waste material generation (quantity/hazardous properties), as well as characteristics/properties of the treated material. Generally, detailed techno-economic (cost) analysis will include all those items related to capital and operations/maintenance (OM) costs.

The differences in capital cost for three presented technologies for oxidative treatment of waste oil could be considered to be approximately negligible; thus, it was neglected in the analysis. MO cost elements, such chemicals costs, labor and energy cost, are of different significance levels to techno-economic analysis. Therefore, selection of the most influential factors, without sacrificing validity of assessments, was made. Oxidative efficiency and market cost of oxidants were selected as critical parameters for selection of the optimal technology. Generally, this cost of used oxidants is as follows: NaOCl ~0.2 \$/kg, H₂O₂ ~0.4 \$/kg, and K₂S₂O₈ ~0.6 \$/kg. According to these data, the preliminary considerations clearly showed that NaOCl was satisfied from the financial point, while, from the ecological point of view, the most satisfactory oxidant is H₂O₂. From a mechanistic point of view, a similar oxidation mechanism of H₂O₂ [32] and K₂S₂O₈ [33, 34] is significantly different from NaOCl [35, 36] which produces higher quantity of chlorinated products. Acidification of effluent water, after oxidation with NaOCl, could generate chlorine gas as potential hazardous gas or produce chlorinated by-products. The third oxidant is the least satisfactory from both financial and ecological points of view. Considering the current price and quantity of all three oxidants, for 1: 5 molar ratio of sulfur, oxidant and weight ratio increased in

the following order S:H₂O₂ (1:5.3)> S:NaOCl(1:11.56)> S:K₂S₂O₈(1:42.28), and the most valid is the use of H₂O₂. These results clearly indicate that both the highest consumption and cost of K₂S₂O₈ make it unacceptable to be considered as an oxidant for waste oil treatment. Accordingly, the obtained results relate to applicative technology for waste oil treatment at a semi-industrial level based on hydrogen peroxide as material of choice due to a balanced contribution to higher cost and almost no ecological impact.

4. Conclusions

This paper presented the optimal laboratory procedure for the treatment of waste engine oil applied for the removal of sulfur containing compounds and heavy metals. After pretreatment of the oil sample by applying physical operations, centrifugation or filtration, desulfurization were performed using three oxidants: hydrogen peroxide, sodium hypochlorite, and potassium peroxodisulfate. The optimal conditions for waste oil treatment using the selected three oxidizing agents were defined. The reaction was performed under mild reaction conditions and without the application of the catalyst.

Based on the reproducibility of results which are characterized by a high degree of conversion, a possible semi-industrial or industrial level of application of a defined laboratory process of treatment of waste motor oil was presented. Regarding the proposed technologies for sulfur removal and metal from waste motor oil, the results indicate that metals removal is highly effective; however, sulfur level reduction is a not suitable, and conventional ODS method could be a better alternative than this method. Also, the additional extraction of acetonitrile

could increase sulfur removal at level 20-35 %. Quality of the obtained products indicates their possibility to be used either in a processes of the blending with raw oil or as a good material in the construction industry. From the techno-economical point of view, the price of oxidizing agents and oxidative efficiency play a decisive role in the design/selection of the appropriate technology. According to preliminary analysis, the most effective oxidant was potassium peroxodisulfate which is not acceptable from techno-economical point of view. In summary, the highest possible applicability was found for hydrogen peroxide.

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References

- [1] European automobile manufacturer's association (ACEA), Service fill oils for gasoline engines, light duty diesel engines, engines with after treatment devices and heavy duty diesel engines, Bruxelles, (2012).
- [2] Babich, I. V. and Moulijn, J. V., "Science and technology of novel processes for deep desulfurization of oil refinery streams: A review", *Fuel*, **82** (6), 607 (2003).
- [3] Song, C., "An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel", *Catal. Today*, **86** (1-4), 211 (2003).
- [4] Guoxian, Y., Shanxiang, L., Hui, C. and Zhongnan, Z., "Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon", *Carbon*, **43** (11), 2285 (2005).
- [5] Pfüller, O. and Walstra, F. P., DE 10217469 C1, Clariant Gmbh, (2003).
- [6] Funakashi, I. and Aida, T., EP 711819 B1, Jpn. Kokai Tokkyo Koho, (2002).
- [7] Morel, F., Boulet, M., Zuliani, M., Company, J. C., Nikitenko, P. and Loutaty, R., EP 621334 A1, Eur. Pat. Appl., (1994).
- [8] Forte, P., US 5582714 A, Uop, (1996).
- [9] Pfüller, O. and Walstra, F., DE 10217469 C1, Clariant Gmbh, (2003).
- [10] Yuje, H., Onuki, H., Sato, H. and Sugavara, T., US 5494572 A, General Sekiyu Kabushikikaisha, (1996).
- [11] Ford, J. F., Rayne, T. A. and Adlington, D. G., GB 972803, British Petroleum Co. Ltd., (1964).
- [12] Rayne, T. A., Ford, J. F. and Adlington, D. G., US 3341448 A, British Petroleum Co. Ltd., (1964).
- [13] Cole, E. L., Herbstman, S. and Wilson, R. F., US 3551328, Texaco Inc., (1970).
- [14] Guptill, F. E., Herbstman, S., Peck, R. A. and Wilson, R. F., US 3565793 A, Texaco Inc., (1971).
- [15] Yoo, J. S., US 3847798 A, Atlantic Richfield Co., (1974).
- [16] Fierce, W. L. and Weichman, R. L., US 3135680 A, Pure Oil Co., (1964).
- [17] Aida, T., Yamamoto, D., Iwata, M. and Sakata, K., "Development of oxidative desulfurization process for diesel fuel", *Rev. Heter. Chem.*, **22**, 241 (2000).
- [18] Mei, H., Mei, B. W. and Yen, T. F., "A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization", *Fuel*, **82** (4), 405 (2003).
- [19] Yu, G., Lu, S., Chen, H. and Zhu, Z., "Diesel fuel desulfurization with

- hydrogen peroxide promoted by formic acid and catalyzed by activated carbon”, *Carbon*, **43** (11), 2285 (2005).
- [20] Gunnerman, R. W., US 6500219 B1, Sulphco, Inc., (2002).
- [21] Gore, W., Bonde, S., Dolbare, G. E. and Skov, E. R., US 6596914 B2, (2003).
- [22] Cullen, M., US 20040074812 A1, Mark Cullen, (2004).
- [23] Rang, H., Kann, J. and Oja, V., “Advances in desulfurization research of liquid fuel”, *Oil Shale*, **23** (2), 164 (2006).
- [24] Sampanthar, J. T., Xiao, H., Dou, J., Teo, Y. N., Rong, X. and Kwan, W. P., “A novel oxidative desulfurization process to remove refractory sulfur compounds from diesel fuel”, *Appl. Catal., B*, **63** (1-2), 85 (2006).
- [25] Dehkordi, A. M., Kiaei, Z. and Sobati, M. A., “Oxidative desulfurization of simulated light fuel oil and untreated kerosene”, *Fuel Process. Technol.*, **90** (3), 435 (2009).
- [26] Mjalli, F. S., Ahmed, O. U., Al-Wahaibi, T., Al-Wahaibi, Y. and Al-Nashef, I. M., “Deep oxidative desulfurization of liquid fuels”, *Rev. Chem. Eng.*, **30** (4), 337 (2014).
- [27] Farshi, A. and Shiralizadeh, P., “Sulfur reduction of heavy fuel oil by oxidative desulfurization (ODS) method”, *Pet. Coal*, **57** (3), 295 (2015).
- [28] Milisavljević, S. S., Marinković, A. D. and Milosavljević, M. M., “New method for synthesis of N-alkyl and O-isopropylthiocarbamates by oxidation of ammonium salt of xanthogenic acid”, *Chem. Ind.*, **64** (5), 401 (2010).
- [29] ASTM D4294, Standard test method for sulfur in petroleum and petroleum products by energy dispersive X-ray fluorescence spectrometry, ASTM International, West Conshohocken, Pensilvanya (USA), (2016).
- [30] Shen, Y., Elele, E. and Khusid, B., “A novel concept of dielectrophoretic engine oil filter”, *Electrophoresis*, **32** (18), 2559 (2011).
- [31] Marinković, A. D., Milosavljević, M. M., Milenković, D. and Ivanović, G., “The optimization of zinc dialkyldithiocarbamates synthesis and determination of their antioxidant activity”, *Chem. Ind. Chem. Eng. Q.*, **14** (4), 251 (2008).
- [32] Kok, G. H., Wan Abu Bakar, W. A., Rusmidah, A., Chong, J. F. and Abdul Kadir, A. A., “Catalytic oxidative desulfurization of diesel utilizing hydrogen peroxide and functionalized-activated carbon in a biphasic diesel-acetonitrile system”, *Fuel Process. Technol.*, **91** (9), 1105 (2010).
- [33] Srinivasan, C., Kuthalingam, P. and Arumugam N., “Substituent and steric effects in the oxidation of alkyl aryl sulfides by peroxydisulfate”, *Can. J. Chem.*, **56** (24), 3043 (1978).
- [34] Trost, B. M. and Curran, D. P., “Chemoselective oxidation of sulfides to sulfones with potassium hydrogen persulfate”, **22** (14), 1287 (1981).
- [35] Irum, S., Akhtar, J., Sheikh, N. and Munir, S., “Oxidative desulfurization of Chakwal coal using potassium permanganate, ferric sulfate and sodium hypochlorite”, *Energ Source, Part A*, **39** (4), 426 (2017).
- [36] Wendi, L. and Eung, H. C., “Coal desulfurization with sodium hypochlorite”, *Energy Fuels*, **19** (2), 499 (2005).