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THERMOOXIDATIVE REGENERATION OF USED MINERAL MOTOR OILS

Bohdan Korchak[1, ✉], Oleg Grynyshyn[1], Taras Chervinskyy[1], Pavlo Shapoval[1], Andriy Nagurskyy[1]

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Abstract. The physico-chemical properties and group composition of the used mineral motor oils M-10DM and NORMAL 15W40, as well as the fractions obtained as a result of their thermooxidative regeneration have been studied. The results of IR-spectroscopic and X-ray fluorescence analysis of used oils and fractions obtained during thermooxidative regeneration are presented. The changes in the composition and properties of regenerated oils are described.

Keywords: thermooxidative regeneration, used oil, IR-spectroscopy.

1. Introduction

Used mineral motor oils (UMMO) are toxic, complex, multicomponent systems which are formed during the operation of a combustion engine. More than 140 types of carcinogenic polycyclic hydrocarbons have been identified in UMMO, the number of which increases in direct proportion to the duration of its life cycle [1, 2]. That is why UMMO are categorized as hazardous waste of the 4th grade of toxicity. The decisions of Stockholm and Basel Conventions [4], which demand control of UMMO formation and utilization, are in force in the world, including Ukraine. According to [3] the production of hazardous wastes should be minimized, adequate disposal plants should be installed, and eco-friendly utilization of waste containing hazardous carcinogens should be provided.

Today in Ukraine about 1 mln. tons per year of fresh oils are consumed and about 500,000 tons per year of used oils are officially collected. Such considerable bulk of UMMO is one of the most acute environmental problems, arising due to the insufficiently developed collection system and almost undeveloped capacities for their regeneration [4].

It is well-known that the chemical composition of oil during operation changes slightly. Approximately 75–80 % of oil components remain unchanged; the products of oil physico-chemical transformations, as well as impurities which make oils unsuitable for further use, are ~20–25 %. Owing to "aging" products removal from UMMO it is possible to obtain oil, the properties of which should correspond to those of fresh oil produced from petroleum raw materials. Therefore, the development of regeneration technology for used oils with a high yield of resulting product and ability to adjust it to domestic refineries without significant upgrading of existing equipment is an urgent problem [5]. The thermooxidative process is one of such methods. In works [6, 7] the authors show the possibility of using thermooxidative method to purify diesel and kerosene fractions from sulfur compounds and resins. It would be interesting to know if this method is suitable for the UMMO regeneration.

The essence of the process is to oxidize the primary products of UMMO aging to the formation of condensation products and their extraction using vacuum distillation. Previously [8] we established the optimal parameters of the thermooxidative regeneration for industrial oils, but they are not sufficient to assert that the base oil is produced as a result of UMMO regeneration. Moreover, the change in operational properties for motor oils M-10DM and NORMAL 15W40 as well as their group hydrocarbon composition were studied [9, 10]. The formation of oxygen-containing products of oils "aging" was confirmed during their prolonged use in internal combustion engines and the changes in the composition of inorganic part were observed, which are explained by the action of additives and wear products of the engine. The obtained results can serve as the source information for choosing the optimum technology for used oils regeneration.

So, the purpose of this work was to establish optimal conditions for the thermooxidative regeneration of waste motor oils and to study the characteristics of regenerated oils.

[1] Lviv Polytechnic National University
12, S.Bandery St., 79013 Lviv, Ukraine
✉ *kor4ak93@gmail.com*

2. Experimental

Used motor oils M-10DM and NORMAL 15W40, removed from the crank case of diesel and gasoline engines, respectively, after the expiration of their operation were the starting materials for researches.

UMMO thermooxidative regeneration was carried out on a laboratory setup consisting of a reactor unit, a system of compression and air purification, cooling and trapping of gaseous reaction products, devices for control and measurement of temperature, pressure, *etc*. Vacuum separation into fractions was carried out at 623 K and a residual pressure of 1.07–1.20 kPa. The following fractions were obtained: strippant, regenerated oil and residue. The obtained products were studied and analyzed according to standard methods described below.

The density of the samples was determined picno-metrically, the refraction index – using a refractometer, viscosity – using a viscosimetry method, flash point in the device of the open type [11]. Group hydrocarbon composition was studied by a chromatography. The silica alumina gel of ASK type was used as an adsorbent. Fractions of hydrocarbons were washed out by petroleum ether and benzene, and asphalt-resinous substances were desorbed by alcohol-benzene mixture.

X-ray fluorescence was used to determine the elemental composition of oils. A mobile precision analyzer EXPERT 3L was used, the assignment of which is to determine the mass fraction of chemical elements in monolithic and homogeneous powder objects [12]. For the analysis we prepared the samples, which were burned at 723 K for 4 h, cooled in a desiccator and then grinded.

IR spectroscopy was performed on Spectrum Two FT-IR spectrometer (PerkinElmer) using Spectrum v.10.03.06 program. The thickness of the cell made of zinc selenide was 0.1036 mm.

For mathematical modelling of the process Mathcad 15.0 was used [13].

3. Results and Discussion

3.1. Determination of Optimum Parameters

To determine the optimum parameters of thermooxidative regeneration, a series of experiments was carried out varying temperature, pressure and process time. The experimental results are represented in Table 1.

Table 1

Determination of optimum parameters

Process parameter		Viscosity, mm^2/s		ν_{50}/ν_{100}	Viscosity index	Acid number, mg KOH/g	Yield, wt %
		ν_{50}	ν_{100}				
Temperature, K*	standard conditions	51.65	10.22	5.05	88	2.71	–
	453	58.27	11.17	5.21	93	2.19	78.40
	473	62.05	11.67	5.30	98	1.45	73.50
	493	63.35	12.00	5.43	100	1.28	69.94
Time,h**	standard conditions	51.65	10.22	5.05	88	2.71	–
	1.0	58.51	11.03	5.28	92	1.98	78.37
	2.0	61.65	11.47	5.30	98	1.62	75.34
	3.0	62.05	11.67	5.32	101	1.45	72.50
Pressure, MPa***	standard conditions	51.65	10.22	5.05	88	2.71	–
	1.0	59.61	10.95	5.44	94	2.11	77.95
	2.0	62.05	11.67	5.32	98	1.45	73.50
	3.0	62.67	11.94	5.03	101	1.39	70.12

Notes: * process time is 2.0 h, pressure is 2 MPa; ** temperature is 473 K, pressure is 2 MPa; *** temperature is 473 K, time is 2 h

To study the effect of optimum parameters on the viscosity index, acid number and ratio ν_{50}/ν_{100} the mathematical model was built [16]. In this case the regression equations are possible:

$$y_1 = b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 - b_{23}x_2x_3 + \gamma_{12}x_1x_2(x_1-x_2) + \gamma_{13}x_1x_3(x_1-x_3) + \gamma_{23}x_2x_3(x_2-x_3) - b_{123}x_1x_2x_3$$

$$y_2 = b_1x_1 + b_2x_2 - b_3x_3 - b_{12}x_1x_2 - b_{13}x_1x_3 - b_{23}x_2x_3 + \gamma_{12}x_1x_2(x_1-x_2) - \gamma_{13}x_1x_3(x_1-x_3) - \gamma_{23}x_2x_3(x_2-x_3) + b_{123}x_1x_2x_3$$

$$y_3 = -b_1x_1 + b_2x_2 - b_3x_3 - b_{12}x_1x_2 + b_{13}x_1x_3 - b_{23}x_2x_3 + \gamma_{12}x_1x_2(x_1-x_2) - \gamma_{13}x_1x_3(x_1-x_3) - \gamma_{23}x_2x_3(x_2-x_3) + b_{123}x_1x_2x_3$$

where parameters of the model are: x_1 is a process temperature, ºC; x_2 is time, h; x_3 is pressure, MPa and response functions are: $y_1 = \nu_{50}/\nu_{100}$; y_2 is viscosity index; y_3 is acid number, mg KOH/g.

When substituting in the equation for y_1 all values of the parameters x_1, x_2 and x_3 and the values of y_1 corresponding to each set of parameters, we obtain a system of equations, the solution of which gives the value of the regression coefficients for the given response function. Similar systems of equations are obtained for other response functions of the mathematical model (y_2 and y_3). When solving each of these systems of equations, we obtain a set of regression coefficients for each response function. To verify the adequacy of the mathematical model, we substitute the parameters values and compare the calculated response functions with the experimental data.

Substituting regression coefficients into regression equations and denoting the model parameters and the response functions by the symbols representing their physical content, we obtain the final form of the mathematical model:

– for ν_{50}/ν_{100}:

$$y_1 = 0.00975x_1 + 0.322x_2 + 0.00701x_3 + 0.001607x_1x_2 + 0.000250x_1x_3 - 0.301x_2x_3 + 0.00000037x_1x_2(x_1-x_2) + 0.00000658\,x_1x_3(x_1-x_3) + 0.00000457x_2x_3(x_2-x_3) - 0.000667\,x_1x_2x_3;$$

– for viscosity index:

$$y_2 = 0.00234x_1 + 3.245x_2 - 0.0035x_3 - 0.0097x_1x_2 - 0.0559x_1x_3 - 0.0452x_2x_3 + 0.000303x_1x_2(x_1-x_2) - 0.000507x_1x_3(x_1-x_3) - 0.000451x_2x_3(x_2-x_3) + 0.00157x_1x_2x_3;$$

– for acid number:

$$y_3 = -0.0000114x_1 + 0.393x_2 - 0.0113x_3 - 0.000296x_1x_2 + 0.000450x_1x_3 - 0.0452x_2x_3 + 0.00000151x_1x_2(x_1-x_2) - 0.00000167x_1x_3(x_1-x_3) - 0.0000154x_2x_3(x_2-x_3) + 0.000517x_1x_2x_3.$$

The obtained regression equations enable to determine the dependence of viscosity index, acid number and ratio ν_{50}/ν_{100} on the process parameters (pressure, temperature, time) by the calculation method.

According to the data of Table 1 it is established that the thermooxidative regeneration of UMMO for 2 h at 473 K and pressure of 2 MPa have a positive effect on the target product. The regenerated mineral oil can serve as a base component for the production of oils, or in other industries. By-products (strippant and residue after vacuum distillation) may be raw material components to produce fuel and bitumen, respectively.

3.2. Physico-Chemical Properties

The operational properties of the target and by-products of UMMO thermooxidative regeneration are given in Tables 3 and 4.

As can be seen from Tables 3 and 4, the oils regenerated *via* thermooxidative regeneration have better properties than used oils. They are characterized by lower values of acid and base numbers, lower ash content, coking ability and content of mechanical impurities.

Unlike used oil, the regenerated oil does not contain water; its viscosity index is higher. At the same time, the residue after vacuum distillation is characterized by higher values of ash content, coking ability, mechanical impurities content and acid number to compare with regenerated oil.

3.3. Change in Group Hydrocarbon Composition

The results of studying the group composition of used oils and fractions obtained during thermooxidative regeneration are shown in Figs. 1 and 2.

Regenerated oils are characterized by a higher content of paraffin-naphthenic hydrocarbons and a lower content of aromatic hydrocarbons as compared with used oils. The amount of paraffin-naphthenic hydrocarbons passed into residue is smaller but the amount of aromatic hydrocarbons is greater.

Table 2

Values of calculated regression coefficients

	ν_{50}/ν_{100}	Viscosity index	Acid number
b_1	0.00975	0.00234	0.0000114
b_2	0.322	3.245	0.393
b_3	0.00701	0.0035	0.0113
b_{12}	0.001607	0.0097	0.000296
b_{13}	0.000250	0.0559	0.000450
b_{23}	0.301	0.0452	0.0452
γ_{12}	0.00000037	0.000303	0.00000151
γ_{13}	0.00000658	0.000507	0.00000167
γ_{23}	0.00000457	0.000451	0.0000154
b_{123}	0.000667	0.00157	0.000517

Table 3

Operational properties of M-10DM and products after its thermooxidative regeneration

Index	UMMO	Thermooxidative regeneration		
		Strippant	Regenerated oil	Residue
Viscosity, mm^2/s:				
– at 323 K, ν_{50}	51.65	18.15	62.05	117.18
– at 373 K, ν_{100}	10.22	5.05	11.67	16.66
– ν_{50}/ν_{100}	5.05	3.59	5.30	7.03
Viscosity index	88	102	98	74
Density, kg/m^3	884	857	863	910
Acid number, mg KOH/g	2.71	2.49	1.45	2.29
Base number, mg KOH/g	0.35	0.23	0.18	0.12
Water content, %	0.14	–	–	–
Mechanical impurities content, %	0.062	traces	0.015	0.198
Coking ability, %	2.30	0.16	1.63	6.84
Ash content, %	0.940	0.001	0.022	4.21
Freezing point, K	254	251	250	259
Flash point, K	488	471	513	543
Fraction yield, wt %	–	7.23	73.50	14.77

Table 4

Operational properties of NORMAL 15W40 and products after its thermooxidative regeneration

Index	UMMO	Thermooxidative regeneration		
		Strippant	Regenerated oil	Residue
Viscosity, mm^2/s:				
– at 323 K, ν_{50}	69.81	37.85	70.13	81.30
– at 373 K, ν_{100}	13.96	8.96	14.17	13.56
– ν_{50}/ν_{100}	5.0	4.22	4.94	5.99
Viscosity index	110	115	104	75
Density, kg/m^3	896	862	895	918
Acid number, mg KOH/g	1.96	1.73	0.97	1.62
Base number, mg KOH/g	3.46	2.87	2.27	1.89
Water content, %	0.15	–	–	–
Mechanical impurities content, %	0.039	traces	0.012	0.165
Coking ability, %	1.71	–	1.04	6.73
Ash content, %	0.534	0.003	0.036	1.58
Freezing point, K	255	252	253	258
Flash point, K	511	478	521	533
Fraction yield, wt %	–	8.38	74.25	13.37

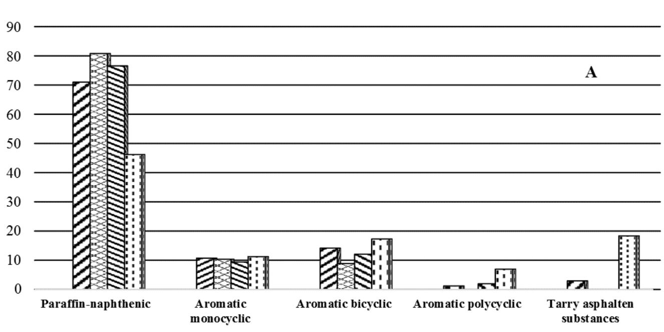

Fig. 1. The group hydrocarbon composition of M-10DM and its products after thermooxidative regeneration

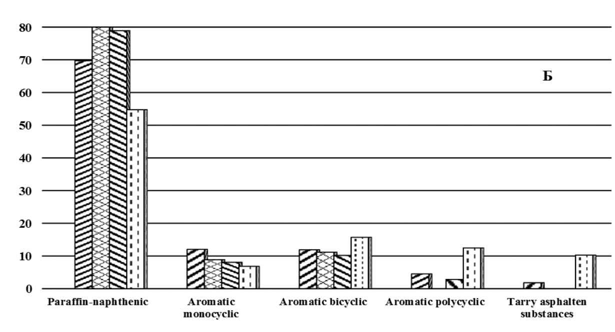

Fig. 2. The group hydrocarbon composition of NORMAL 15W40 and its products after thermooxidative regeneration

Thus, we can state that regenerated mineral oils which are characterized by the low content of undesirable polycyclic aromatic hydrocarbons and the absence of tarry asphaltene substances allows them to be used as components of base oils or as lubricants in various industries.

Table 5

XRF analysis of UMMO thermooxidative regeneration

Element	Content, ppm			
	M-10DM		NORMAL 15W40	
	in used oil	in residue	in used oil	in residue
Mg	–	–	549.75	2336.44
Si	–	–	139.97	594.87
P	2950.99	12541.71	2797.05	11887.46
S	6166.21	26206.39	6401.21	27205.14
Ca	16006.38	68027.12	1445.68	6144.14
Cr	–	–	52.63	223.68
Mn	7.09	30.13	8.8	37.40
Fe	307.10	1305.18	696.36	2959.53
Ni	–	–	5.81	24.69
Cu	–	–	74.05	314.71
Zn	4033.07	17140.55	4360.95	18534.04
As			2.99	12.71
Rb	–	–	1.99	8.46
Zr	0.17	0.72	–	–
Sr	4.14	17.60	2.16	9.18
Mo	1.48	6.29	48.15	204.64
Pb	26.90	114.33	16.11	68.47

3.4. X-Ray Fluorescence Analysis

The strippant and the basic oil fraction obtained as a result of thermooxidative regeneration are characterized by low ash content and coking ability (Tables 3 and 4). At the same time, the residues after vacuum distillation have much higher values of these indices. Therefore, the next step was to establish the inorganic composition of the residues. The experimental results are given in Table 5.

The obtained regenerated oils are characterized by low ash content and coking ability, indicating the decrease of inorganic components in their composition. At the same time, the products of additives and wear parts decomposition are concentrated in the residue [14].

3.5. IR Spectroscopy

To confirm the changes in the group composition of regenerated oils IR spectroscopy was used. The results are shown in Figs. 3 and 4.

As can be seen from Fig. 3, IR spectra of used and regenerated M-10DM differ by the absorption bands. Paraffin-naphthenic hydrocarbons were identified by stretching vibrations at 2935–2915 cm^{-1}, as well as deformation vibrations of CH group at 1470–1445 cm^{-1} and stretching vibrations of C–C group at 1740–1720 cm^{-1}. The presence of aromatic hydrocarbons in oils was confirmed by an intensive absorption band of CH group at 860 cm^{-1}. In addition, skeletal vibrations of C–C bond of the aromatic nucleus are observed in the region of 1610–1600 cm^{-1} [15-17].

Oxygen-containing products (alcohols, aldehydes, ketones, organic acids, *etc.*) were identified in both used and regenerated oils. Their presence is confirmed by the change in absorption bands intensity of C=O stretching vibrations in the region of 1740–1690 cm^{-1}, as well as by stretching vibrations at 1820–1740 cm^{-1} and by asymmetric stretching vibrations of C–O bond in the region of 1260–1150 cm^{-1}.

The IR spectra of regenerated NORMAL 15W40 oil (Fig. 5) have a similar relationship.

As can be seen from Fig. 5, infrared spectra of used and regenerated oil NORMAL 15W40 differ by their absorption bands. For regenerated oil we observe the change in the absorption bands typical of oxygen-containing products. It means that the content of oxygen-containing products is decreased. The presence of mentioned products in IR spectra is confirmed by absorption bands of C=O stretching vibrations in the region of 1740–1690 cm^{-1}, as well as by stretching vibrations at 1820–1740 cm^{-1} and asymmetric stretching vibrations of C–O bond in the region of 1260–1150 cm^{-1}.

4. Conclusions

The optimum parameters of thermooxidative regeneration process of used mineral motor oils (UMMO) were determined: temperature is 473 K, pressure is 2 MPa and process time is 2.0 h. In comparison with used oils the regenerated oils are characterized by higher viscosity index (by 7.2–11.3 %), lower ash content (by 93.3–97.6 %), lower coking ability (by 29.1–39.1 %) and lower acid number (by 46.5–50.5 %).

The operational properties and the group hydrocarbon composition of M-10DM and NORMAL 15W40 oils, as well as fractions obtained as a result of their thermooxidative regeneration, were studied. The change in the distribution of the hydrocarbon part of used oils in the resulting fractions was established. The results of XRF confirmed that the metals included in the additives are concentrated in the residue due to UMMO thermooxidative regeneration. The hydrocarbon composition and the change in the amount of oxygen-containing products were confirmed by IR spectroscopy.

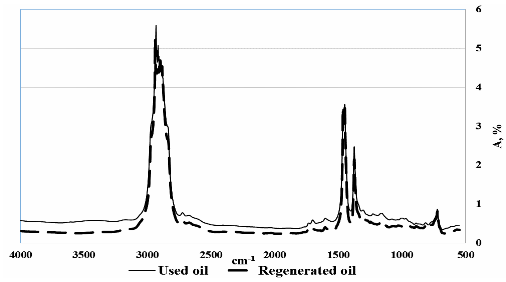

Fig. 3. IR spectra of used and regenerated oil M-10DM

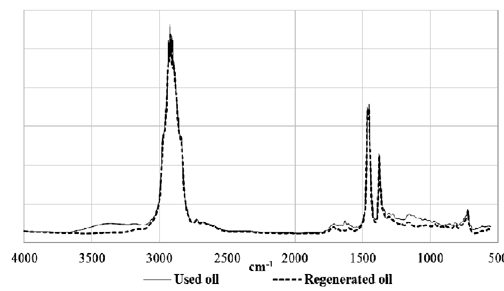

Fig. 5. IR spectra of used and regenerated oil NORMAL 15W40

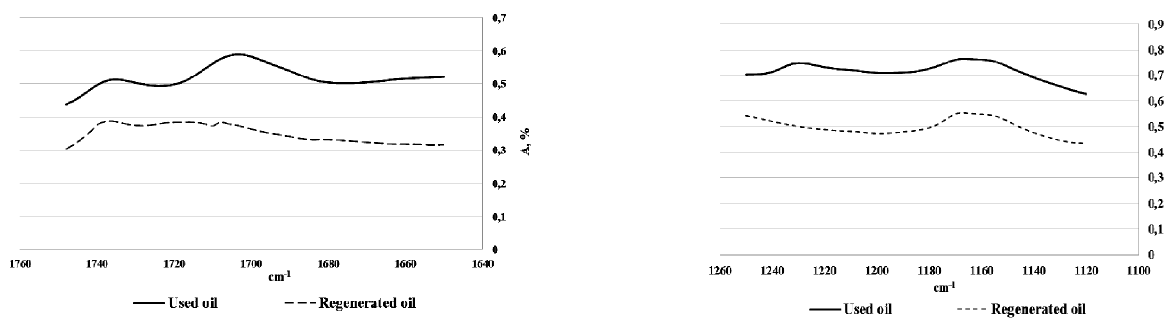

Fig. 4. Changes in the absorption bands intensity of carboxylic acids (1740–1640 cm-1) and their derivatives (1250–1110 cm^{-1}) as a result of thermooxidative regeneration of M-10DM

Thermooxidative regeneration has a positive effect on restoring the UMMO operational properties. However, in most cases it cannot be used as an independent process, since regenerated oils require an additional aftertreatment. However, it can serve as an intermediate stage of a certain complex process of regeneration of used mineral motor oils.

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ТЕРМООКИСНЮВАЛЬНА РЕГЕНЕРАЦІЯ ВІДПРАЦЬОВАНИХ МІНЕРАЛЬНИХ МОТОРНИХ ОЛИВ

***Анотація**. Вивчено фізико-хімічні властивості та груповий склад відпрацьованих мінеральних моторних олив М-10ДМ та NORMAL 15W40, а також фракцій, одержаних внаслідок їх термоокиснювальної регенерації. Наведено результати ІЧ-спектроскопічного та рентгенофлуоресцентного аналізу відпрацьованих олив та одержаних фракцій. Описано зміну складу і властивостей регенерованих олив внаслідок термоокиснювальної регенерації.*

***Ключові слова:** термоокиснювальна регенерація, відпрацьована олива, ІЧ-спектроскопія, рентгенофлуоресцентний аналіз.*