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Chapter 18

REFINING OF PETROLEUM PRODUCTS USING INORGANIC MEMBRANES

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ABSTRACT

The level of use of natural resources and the degree of environmental degradation are the main problem of modern society that's why this chapter discusses some aspects of the development, operation and environmental-economic efficiency of such local systems for machine-building en-terprises, namely, the technology and hardware design of the process of waste oil regeneration and fuel purification with the use of inorganic membranes and making creation of local systems with high characteristics possible.

Keywords: petroleum products, inorganic membranes, regeneration, oil, wastewater

INTRODUCTION

The widespread use of oils and petroleum products (hydraulic fluids, fuels, lubricants, etc.) in industrial enterprises leads to the fact that the waste water (SV) of any enterprise contains more or less petroleum products. Therefore, full or partial recovery and use of used oils (OM) and petroleum products in production ensures environmental protection, saving of natural and energy resources [1-3]. For enterprises of the machine-building complex, pulp and paper, microbiological and other industries, this problem is solved by creating local systems for the treatment and regeneration of wastewater, oils, solutions and process liquids containing petroleum products. The combination of traditional and membrane processes in these systems ensures not only environmental protection, but also rational use of natural resources-the return of water, oils or process fluids to production and the recovery of valuable components from waste.

During operation in machines and mechanisms, oils come into contact with metals, air, are polluted with water and dust, are liquefied with fuel, are exposed to temperature, pressure, electric field and other factors that change the properties of oils over time: viscosity changes, acid number increases, ash content and cokingability, the flash point decreases, the content of water and mechanical impurities increases, color and performance properties deteriorate.

According to data from 1989, about 6 million tons of waste oil products enter the biosphere every year, of which more than half was spent oil (OM). This is confirmed by the approximate data on the world production of fresh and used lubricants [4].

Production of fresh products (million tons / year):

petroleum oil	30
synthetic oil	0.7
lubrications	1
concentrates (for cutting fluids)	1.5

Collection of waste products (million tons / year)

petroleum oils	15
of them:	
is being processed	1.5
used as fuel	10.5
gets into the biosphere	3

In accordance with the data presented, the regeneration of about 1.5/30 = 5% used petroleum oils.

Table 1. Education and consumption of used oils in different countries, thousand tons / year (2019 data)

Country	Oil consumption	Waste Oil Collection	Waste oil recycling	Recycling of used oils from collected ones, %
Russia and CIS countries	7800	1700	260	15
USA	10000	4000	around 400	10
Canada	1400	-	around 250	-
Germany	1460	730	400	55
Great Britain	800	200	150	75
France	850	250	200	80
Italy	630	200	150	75
Holland	500	200	15	7.5

Comparison of the above-mentioned balance of production of fresh and regenerated waste oil products with similar indicators for 2019, which are illustrated in Table 1, shows:

- annual production of fresh oils increased by 30% from 30 million tons to 40 million tons;
- the countries indicated in table 1 process from 7.5% to 80% of the collected waste oils;
- France, Great Britain and Italy are the leaders in the recovery and reuse of used oils. In the UK there are more than 1000 small sized installations for restoring the properties of used technical oils to the level of basic ones;
- the degree of oil regeneration in Russia and the CIS countries was 260/1700 = 15.3%, which is much less than in the USSR. For example, only one plant in the city of Kremenchug had a capacity of up to 240 thousand tons / year.

The main conclusion from the analysis of the above and other data is that over 30 years, the degree of regeneration and reuse of used mineral oils has increased slightly, namely from 5% to (2.4 million tons / year)/(40 million tons / year) = 6%.

In this regard, our developments in this area are very relevant and quite promising in terms of opening our own business. Refining using our technologies and reusing used mineral oils only reduces energy consumption by 15-20 times than those needed to obtain the same amounts of base oil from crude oil.

EXPERIMENT

Used lubricating oil (ULO) refers to liquid waste. UO and ULO - this is any oil obtained from crude oil or synthetic oil, contaminated as a result of exploitation by physical and chemical impurities, for example, metal particles, water, dirt and chemicals. Gradually, their number increases and exceeds that border to which it is still possible to use lubricant for its intended purpose.

Environmentally friendly disposal of ULO is their cleaning and processing in order to obtain various marketable products of both base oils and greases, fuels, preservation materials and other petroleum products.

In the technical literature, when considering the issues of processing UO, different terms are used - *cleaning, regeneration and recycling*.

The term *cleaning* (reclaiming, reclamation) refers to the continuous or periodic cleaning of a working lubricant in existing equipment, carried out using sedimentation tanks, filters, centrifuges and adsorbents. Such cleaning does not always lead to the production of oil, in quality corresponding to the level of fresh lubricant.

The term *regeneration* (replication) refers to restoring the quality of an individual, fully spent material to the level of fresh. It is used in relation to the cleaning of lubricants, mainly containing no additives. To conduct regeneration, more complex physical and chemical processes are used - coagulation, sulfuric acid and adsorption treatment.

In the case of processing mixtures of various oils collected centrally from industrial enterprises, *the term recycling* is used. (rerunning). From such raw materials, it is possible to obtain base oils of various compositions and purposes, as well as diluents and other by-products. Recycling is carried out only at large specialized enterprises and involves the use of a complex of processes - vacuum distillation, extraction, hydrotreating [1-5].

In addition to the low yield of regenerated oil, traditional technologies also have another significant drawback - the formation of difficult to recycle and environmentally hazardous waste. For example, during adsorption treatment it forms 50-360 kg / t of spent sorbent, and in case of acid-contact cleaning, up to 200 kg / t of hard-to-recover tar. In the processes of UO recycling, the formation of 200-300 kg / t of wastewater containing phenols, mercaptans and other harmful substances occurs. Therefore, the improvement of UO regeneration technological processes is an urgent and economically feasible problem, and the use of membrane technology is a key condition that provides a solution to this problem.

The results of purification and regeneration of UO using inorganic membranes based on ceramics and carbon with membrane layers of aluminum and titanium oxides, respectively, were obtained from the operation of industrial plants of various capacities and are presented in Tables 2-5.

Tables 2-5 summarize the test results of membrane plants for the regeneration of used industrial (OUI), transformer (OUT), and motor (OUM) oils for passenger cars VAZ.

From the Tables 2 and 3, it is seen that inorganic membranes make it possible to restore the quality of industrial and transformer oils and to ensure their reuse.

The use of inorganic membranes allows you to effectively clean engine oil (see Table 4).

The indicators of refined m fresh oil are the same (except for viscosity). This is due to the fact that during cleaning, the used additives are removed from the oil and due to this, the viscosity decreases. It is supposed to have a device for the preparation of oil purified using membrane technology for reuse, where necessary additives will be introduced. When oil was refined using inorganic (carbon or ceramic based) membranes, the yield of purified oil was 85–90%.

Table 2. The results of the regeneration of waste oils

	Oil		
	used	**purified**	**new**
Viscosity (50 °C), cСт	18 ÷ 45	22 ÷ 50	22÷50
Content of mechanical impurities, %	0,03 ÷ 0,9	0 ÷ 0,005	0÷0,005
Ash content, %	0,01 ÷ 1,3	0,003 ÷ 0,007	0,005
Acid number, mg KOH/g	0,1 ÷ 2,0	0,01 ÷ 0,12	0,005

Table 3. The results of regeneration of used transformer oil

Characteristic	**Oil**		
	used	**purified**	**new**
Viscosity (50 °C), cСт	6,81	6,6	8 (no more than)
Content of mechanical impurities, %	0,01	absent	absent
Acid number, mg KOH/g	0,08	0,05	0,05
Flash point, °C	148	138	135(nevertheless)
Optical density (natron sample)	2,8	1,8	1,8
Density (20 °C), g / cm^3	0,870	0,864	0,900

Table 4. The results of the cleaning of used engine oil

Characteristic	Oil		
	used	**purified**	**new**
Viscosity (50 °C), cCт	6,5 ÷ 10	6 ÷ 9	12 ÷ 13
Content of mechanical impurities, %	0,04 ÷ 1	0 ÷ 00,5	up to 0,01
Ash content, %	0,5 ÷ 1,3	0,07÷0,3	0,4 ÷ 0,7
Acid number, mg KOH/g	0,4 ÷ 1,8	0,2÷0,6	0,2 ÷ 1,2

Membrane cleaning plants (MCP) with ceramic membranes have higher technical characteristics compared to polymer membranes, as can be seen from Table 5.

For example, the permeability of inorganic membranes in the treatment of industrial waste oil was 6 l/m^{2}h.

Currently, the permeability of ceramic membranes ranges from 5 to 400 l/m^{2}h depending on the type of oil and its contamination, temperature, operating pressure and other factors. Therefore, the use of membrane technology makes it possible to simplify and make more economical schemes for cleaning, regeneration and recycling of used oils.

Table 5. Cleaning of waste oils using inorganic membranes and polymer hollow fibers

Characteristic	Selectivity of oil purification by indicators φ, %	
	Plant MCP	**Installation of company ITO (Japan) and polymer membranes (USA)**
Content of mechanical impurities	98÷100	65÷68
Ash content	72÷94	60÷68
Optical density	60÷93	25÷35
Asphalt-resinous compounds	25÷40	0÷15
Permeability G, l/m^2·h	4÷6	1÷1.5

The block diagram of the regeneration process using the UO membrane technology and the preparation of fresh (commercial) oil on its basis is shown in Figure1.

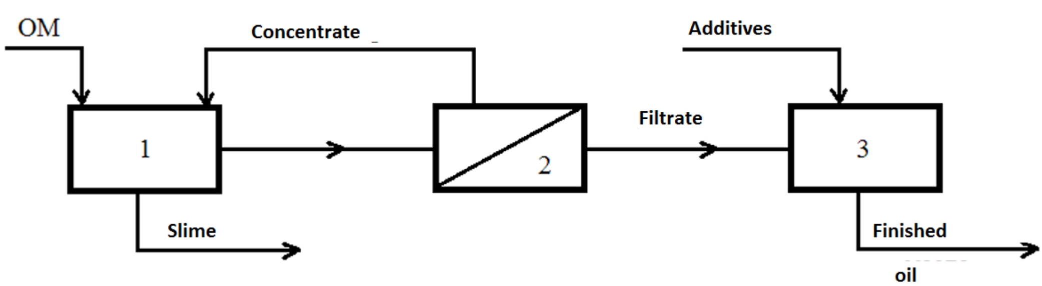

Figure 1. Block diagram of UO regeneration and preparation of fresh (boiled) oil on its basis: 1-OM pretreatment unit; 2-membrane cleaning unit; 3-additive injection unit (compounding).

At the pre-treatment stage of the OM, coagulation or settling processes occur, or some other traditional process. Then the membrane cleaning is carried out, which allows you to get an oil base. At the third stage, the necessary additives are introduced into the oil base, resulting in a ready-made commercial oil.

For the regeneration of industrial, transformer, compressor, turbine and other types of oils, diesel fuel purification, 220 installations for various purposes and capacities were manufactured and operated without replacing the membrane elements for 7-9 years. Oil recovery units had a capacity of 25-270 l / hour, and for fuel purification-25-8000 l / hour. For example, low-performance devices were used in running turbines or engines of buses and tanks. In the oil system of a turbine with synthetic oil, inorganic membranes continuously maintain the properties of the oil in working condition.

Table 6. Cleaning of fuel with the use of membranes based on ceramics

Diesel fuel	**Content, %**		**Ash content, % (mass.)**	**Acid number, mg KOH/100g**	**Membrane permeability, l/(m²h)**
	mechanical admixture	**sulfur**			
Cleaning at 25 °C					
Before cleaning	0.09	0.76	0.0034	0.06	-
After cleaning with membranes					
1	absent	0.76	0.003	0.041	12 ÷ 30
2	absent	0.76	0.0033	0.046	17 ÷ 35
Cleaning at 50 °C					
Before cleaning	0,041	0,8	0,032	0,062	-
After cleaning with membranes					
1	absent	0.78	0.0023	0.041	37 ÷ 40
2	absent	0.79	0.0024	0.051	37 ÷ 50
3	absent	0.76	traces	0.039	37 ÷ 40
Membrane designations: 1,2-ceramic with pore diameters respectively 0.7-1 microns and 0.1-0.3 microns, 3-electrically conductive. Working pressure-4-4. 5 MPa.					

Ceramic membranes are effectively used, as can be seen from table 6, and when cleaning the fuel immediately before feeding it to the engine, the economy of diesel fuel was provided from 3% (bus fleet in Istanbul) to 10% (Russian tanks) and an increase in the motor life of such an engine by 1.5-3 times.

CONCLUSION

MCP -type installations are easy to install and operate and can be recommended for industrial implementation in enterprises with oil consumption of more than 20 tons per year.

With such an annual volume of oil consumption, capital investments for cleaning and regeneration at the place of consumption will fully pay for themselves within 8-12 months, depending on the contamination of waste oil and the cost of spent (regenerated) oil. This also applies to large lubrication systems with a tank volume of more than 0.8 m^3 [4, 5].

According to our data, the highest payback is achieved when regenerating turbine synthetic oils. In this case, the payback for the installation of MCP is about 15 days. As an example, we can cite the operation of the MCP unit for maintaining synthetic turbine oil in working condition at a thermal power station with the highest efficiency coefficient in Russia – 42%. In this case, the payback of the installation was achieved in 5 days.

Thus, the use of MCP installations for cleaning used oils will ensure their reuse and reduce energy consumption by 15-20 times, which will significantly reduce environmental pollution and save oil resources of any country. The latter conclusion is confirmed by data from Total (France), which showed that 1 ton of oil refined for reuse makes it possible to save 7-9 tons of crude oil.

It was found that the use of ceramic membranes provides almost complete removal of water and mechanical impurities from the fuel, reduces the content of sulfur, reduces the value of the acid number and the ash content. As a result, it is achieved: an increase in engine life by 1.5-3 times, a reduction in fuel consumption (economy) by 3-10%, an increase in the service life of exhaust afterburning catalysts by 1.5-2 times and a reduction, due to these factors, of the amount of harmful emissions from the use of these catalysts by 50-80%.

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