

# Petroleum and Coal

## Article

## Open Access

### TECHNOLOGY OF RECYCLING WASTE LUBRICANT GREASES

Andrey Grigorov<sup>1</sup>, Ivan Nahliuk<sup>2</sup>, Oleg Zelenskii<sup>1, 3</sup>, Natalia Ponomarenko<sup>4</sup>

<sup>1</sup> National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine

<sup>2</sup> Kharkiv National Automobile and Highway University, 61002, 25 Yaroslava Mudrogo str, Kharkov, Ukraine

<sup>3</sup> Ukrainian State Research Institute for Carbochemistry, 61023, 7 Vesnina str., Kharkov, Ukraine

<sup>4</sup> Ukrainian State University of Railway Transport, 61050, 7 Feuerbach square, Kharkov, Ukraine

Received March 14, 2019; Accepted May 21, 2019

#### Abstract

A scheme for the production of plastic greases based on high-boiling fractions of oil sludge and used lubricating oils, as well as polymer waste, in the form of HDPE, LDPE, and PP, that is used as a thickener, has been proposed. Based on the used lubricating oils and polymer thickeners, grease lubricants were obtained. They can be used in the temperature range, on average, up to 80–130 °C (depending on the polymer) and speed mode in the bearing up to 4000 rpm. These greases are not worse in their properties to classical ones; analogs obtained based on distillate fractions, thickened with metal soaps, which are widely used in industry today.

**Keywords:** Grease; Recycling; Dispersion medium; Thickener; Polymer additives; Waste; Preparation of raw materials.

## 1. Introduction

In the recent decade in the technosphere, so-called recycling technologies have been widely developed. They allow expanding the raw material base for many technological processes, in particular in oil refining, through the use of secondary raw materials. These technologies, compared with those that have been around for more than a decade, have been used in the production of marketable petroleum products, and have a number of significant advantages to which include using of industrial and household waste; reducing the cost of production associated with the purchase of raw materials; increasing the production culture and improving the environmental situation.

## 2. The purpose and objectives of the research

A series of directives [1-2] adopted in the EU and their associate members, in particular in Ukraine, served as an impetus for the development of amendments to the Law of Ukraine "Waste." They governed the behavior of waste based on its sorting by type. Sorting waste by type is the initial stage of any recycling technology, on which its effective implementation largely depends. Also, a lot of important requirements for waste, as the raw material of recycling technology, are its quantity, which is able to provide the necessary production volumes of processing.

Today, the leading place in the world among multi-ton liquid industrial wastes, consisting mainly of hydrocarbons, is oil slime – oil sludge, which is formed when using technological equipment at refineries and used lubricating oils. The peculiarities of their chemical composition make it possible to apply thermo-destructive processing technologies to them, using catalysts, aimed at obtaining different types of fuels. An example is the pyrolysis-reforming technology of oil sludge, which allows you to get up to 35.5 wt% of fuel, its chemical composition (C<sub>7</sub>–C<sub>26</sub>) is similar to diesel fuel and having a value of higher heat of combustion of 46.1 MJ/kg

and cetane index 38.51. As a catalyst in this process, it is proposed to use ash, which, due to the content of elements of iron and sulfur, has catalytic properties [3]. A variant of the technology of pyrolysis of oil sludge using a nitrogen carrier gas, in the temperature range of 378–873 K, is proposed. The gaseous products of this technology are 50.88 wt% CO<sub>2</sub>; 17.78 wt% H<sub>2</sub>O; 6.11 wt% CO and 25.23 wt% of low molecular weight paraffins and olefins (C<sub>1</sub>–C<sub>2</sub>). The liquid distillate has a calorific value of 45.35 MJ/kg, and its characteristics resemble diesel fuel [4]. Also, it is a very interesting technology of turning oil sludge into pyrogas, which can be used as fuel, by heating it to 1000°C in a plasma arc, without oxygen access [5].

There is a technology for producing fuel, in its characteristics similar to diesel fuel, through pyrolytic distillation, used engine oil. The fuel yield is up to 60 % of the raw materials [6]. In work [7], it was proposed to obtain fuel according to its characteristics (octane number 96 units, flash point 245 K) similar to gasoline, from used engine oil using catalytic pyrolysis technology on an aluminosilicate catalyst. It should be noted that along with the production of fuels, which is important and in demand, is the direction for the production of lubricants, in particular, plastic lubricants. As shown by the analysis of data on the use of recycling technologies, this issue is not given enough attention, and it is precisely the plastic lubricants that are petroleum products that perform their functions in those conditions (high temperatures, loads and rotational speeds) in which no other lubricant is suitable. In this regard, in this paper, we will propose a flow chart for the production of recycling greases; various functional purposes based on oil sludge and used lubricating oils.

### 3. Results and discussion

As is well known, classic plastic lubricants consist of a base component (dispersion medium), a thickener and additives. As a dispersion medium, you can use waste lubricating oils of any functional purpose: industrial, hydraulic, turbine, engine, and transmission. As for oil sludge, it must be pre-cleaned from water, mechanical impurities, and acidic components that cause corrosion of the equipment. Given its presence in it of light hydrocarbon fractions in the production of greases, it is advisable to use only the fractions obtained during its processing.

The choice as a dispersion medium, oil sludge, and waste oils, which contain a significant amount of high molecular weight resinous asphaltene substances, makes it impossible to use classical thickeners – metal soaps, without prior deep cleaning of raw materials. It should be noted that these substances have high adhesion properties and can act as a natural antiwear additive in the final product, and therefore, their removal from the base component is highly undesirable. In this case, it is necessary to use a thickener, less demanding of the chemical composition of the dispersion medium, which would be distinguished by its availability, cheapness, and of course, a significant amount. Such a thickener can be solid polymeric household waste, represented mainly by -products from high-density polyethylene (HDPE) and low-density polyethylene (LDPE) pressure, as well as polypropylene (PP) [8]. This waste fully meets all the requirements that can be presented to the thickener, alternative to metal soaps. So, along with comparative cheapness and a huge amount, allowing them to be used on an industrial scale, positive physical and chemical properties should also be noted (a melting point not less than 110°C, resistance to water and corrosive media).

It is known that the final properties of the grease will depend not only on the properties of the main components (dispersion medium and thickener) but also on the correct selection of the concentration of the thickener. For used lubricating oils, the range of application of polymeric thickeners is in a rather narrow margin to 10 wt%, the excess of this concentration results in the manifestation of polymer properties in the final product, due to the formation of a polymer matrix in its structure. In this case, talking about the resulting product as grease is no longer has a sense. The concentration of the thickener largely determines the viscosity of the dispersion medium. Thus, a lubricant of a certain consistency (class NLGI) of the base of used hydraulic oil (HLP 46) will contain a higher concentration of polymer thickener than a lubricant of the same consistency based on transmission oil (SAE 85W-90). The viscosity of the dispersion medium and the ability of the thickener to prevent the separation of the dispersion medium from the total amount of grease depend on such an important indicator of

greases, which characterizes their storage stability as their colloidal stability. It is established that the lubricant obtained on the bases of used hydraulic oil HLP 46, thickened with 5 % low-pressure polyethylene, has the worst colloidal stability, with the same amount of thickener compared to lubricant based on used SAE90W-140 transmission oil [9]. Typically, to obtain recycling greases, which are analogs of industrial designs, the concentration of polymer thickener should be in the range of 5.0-7.0 wt%. Taking into account the high viscosity of high-boiling fractions of oil sludge, up to 2.0 wt% of polymeric thickener is used for thickening.

However, the total range of concentrations of a polymeric thickener in greases can be significantly expanded when using low viscosity oil fractions or fractions obtained from thermodestructive processing of waste oil as a dispersion medium.

Prediction of the properties of the resulting greases should be carried out while taking into account changes in the composition and properties of raw materials in the process of its technological processing. So, for example, industrial oil I-40 has higher viscosity values compared to hydraulic oil HLP 46, which should determine the higher colloidal stability of the resulting grease. However, an oil I-40 has low thermal stability and in the temperature range of 130–200°C, necessary for obtaining grease, undergoes thermal destruction, which is accompanied by a decrease in the yield of the resulting lubricant and viscosity of the dispersion medium. Therefore, this plastic has the worst colloidal stability in comparison with the lubricant based on oil HLP 46 [9].

Thus, the technology for obtaining recycling greases is a technological process consisting of successive stages, closely related to each other, and is presented in Fig. 1.

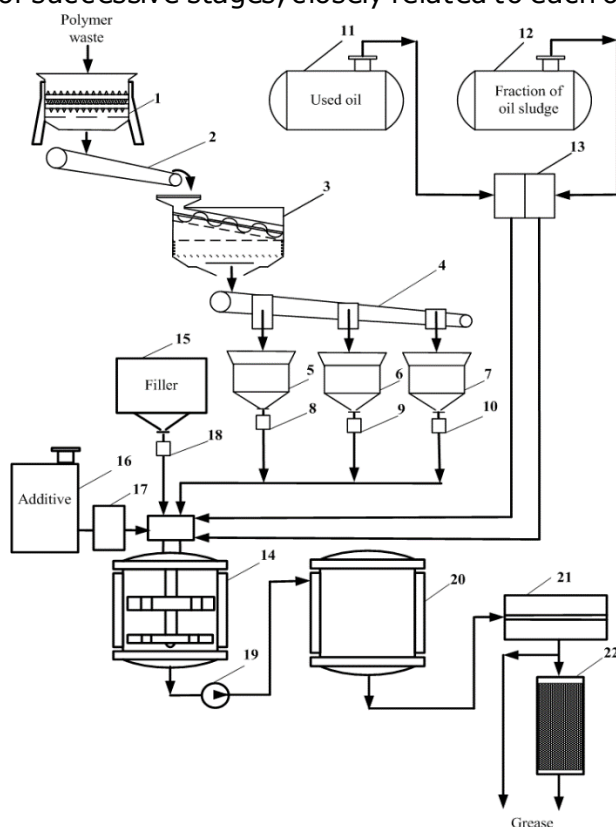


Fig. 1. The scheme for obtaining recycled grease: 1 – chopper; 2, 4 – belt conveyors; 3 – apparatus for washing and drying polymer waste; 5-7, 15 – bunkers; 8-10, 18 – dispensers; 11, 12, 16 – tanks; 13, 17 – dosing pumping devices; 14 – reactor; 19 – pump; 20 – cold-storage space; 21 – homogenizer; 22 – filter

**Stage I.** At this stage, preparation of the dispersion medium of the grease, thickener, as well as fillers takes place. For used lubricating oil and oil sludge at this stage, water and mechanical impurities are separated by various physicochemical methods described in work [10]. Also, it is necessary to separate the high-boiling fraction from the oil sludge, which will be used as a dispersion medium for the production of plastic lubricants [11]. After these operations, the prepared dispersion medium enters the raw material tanks **11** and **12**.

At this stage, in order to obtain a homogeneous mass with unified properties, in apparatus **1**, the sorted polymeric solid household waste is crushed to particles no larger than  $2 \times 2$  mm. The grinding process can significantly reduce, shorten the duration of the subsequent stages, reduce the size of the apparatus, improve plant performance, due to a full load of raw materials and improve the quality of the lubricants produced due to the homogeneity of the structure. This process is carried out using mainly cutting and impact devices, taking into account the initial characteristics of the polymers. Next, the crushed polymers through the conveyor belt **2** are fed into the apparatus **3**, performing the function of cleaning from contamination with the subsequent removal of moisture from the polymers. First, the crushed polymer waste is fed into a screw

washer, where the preliminary soaking of the material is carried out, followed by transportation to the separation bath, where contaminants are separated from the polymer. Next, the waste is fed to the filter press, where the moisture is completely squeezed out, after which the crushed, cleaned and dehydrated polymeric materials are fed to the belt conveyor **4** and then to storage hoppers **5, 6, 7** for different types of polymers (HDPE, LDPE, PP).

To improve the physicochemical and performance properties, greases, along with the main components, may contain various fillers, which can also be chosen from several numerous wastes, for example, used automobile tires or cardboard-paper wastes are suitable for this purpose.

Adding ground tires due to physical interaction with the dispersion medium improves the rheological and adhesive properties of greases, storage stability, and also increases the temperature range of their application. Also, a noticeable improvement in rheological properties and storage stability is observed when paper industry waste is added in the form of cellulose. However, before using them as filler, they must be prepared. So, used car tires are necessary to grind, remove fabric or metal cord (magnetic removal is used), wash and dry, in general, carry out almost the same stages as in the preparation of polymer waste, but using more complex equipment (there is a need for grinding, use more expensive equipment using durable knives and crowns).

The situation is different from paper waste because they contain glue, which must be disposed of to obtain cellulose. In this case, with constant mixing, alkaline washing is carried out with a 10 % solution of NaOH, previously crushed waste. After that, it is necessary to rinse with water and dry the obtained cellulose, followed by its grinding to the required size. The implementation of such preparation, from an environmental point of view, is seen as a complex process, in which it is necessary to provide both the regeneration technology of the spent NaOH solution and the cleaning of the wash water.

At *Stage II*, the prepared components are fed into the reactor **14** in the strict sequence, they are heated, and the compounding itself by means of a paddle stirrer operating at high speeds. The sequence is such that into the reactor **14**, through a mixer, using a multi-flow dosing pumping device **13**, the prepared dispersion medium from tank **11** or **12** is fed. Here, depending on the desired characteristics of the final product, the crushed polymer is fed through hoppers **5, 6, 7** through dispensers **8, 9, 10**. In the reactor **14**, depending on the melting point of the polymer thickener, the mixture is heated to 130–200°C with constant stirring, for 1.5–3.0 hours.

Moreover, for the quality of the finished product, in particular for its colloidal stability, an important is the degree of dispersion of the polymer thickener and the uniformity of its distribution over the volume of lubricant. The thickener is dispersed by using a mechanical paddle propeller stirrer, which can provide a laminar and turbulent dispersion mode. Along with mechanical dispersion, it is possible to apply ultrasonically, which is carried out by creating a cavitation effect and acoustic flow, in which the structure and properties of the lubricant are changed, that leads to an increase in its homogeneity <sup>[12]</sup>.

Further, from the hopper **15**, a filler is added through the dispenser **18**, and from the tank **16**, an additive is introduced through the dosing pumping device **17**.

Next comes the final *stage III* – this is the cooling of the resulting reaction mixture in the tank-cooler **20**, and the final formation of the structure of the grease in the homogenizer **21**. The cooling process, depending on the desired properties of the final product, can be carried out within 5–24 hours.

Homogenization of plastic grease occurs under mechanical action (punching under pressure through holes 30–50 μm in size) in the valve or rotary-slot homogenizers. In this case, there is an improvement in its appearance and colloidal stability <sup>[13]</sup>. Further, if necessary, the lubricant may be subjected to filtration in the apparatus **22**.

According to the proposed technology, depending on the properties and degree of preparation of used oils, as well as the selected process parameters, greases can be obtained, whose properties are in the range of values given in Table 1.

Table 1. Properties of recycling greases

Indicator name	Numerical values of indicators		
Dispersion medium	used oils		
Type of thickener	LDPE	HDPE	PP
The concentration of the thickener, wt%	5-7		
Appearance	Homogeneous ointment, black		
Penetration at 25°C, 0.1·mm	215-325		
Drop point, °C	95-100	110-115	135-140
Evaporation at 120°C	0.10-0.75		
Colloid stability, %	3.5-14.0		
Corrosive effects on metals:	Endures		
- Steel	No corrosion traces		
- Copper			
Working speed mode in the bearing, rpm	up to 4000		
Solubility:			
- in water at 100 °C	not dissolve		
- in gasoline at 60 °C	dissolves		

#### 4. Conclusions

The application of recycling technologies in the production of commercial petroleum products allows, not only, to expand the raw material base of the technological process significantly, but also to improve the environmental situation. The studies have shown that industrial waste such as oil sludge and spent oils can be successfully applied in the production of plastic lubricants along with the production of fuels. The production scheme of plastic lubricants based on high-boiling fractions of oil sludge and spent lubricating oils has been proposed; the scheme involves using as a thickener, waste polymer from LDPE, HDPE and PP. The implementation of this scheme will allow obtaining plastic greases that can be used in the temperature range, on average, up to 80–130°C (depending on the polymer) and speed mode in the bearing up to 4000 rpm, and their properties are not worse than ones of classical industrial analogs.

#### References

- [1] Council Directive 1999/31/EC on the landfill of waste. Official Journal L 182, 16 July 1999: 1-19.
- [2] Directive 2008/98/EU of the European Parliament and of the council. Official Journal of EU L 312/3, 22 November 2008: 3-30.
- [3] Shen Y, Chen X, Wang J, Ge X, Chen M. Oil sludge recycling by ash-catalyzed pyrolysis-reforming processes. *Fuel*. 2016; 182: 871-878.
- [4] Chang CY, Shie JL, Lin JP, Wu CH, Lee DJ, Chang CF. Major products obtained from the pyrolysis of oil sludge. *Energy Fuels*. 2000; 14(6): 1176-1183.
- [5] Diederich R. Advance sludge treatment system by ultrahigh temperature gasification. Proc. in Biomass and Conversion Technologies on Emerging Technology Forum, California, 17-18 April 2006.
- [6] Arpa O, Yumrutas R, Demirbas A. Production of diesel-like fuel from waste engine oil by pyrolytic distillation. *Applied Energy*. 2010; 87(1): 122-127.
- [7] Demirbas A. Gasoline-like fuel from waste engine oil via catalytic pyrolysis. *Journal Energy Sources*. 2008; 30(16): 1433-1441.
- [8] Grigorov AB, Zelenskii OI, Sytnik AV. The prospects of obtaining plastic greases from secondary hydrocarbon raw material. *Pet Coal*. 2018; 60(5): 879-883.
- [9] Grigorov A, Zelenskii O, Saienko L, Zhynova S. Production of plastic lubricants on the basis of waste lubricated oils. *Pet Coal*. 2019; 61(2): 319-323.
- [10] Khmelev VN, Leonov GV, Barsukov RV, Tsyganok SN, Shalunov AV. Ultrasonic multifunctional and specialized equipment for intensification of technological processes in industry. Barnaul: AltGTU, 2007; 416 p.
- [11] Hu G, Li J, Zeng G. Recent development in the treatment of oily sludge from petroleum industry: A review. *Journal of Hazardous Materials*. 2013; 261: 470-490.
- [12] Mardupenko A, Grigorov A, Sinkevich I, Tulskaia A. Oil sludge as source of a valuable carbon raw material. *Pet Coal*. 2018; 60(3): 353-357.
- [13] Fuks IG, Shibryayev SB. Composition, properties and production of greases; Moscow: Gosudarstvennaya akademiya nefi i gaza im. I.M. Gubkina, 1992; p. 153.

To whom correspondence should be addressed: Dr. Oleg Zelenskii, Ukrainian State Research Institute for Carbochemistry, 61023, 7 Vesnina str., Kharkov, Ukraine, [zelenskii.ukhin@gmail.com](mailto:zelenskii.ukhin@gmail.com)