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MODERN RECOVERY METHODS IN USED OIL RE-REFINING

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Abstract
Used oil – as its name implies – is any petroleum -based or synthetic oil that has been used. During normal use, impurities such as dirt, metal scrapings, water or chemicals can get mixed in with the oil or be generated in it due to thermal degradation or oxidation[1]. Therefore, the oil quality gradually decreases to a level that the used oil should be replaced by a new one. Disposing the used oil off in nature creates an intense dangerous pollution. But by proper recovery and refinement of it, a lot of valuable product can be obtained. This article studies one of the best methods of used oil re-refining and compares its product specifications with those of a virgin base oil.

Key Words : used oil re-refining , hydrotreating , waste oil recovery

Introduction

Used oil is defined as the petroleum-derived or synthetic oil remained after applications in lubrication, cutting purposes, heat transfer, hydraulic power or insulation in dielectric transformers (not including used solvents and used ethylene glycol)[2]. Improper disposal of used oil pollutes environment to a great extent; for example, each volume of it can pollute at least 250’000 volumes of water. This is believed that an important part of water pollution in the North and South poles of the earth is due to the accumulation of this pollutant, because of its high toxicity and very low temperature of water there, which inhibits water biological refinement.
But, by proper recovery of this precious material, a considerable economic benefit, a vast amount of petroleum conservation, besides the environmental preservation can be obtained. One of the most efficient processes for this purpose is hydro-treating, which is discussed in the present article.

Theoretical Background

During normal use, impurities such as dirt, very fine metallic scrapings due to engine erosion, water or chemicals, etc., can get mixed in with the oil. Also, due to oxidation or thermal degradation, a lot of impurities are generated in lubricating oil, during its application in internal combustion engines. These impurities contain: unsaturates, polar, asphalt-like, acidic compounds, aldehydes, phenolic compounds, alcohols, non-stable products of hydrocarbons poly-condensation (gums, poly-nuclear aromatics, etc.). Besides, it absorbs NOx and the acidic fuel combustion exhaust gas. These compounds besides dust, fuel, lubricating oil additives degradation products, fuel additives and soot gradually reduce the lubricating oil quality. Moreover, the metallic scrapings act as catalysts at the high combustion temperature and oxygen vicinity, and produce an asphalt-like sludge which increases the viscosity.

The used oil drained from electrical transformers contains a very dangerous material called PCB. (polychlorinated biphenyl). This material is toxic by inhalation, potable water or skin adsorption, so that its allowable limit is 2 ppm (mg/kg)[2]. This compound is degraded at 300-400^{o}C and produces a compound called dioxine, which is very toxic and very dangerous. Therefore, burying used oils containing PCB, or using it in road pavements are not good ways for its disposal[2]. Many decades ago, used oil was burnt, but now this way is not acceptable, because of emitting a lot of pollutants, specially heavy metals ash.

Considering the above points, the importance of the used oil re-refining processes for environmental preservation is approved. At least 600 tons of lubricating base oil can be recovered from each 1000 tons of used oil, whereas 6000 tons of crude oil is required to produce this amount of lubricating base oil. The importance of used oil re-refining is such that the U.S. government prepared a set of tax regulations many years ago which resulted in the minimum tax for a mixture of 25% re-refined oil and 75 % virgin base oil[3].

The re-refined base oil properties are comparable with those of the virgin base oil (directly produced from crude oil), as long as the re-refinement is done properly. Used oil re-refining is not a new process, but some of its applied old versions produce pollutants which are not less environmentally harmful than the used oil itself.

Generally speaking, there are 3 categories for waste oil disposal:

1- Reuse , including re-refining
2- Thermal cracking
3- Incineration / Use as a fuel[1]

The first one , is the best one and is the subject of this study . The second one – although produces acceptable (cracked) products , but is not as good as re-refining. The third one produces a lot of ash, which contains heavy metals and pollutes the environment.

In Europe, three groups of technologies can be considered as representatives of existing regeneration methods:

A) Vacuum distillation plus clay treatment
B) Vacuum distillation plus chemical treatment
C) Hydrogen pre-treatment plus vacuum distillation

At this time, the most common two technologies for used oil re-refining are: Sulfuric Acid plus Bleaching Earth and the Propane Extraction plus Sulfuric Acid plus Bleaching Earth. Both processes generate significant amounts of residues, such as sludge from sedimentation, acid tars, filter cake from bleaching earth and wastewaters, which contained high concentration heavy metals or sulfuric acid (in the range of 17 % w/w). In the first method, some references[4] imply about 200 tons of environmentally harmful by-products generation, versus each 1000 tons of used oil processed. Acid tars were burned in rotary kilns or other furnaces[1].

Therefore, some modern processes should substitute them. One of the best ones is hydro-treating. The method used by our team, consists of the following steps:

1- Heating the used oil up, to separate water and light compounds
2- Vacuum distillation for the separation of gas oil, base oil and the distillation residue
3- Passing the base oil through a guard bed, to eliminate the catalyst bed plugging constituents
4- Hydro-treating of the obtained base oil

The last step aims at removing or reducing organic acids, chlorine, sulfur or nitrogen, metals (and metalloids) compounds under severe hydro-treating conditions. Also, a lot of the aromatics and other unsaturates (which were not eliminated by previous steps) are saturated to an acceptable low level. This not only improves its quality to a great extent, but also decreases its evaporation (loss) in engines; specially for multi – grade lube oils[5].

The lube oil hydro-treating chemistry is different from those of light and middle petroleum cuts .The main target of virgin base oil hydro-treatment (before being used) is controlling its color stability. Therefore, polar (oxygen-containing, unsaturated, etc.) compounds which produce the brown color in lube oil and also make this color unstable, are eliminated by low temperature – low intensity hydrogenation[6]. Under more severe conditions (higher pressures and temperatures); nitrogen and sulfur are eliminated (as NH_3 and H_2S) and aromatics are saturated[1].

This process has many advantages: Production of a high Viscosity Index lube oil with a good and stable color and well oxidation resistance; yet having low or no discards. At the same time, it consumes bad quality feed.

Another important aspect of this method is that all of its hydrocarbon products have good applications. In other words, the product recovery is high with no (or very low) disposals. Other hydrocarbon products are:

Light –cuts can be used as fuel in the plant itself. Gas oil may be consumed after being mixed with heating gas oil. The distillation residue can be blended with bitumen and consumed as the paving asphalt, because it upgrades a lot its rheologic properties. Also, it can be used as a concentrated anticorrosion liquid coating, for vehicles frames. Moreover, it has some applications in metal smelting industries.

Equipment and Experimental Method

In this experimental research, a spent (i.e., regenerated many times and ready to be discarded) middle – distillate hydro-cracking catalyst (HC – 102) was used. Therefore, the economic benefits can be greatly enhanced for refineries having such plants. But of course, for other refineries a fresh "lube oil hydro-finishing" catalyst should be used instead (e.g., DN-190 or C-411).

The operating conditions used were:
Temperature: 250 – 370°C
Pressure: 60-73 bar (gauge)
Liquid Hourly Space Velocity: 1 – 2.3
H_2 purity: 70 % mole (min.)

The apparatus is a 60 c.c. high pressure hydro-treating reactor (Fig. 1). In this reactor test, when using the spent catalyst, a special preparation process(rejuvenation) should be done on it.

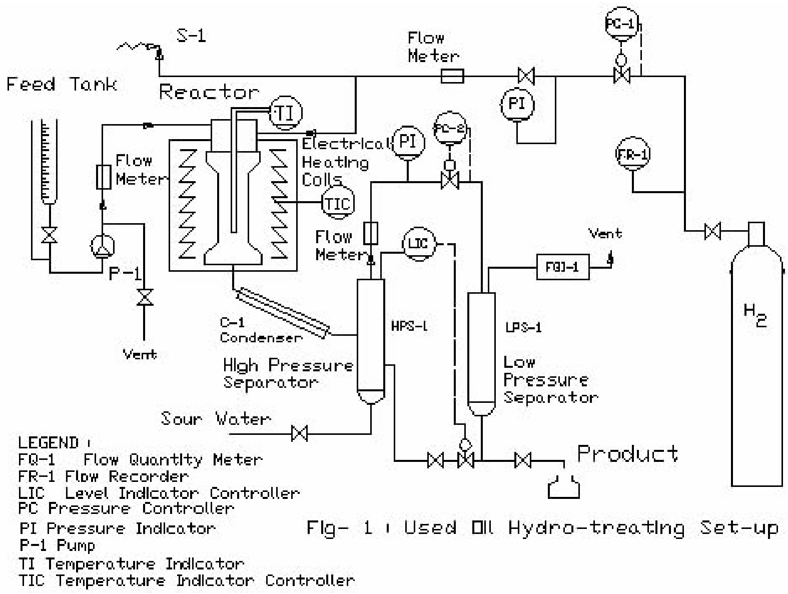

Fig- 1 : Used Oil Hydro-treating Set-up

At first, the catalyst is washed by naphtha in a vessel (equipped with a mechanical mixer) to clean hydrocarbons on its surface. Then, it is dried for 24 hours in an oven at 120°C. At this step, the catalyst is washed by 0.1 normal solution of acetic acid for 3 hours, to eliminate the disturbing metals, previously precipitated on the spent catalyst (due to the small amounts of these metals in hydro-cracking service). After this step, by using a continuous air flow, decoking is done in a cylindrical electrical furnace .The temperature should be kept at 425°C, for 5 hours. Now, a pre-sulfiding step should be done on it. After loading the catalyst into the 60 c.c. reactor, a 30 bars pressure and 12 l/hr hydrogen flow at 180°C is passed for 4 hours, through it. Then, hydrocracker gas oil (containing 1 to 2 wt.% dimethyldisulfide) is injected into the reactor, and the temperature is gradually increased to 260°C, during 4 hours, and then to 310°C, during another 5 hours. After remaining for 12 hours in these conditions, the pre-sulfiding stage is finished. Then, the sulfiding step is done, by the injection of hydrocracker gas oil (containing 1 to 2 wt.% dimethyl disulfide) at 340°C and at the rate of 12 ml/hr. These conditions are maintained for 12 hours, and gives us the required catalyst.

Results

Table (1) shows the expected standard specifications for some lube oils. Table (2) compares the re-refined oil obtained by our method and SAE 30 virgin base oil specifications.

In order to obtain more assurance about the PCB elimination in this method, intense studies were conducted. Since direct measurement of PCB is not easy, indirect one was used. In fact, the chlorine content of the re-refined oil was done. Obviously, all the existing chlorine in the re-refined oil is not necessarily indicate the presence of PCB in it. Therefore, the above method is an acceptable one, with respect to the PCB existence. Table (3) shows the results.

Table 1- Specifications of some lube oils

Specifications	***SAE 20***	***SAE 30***	***SAE 40***
Specific Gravity at 15.56°C	0.8700	0.8801	0.8826
Kinematic Viscosity at 100°C, cSt.	5.65	10.15	11.50
Kinematic Viscosity at 40°C, cSt.	37.0	88	110
Viscosity Index	95	94	96
Flash Point, °C	224	264	268
Pour Point, °C	-10	-10	-12

Table 2- The comparison between (this method) re-refined and SAE 30 base lube oils

Specifications	SAE 30	Re-refined Oil
Appearance	Clear& Homogeneous	Clear& Homogeneous
Color	max. 2,5	1
Flash Point (Deg. C)	min. 215	234
Pour Point (Deg. C)*	max. -6	-3
Kinematic Viscosity @100°C (c.St.)	min. 9,5	9,63
Viscosity Index	min. 90	92
Foaming Characteristics	0	0
Water & Sediments (Vol.%)	max. 0,02	trace
Neutralization Number (mg KOH/g lube)**	max. 0,02	<0,05

* *Additive addition corrects this problem*

***The maximum standard value for the virgin base oil is 0.02 and for the re-refined oil is 0.05*

Table 3- The chlorine content measurement in some lubricating oils

Lube Oil	Chlorine Content (ppm)
Base Lube Oil (before additives blending)	2.1
Lube Oil (with additives, during application)	38
Used Oil	14
Our Re-refined Oil (after the hydro-treating step)	2.9

Discussions and conclusions

The above method (specially for crude oils which are mainly paraffinic) causes favorite changes in the re-refined oil product, which are compatible with the coming specifications. All required technical and environmental specifications of the re-refined oil product are met by this method product , and also it can have the extra economic benefit of using spent hydro-cracking catalysts, instead of buying fresh hydro-treating ones.

Moreover, almost no harmful or useless byproduct hydrocarbon is produced via this method. Light fuel, gas oil and asphalt blending / improving material are valuable other products of this re-refining method.

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