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Re-Refining Recovery Methods of Used Lubricating Oil

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Abstract

Used lubricating oil (ULO) is any petroleum based or synthetic oil that has been used and during operation oil losses effectiveness due to the presence of certain contaminants from air, fuel combustion, oxidation and additives. Thus, decreases the oil quality gradually to a level that the used oil should be replaced by a new one, in order to maintain the engines in good condition, it is necessary that the engine oil must be replaced by new oil after certain period of service. Waste oil creates environmental pollution if not disposed-off properly. This article describes one of the best methods of used oil re-refining and compares its product specifications with those of virgin base oil.

Keywords: waste oil, hydrotreating, re-refining

Introduction

Automotive used oil is generated from the transport sectors when oil loses its effectiveness during operation because oil after a time of use degrade the fresh lubricant components and the contamination from the combustion chamber, metallic particles resulting the wear and tear of the engine parts, together with water, varnish and gums from in over lay on bearing surfaces and other asphaltic compounds due to degradation of additives, light hydrocarbons, resinous material, mono-and polyaromatic compounds, carbon black and used base oil made it toxic chemicals [Klaman-1983], arising mostly in urban area at filling stations and motor repair shops. Used oil creates environmental pollution if not disposed-off properly, there is a possibility that other substances that it may contain, enter natural cycles through the food chain via water, soil and the air. In this way used oil pose risk to human health and impede the growth of plants and their ability to take up water as sometimes used oil contained hydrocarbons, heavy metals, polyclorinated biphnyls (PCBs) and other halogen compounds [M.El-Fadel 2001].

This hazardous waste oil needs proper management to maximize the amount of used oil recovered by recycling to make it useful as value added product and to minimize the quality of oil being improperly disposed off and to reduced the waste oils environmental pollution from waste oil [Dang,G.S, 2006]. To convert the harmful wastes into harmless substances, it is necessary to increase the collection and re-processing of the oils, in order to extract useful materials. In case of re-refining of used oil, 2.5 quarts of lube oil can yield from one gallon of used motor oil the same may be obtained from refining 42 gallons (one barrel) of crude oil and one gallon of used oil processed for fuel contains about 140,000 BTUs [Holmes et al., 1993]. Therefore, burying used oils containing PCB, or using it in road pavements are not good ways for its disposal [Missouri Department, 2003]. 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.

In Pakistan, until now, no used oil management systems are available and the level of public awareness is very low in respect of environment impacts of waste lubricating oils. According to relatively recent studies, estimated 80,000 to 100,000 tonnes of used oils generated each year from the vehicles that is being improperly disposed off in Pakistan. [Durrani, Panhwar and Kazi 2008], 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.

Background

Used lubricant oil as used product of any semi solid liquid, consists of completely or partially mineral oil or synthesized hydrocarbons (synthetic

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oil), loses its effectiveness during operation due to the presence of certain contaminants from air, fuel combustion, oxidation and additives. The principal source of contamination during oil use is the chemical breakdown of additives and the subsequent interaction among the resultant components to produce corrosive acids and other undesired substances. This used lubricating oil has higher values of ash, carbon residue, asphaltenic materials, like, aldehydes, alcohols, phenolic compounds, acidic compounds, non-stable products of hydrocarbons poly-condensation (poly-nuclear aromatics, gums, water, and other dirty materials; which are built during the course of lubrication inside the engine. Wang et al [Fiedler H 2004]. It absorbs NOx and the acidic fuel combustion exhaust gas also, besides these compounds fuel, lubricating oil additives degradation products, fuel additives, dust, and soot gradually reduces the lubricating oil quality. Furthermore, the metallic scrapings act as catalysts at the high combustion temperature and oxygen vicinity, produce an asphalt-like sludge which increases the viscosity.

The used oil draw off from electrical transformers especially contains hazardous material called PCB (polychlorinated biphenyl). This material is very toxic by inhalation, potable water or skin adsorption, therefore its permissible limit is 2 ppm (mg/kg) and degraded at 300-400oC and produces a compound called dioxine, which is very toxic and very dangerous, so burying or using it in road pavements are not good ways for its disposal[2 Missouri Department,2003]. Used oil was burnt many decades ago as a low grade fuel, but now this way is not acceptable, because of emitting a lot of pollutants, particularly heavy metals ash released in to air.

Considering the above environmental issues, it is necessary to convert the harmful wastes into harmless substances through combustion process [Durrani 2013] or re-refining processes for environmental preservation as re-refining requires the conversion of waste oil to a product with similar characteristics to those of virgin oil and from 6000 tons of crude oil are needed to obtain 1000 tons of motor 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. [Bowman L.O. 1982].

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

So far the following 3 categories for used oil disposal methods have been in common use:

1- Reuse, including re-refining
2- Thermal cracking
3- Incineration / Use as a fuel [Fiedler H 2004]

The first category is one of the best one and is the subject of this study. The second one is not good as re-refining though produces acceptable (cracked) products, where as the third one pollutes the environment, as produces a lot of ash, which contains heavy metals. In developing the following 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 present, there are two most common technologies for used oil re-refining are: Sulfuric Acid plus Bleaching Earth and the Propane Extraction plus Sulfuric Acid plus Bleaching Earth. Both these processes generate significant amounts of residues, such as sludge from sedimentation, acid tars, filter cake from bleaching earth and waste waters, which contained high concentration heavy metals[Durrani et al 2011,12] or sulfuric acid (in the range of 17 % w/w) [Durrani et al 2009]. In the first re-refining method, some references quoted around 200 tons of environmentally harmful by-products generation, versus each 1000 tons of used oil processed [Whisman M.L., et. al.], and Acid tars were burned in rotary kilns or other furnaces [Fiedler H2004]. To avoid from harmful product some modern processes have been used and the best one is hydrotreating, it consists of the following steps: [Bridjanian.H. et al 2006].

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 is very important in a sense that it improves the quality of oil to great extent by removing or reducing the organic acids, chlorine, sulfur or nitrogen, metals (and metalloids) compounds under severe hydro-treating conditions and also, a lot of the aromatics and other unsaturated (which were not eliminated by previous steps) are saturated to an acceptable low level and decreases its

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evaporation (loss) in engines; specially for multi – grade lube oils [Hournac R1981].

The chemistry of hydro-treating lube oil is different from those of light and middle petroleum cuts and the main objective of virgin base oil hydro-treatment (before being used) is controlling its color stability, so 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 [Axens Brochure]. In case of more severe conditions such as higher pressures and temperatures; nitrogen and sulfur are eliminated (as NH_3 and H_2S) and aromatics are saturated [Fiedler H 2004].

Another important aspect of this method is that, this process has many advantages: Produces of high Viscosity Index lube oil with well oxidation resistance and a good stable color and yet having low or no discards. At the same time, it consumes bad quality feed. In addition to that this method has advantage that all of its hydrocarbon products have good applications and product recovery is high with no (or very low) disposals. Other hydrocarbon products are:

In oil refinery the light –cuts can be used as fuel in the plant itself. Gas oil may be consumed after being mixed with heating gas oil and the distillation residue can be blended with bitumen and consumed as the paving asphalt, because it upgrades a lot its rheological properties. Also, it can be used as a concentrated anti-corrosion liquid coating, for vehicles frames.

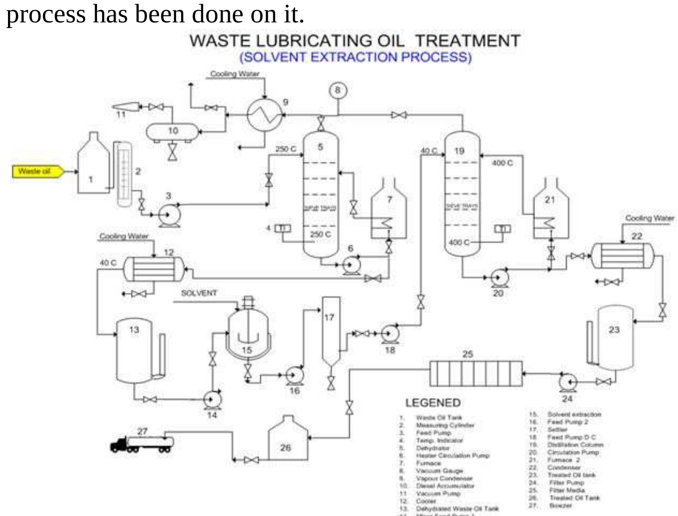
Equipment and Experimental Method

This experimental research work was carried out on pilot scale rig that was designed and fabricated on batch system, the various technologies were studies while designing and fabrication of pilot scale rig, like Meinken technology, KTI technology (Kinetics Technology International), Mohawk technology, BERC or NIPER technology (Bartlesville Energy Research Center USA, renamed the National Institute of Petroleum and Energy Research) and PROP technology (Phillips Petrol Company). This pilot scale rig was developed to treat the used oil by with sulphuric acid or solvent to eliminate the polluting substances and then treatment with clay earth and its operation was similar to laboratory work where the used lubricating oil was treated. This pilot scale rig was installed in Department of Mechanical Engineering, Mehran University of Engineering and Technology, Jamshoro, Sindh Pakistan. It was fabricated in stainless steel with brass and copper fittings equipped with safety equipment and 2 liters of used oil was treated per run.

In this experimental research, regenerated distillate hydro-cracking catalyst (HC – 102) was used for the economic benefits can be greatly enhanced for refineries having such plants.

The operating conditions used were:
Temperature: 125 – 400°C
Pressure: 60-73 bar (gauge)
Liquid Hourly Space Velocity: 1 – 2.5
H_2 purity: 70 % mole (min.)

The apparatus is a 2 liters high pressure hydro-treating dehydrator (Fig. 1). In this dehydrator test, when using the spent catalyst, a special preparation process has been done on it.



As in first stage process removes water from the feedstock and in the second stage catalyst is washed by naphtha in a vessel (equipped with a mechanical mixer) to remove hydrocarbons on its surface and then dried it for 24 hours in an oven at 125°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).

In the second step, decoking process took place in a cylindrical furnace and the temperature kept constant at 400°C, for 5 hours and after that pre-sulfiding step was done on it. When loading the catalyst into the distillation column (reactor), a 30-35 bars pressure and 10 l/hr hydrogen flow at 180°C is passed for 5 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 5 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

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done, by the injection of hydrocracker gas oil (containing 1 to 2 wt. % dimethyl disulfide) at 350°C and at the rate of 12 ml/hr. These conditions have been maintained for 12 hours, and give us the required catalyst.

Results and Discussion

The standard specifications for some lube oils are shown in table: 1, whereas table 2 shows the comparison results of re-refined oil obtained by present research work and SAE 30 virgin base oil specifications.

The experimental results obtained were studies to assure the removal of PCB through the indirect measurement method as the direct measurement of PCB is not easy. The chlorine content were taken into consideration in re-refined oil studies, there is no indication of PCB traces found in all chlorine.

The experimental results were compared with the research work carried out by [Bridjanian.H. et al 2006] found in closed agreement. So the above method is good enough with in relation to the PCB existence. The results are shown in Table 3.

Table 1- Some specifications of 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 (COC) °C	min. 215	222
Pour Point, °C	max. -6	-4
Kinematic Viscosity @100°C (c.St.)	min. 9,5	8.33
Viscosity Index	min. 90	94
Foaming Characteristics	0	0
Water & Sediments (Vol.%)	max. 0,02	trace
Neutralization Number (mg KOH/g lube)*	max. 0,02	<0,05

*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	16
Our Re-refined Oil (after the hydro-treating step)	3.2

Conclusion

This method is very useful in a sense that re-refined oil product is compatible with the specifications of new virgin oil; secondly this method also meet all the required technical and environmental specifications of the re-refined oil product and have extra economic benefit to use spent hydro-cracking catalysts, instead of buying fresh hydro-treating ones. Furthermore through this method no harmful or useless byproduct hydrocarbon is produced

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