

Full Length Research Paper

A comparative study of recycling of used lubrication Oils using distillation, acid and activated charcoal with clay methods

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Lubricating oils are viscous liquids used for lubricating moving part of engines and machines. Since lubricating oils are obtained from petroleum – a finite product, and with dwindling production from world oil reserves, the need arises more than ever, to recycle used lubricating oils. Accordingly, this research effort focuses on comparative study of four methods of recycling of used lubrication oils: acid/clay treatment, distillation/clay, acid treatment and activated charcoal/clay treatment methods. Test carried out on the recycled lubrication oil include: flash point, pour point, specific gravity, metal contents, viscosity and sulphur contents. The results from the tests showed that, viscosity increased from 25.5 for used lube oil to 86.2 for distillation, 89.10 for acid/clay treatment and 80.5 is for activated/clay treatment. This is compared with 92.8 cs for fresh lube oil. Other results from the different tests showed varied degrees of improvement with the best results obtained using the acid/clay treatment.

Key words: Lubrication, refining, environmental pollution, viscosity.

INTRODUCTION

Lubricating oils from petroleum consists essentially of complex mixtures of hydrocarbon molecules. They are mostly composed of isoalkanes having slightly longer branches and the monocycloalkanes and monoaromatics which have several short branches on the ring (Cutler, 2009). These hydrocarbon molecules generally range from low viscosity oils having molecular weights as low as 250, up to very viscous lubricants with molecular weight as high as 1000 (Concawe, 1985). The carbon atoms range from 20 to 34. Lubricating oils are viscous liquid and are used for lubricating moving parts of engines and machines. Grease, which is a semi-solid, also belongs to this group. There are three major classes of lubricating oils, namely: lubricating greases, automotive oils and industrial lubricating oil.

When lubricating oils are used in service, they help to protect rubbing surfaces and promote easier motion of connected parts. In the process, they serve as a medium to remove high build up of temperature on the moving surfaces. Further build up of temperature degrade the lubricating oils, thus leading to reduction in properties such as: viscosity, specific gravity, etc. Dirts and metal parts worn out from the surfaces are deposited into the

lubricating oils. With increased time of usage, the lubricating oil loses its lubricating properties as a result of over-reduction of desired properties, and thus must be evacuated and a fresh one replaced. With the large amount of engine oils used, the disposal of lubricating oils has now become a major problem. Many nations are now addressing the problem of environmental pollution posed by waste or used lubricating oils in their countries (Cooke, 1982). In USA, for example, about 2 billion gallons of oils are generated annually (Coyler, 2000). This has led industries and governments to find satisfactory solutions that will reduce the contribution of used lubrication oil to pollution and also recover these valuable hydrocarbon resource (Whisman et al., 1978).

In disposing used oil, many people use it as a dust cure; that is, for dust prevention (Bennet et al., 1960). This method of disposal is in many ways unsatisfactory as the lead-bearing dust and run-off, constitute air and water pollution. Another method by which used oil is being disposed is by incineration. This method represents another poor use of such a valuable product, and the attendant emission of probably carcinogenous products, contribute to environmental pollution (Georgel and La

Tour, 1977). Recycling of used lubricants is now attracting more attention than before. This is partly because of the fear of dwindling of world oil reserves and more as a result of the environment concern which it poses. The following three distinctive reasons explain the interest in the re-cycling of waste lubricating oils (Iarc, 1984):

1. The need to conserve crude reserves.
2. Minimizing unemployment through the building/construction of used lubricating oil recycling plant.
3. The elimination of environment pollution source of used lubricant.

The recycling of used lubricants has been practiced to various degrees since the 1930s and particularly during the Second World War when the scarcity of adequate supplies of crude oil during the conflict encouraged the reuse of all types of materials including lubricants (Asseff, 1961). Environmental considerations regarding the conservation of resources have maintained interest in the concept of recycling up to the present day. The reclamation of spent crankcase oils is now a subject of pressing national interest in some countries. On the other hand, pollution by used lubrication oils is recognized now to account for greater pollution than all oil spills at sea and off-shore put together. Some countries have petroleum storage and spent oils represent a precious commodity, which must not be wasted. It was because of this, the conservation of petroleum resources have been declared national policy for several countries and the benefit of wise resource management are obvious (Mortier and Orszulik, 1994). Recent impetus on waste recovery leads to renewed interest in re-distilling to convert this used lubricating oil into useful original lubricating oils.

Re-distilling or re-finishing is the use of distilling or refining processes on used lubrication oil to produce high quality base stock for lubricants or other petroleum products. The use of this method has increased tremendously in the developed countries, in some countries reaching up to 50% of the countries' need for lubricating oil (Thrash, 1991) and there are different methods developed by different countries in the western countries, on how to refine used lubricating oil for reuse. The basic principle remains the same and utilizes many of the following basic steps:

- Removal of water and solid particles by settling.
- Sulphuric acid treatment to remove gums, greases, etc.
- Alkaline treatment to neutralize acid.
- Water washing to remove "soap".
- Clay contacting to bleach the oil and absorb impurities.
- Stripping to drive off moisture and volatile oils.
- Filtering to remove clay and other solids.
- Blending to specification.

The objective of this research is centered mostly on obtaining a high quality production of lubricating oil from used lubricating oil by the re-refining of used lubricating oil, thereby reducing environmental pollution and also minimizing importation of lubrication oil.

Literature survey

It is essential to recognize that, all used oils should be collected for controlled disposals. Some products, such as transformer oils and hydraulic oils, can be readily collected from large industrial concerns, regenerated to a recognized standard and returned to the original source. Oil from the automotive sources will include mono and multi-grade crankcase oils from petrol and diesel engines, together with industrial lubricants that have been inadequately segregated may also be included (Gergel and La Tour, 1977). Lubrication oil is used to provide a film between the moving parts of machine and engines to prevent wear with little or no loss of power. The conventional steps in lubricating oil manufacture are pretreatment of the crude oil charge, followed by distillation of the crude in two steps (an atmospheric tower and vacuum tower), deasphalting (as required by the nature of the crude oil charge), dewaxing, solvent extraction, filtering and blending including mixing various additives with the final lubricating oil (Bromilow, 1990).

The prime objective in the production of lubricating oil is the separation of wax distillate and cylinder stock without any decomposition or cracking of the lubrication oil fractions, thus a vacuum distillation unit is used to separate the wax distillate and the bottom stock at a lower temperature. The properties which make the high boiling paraffin hydrocarbon suitable for lubricating manufacture include stability at high temperatures, fluidity at low temperature, only a moderate change in viscosity over a broad temperature range and sufficient adhesiveness to keep it in place under high shear forces. The desired fractions for the manufacture of the lubricating oil have high boiling points and its separation into various boiling points range cuts must be accomplished under reduced pressure. The vacuum tower produces some fuel oil overhead which is sold as a separate product or sent to another area of the refinery for further processing and blending. The two main products from the vacuum tower are wax distillate and cylinder stock which is the bottom product. Both streams contain desirable lubricating oil constituents as well as by-products. The wax distillate is charged directly to the dewaxing unit. The vacuum tower bottoms, or cylinder stock are charged to deasphalting unit. These two fractions from the basic stock for lubricating oil manufacture (Hamad, 2005).

General characteristics of lubricating oils

All lubricants are characterized by some properties,

which are very peculiar to them. Such properties include: viscosity index, cloud point, flash point, pour point, total base number (TBN), ash content, water content, corrosive properties, relative density, insolubles, total acid number (TAN) etc.

Viscosity

Viscosity is defined as the force acting on a unit area where the velocity gradient is equal at a given density of the fluid. Viscosity is strongly depending on the temperature. With increasing temperature, the viscosity has to be stated for a certain temperature. The most important fluid characteristic of a lubricant is its viscosity under the operation condition to which it is subjected in the unit. It is the characteristic of a liquid which relates a shearing stress to the viscosity gradient it produces in the liquid.

Lubrication oils are identified by Society of Automotive Engineers (SAE) number. The SAE viscosity numbers are used by most automotive equipment manufacturers to describe the viscosity of the oil they recommend for use in their products. The greater or higher the SAE viscosity numbers, the more viscous or heavier is the lubricating oil (Scapin, 2007). Viscosity numbers are given in terms of saybolt second universal, SSU. The addition of certain additives is for the improvement of viscosity-temperature characteristics.

Specific gravity (Density)

From ordinary theory, we know that density of a substance is equal to the mass of a substance divided by the volume of the substance, that is:

$$\text{Density (d)} = \frac{\text{Mass (m)}}{\text{Volume (v)}}$$

Specific gravity is the ratio of the density of the material to density of the equal volume of water. The temperature at which the density is been measured must be known for density changes as temperature changes.

Cloud point and pour point

Cloud and pour points, ASTM D97 – 47. Cloud point is the temperature at which paraffinic wax and other oil is cooled under a given condition. Pour point is not a measure of the temperature at which the oil ceases to flow under service conditions of a specific system. It is very important to users of lubricants in low temperature environment.

Water content

Water found in lubricating oil in service depends on

where the automobile is being used. In almost all system, traces of water in the lubricant are unavoidable, arising from such sources as leaking oil coolers, engine cooling system leaks and in all types of machinery, from atmospheric condensation. Accordingly, the water content must not exceed the “action” levels (more than 0.5) recommended for the different grades of oil and application. In places where there are bad roads and drainage system, one is bound to see water as part of contaminants of the oil. The water in the radiator may also contribute to the presence of water in lubricating oils in use. The presence of excessive water contamination will affect the viscosity of the oil and this may give rise to emulsion formation and can also lead to gear tooth and bearing problems.

Flash point

Flash point is the minimum temperature at which an oil gives off sufficient vapours to form an explosive mixture with air. The flash point test gives an indication of the presence of volatile compounds in oil and is the temperature to which the oil must be heated under specific conditions to give off sufficient vapour to form a flammable mixture with air. There are various methods of determining flash point of oils as contained in ASTM (Art, 2010). Flash point, open cup is the temperature at which a flash appears on the surface of the sample when a small flame of specified size is passed across the cup at regular temperature intervals while the oil in the cup is being heated at a specified rate.

Fire point

Fire point and flash point are significant in cases where high temperature operations are encountered. The fire point, open cup is the temperature at which the oil ignites and continues to burn for at least 5 seconds. Fire point is obtained as a continuation of the flash point test. The fire and flash points by Cleveland open cup, ASTM D92 – 56.

METHODOLOGY

The following materials were used in the recovery of the used lubricating oil vis-à-vis concentrated sulphuric acid, caustic soda, clay, activated charcoal, ethyl acetate. The apparatus and equipment used include the following:

- Bunchner funnel
- Filtering flask
- Seperating funnels
- Distillation column
- Flash point tester
- Thermometer (360°C)
- Erlenmeyer flask (250 ml)
- Beaker
- Measuring cylinder

Vacuum pump
 Sulphur content analyzer
 Atomic absorption spectroscopy (AAS)
 Coiled condenser
 Ubbelohde viscometer
 Erlenmeyer flask
 Round bottom flask

The methods used in the re-refining of the used lubricating oils include methods such as, filtration to remove impurities, acid treatment, acid/clay treatment, and distillation/clay treatment and activated charcoal/clay treatment.

Collection of test samples

The test samples of used lube oils (premium motor oil SAE-40) and (Quartz 2000-SAE 40) were collected from an oil service station. The used lubrication oil were collected from used oil dumps of a car mechanic.

Experimental procedure

The procedure for the purification of the used lubrication oil consist of filtration of the oil before subjecting to treatment using: acid/clay, distillation/clay, acid and activated charcoal/clay treatment methods. The used lubricating oil was filtered to remove impurities such as metal chips, sand, dust, particles, micro impurities, that are contained in the lube base oil. This was done using a funnel with a filter paper placed in it, then a vacuum pump was connected to the filtering flask to which the funnel was fixed with the aid of a rubber stopper. 2 L of the used lube oil were filtered for the two samples collected respectively. For the acid method, the used lubricating oil was stirred thoroughly to promote homogeneity from the stock 450 ml was measured out and transferred to a beaker and 150 ml of gasoline was also measured and added to the oil.

The lube base oil mixture was transferred to the bucket of the centrifuge and centrifuged at 1500 rpm for minutes. It was then left to settle for another 10 min before decanting into a beaker. The decanting liquid mixture was distilled; to remove water, gasoline and any other liquid that may be present. The content in the flask was cooled and treated with 10 ml of 98% conc.H₂SO₄ in a separating funnel with the mixture strongly agitated. It was then allowed to settle for 48 h after which two layer/phases were formed. The sludge was removed from the bottom of the separating funnel. After which 100 ml solution of 10% NaOH was added to neutralize the acid. It was then allowed to settle for about 30 min without agitation. The alkaline phase, which is formed at the bottom, was removed and the lube oil washed with hot water 2 times (15 ml). The oil was heated with an elemantle burner while connected with a vacuum pump.

For the distillation/clay method, the sample was made moisture free by first carrying out atmospheric distillation. 200 ml of the used oil was poured into the vacuum distillation flask. The pressure was increased slightly to subside the foam encountered. Mild heating was gently applied to remove the dissolved gases. The distillate obtained was weighed leaving a very dark and waxy residue. This lube oil stream was treated by packing 30 g of clay in a plugged funnel. (the funnel inserted with a filter paper) and allowing the lube oil to pass through the bed of clay was disposed off.

For the acid/clay method, the used lube oil was allowed to settle for 12 h. The sample was further filtered by centrifugation for 20 min at 1000 rpm. The suspended particles settled in the used oil at the bottom of the flask and the liquid portion was decanted off. The decanted liquid was thermally pretreated to degrade some of the additives and reduce the workload of the acid. 100 ml of pretreated oil was measured in a separating funnel and treated with 10 ml of

98% conc. H₂SO₄ (see details in acid treatment method). The remaining oil was clay treated using 30 g clay packed in a funnel with filter paper, which was then neutralized. In the activated charcoal/clay method, the waste base lube oil was stirred homogenously and 200 ml of the used lube oil was measured into a separating funnel containing 100 ml of ethyl acetate. The solution was left at room temperature for 24 h. After decanting from the paste the solution was treated with clay and activated charcoal. Filtration and evaporation was carried out under reduced pressure (see details in acid treatment).

Quality test

Flash point (ASTM D92)

10 ml of the re-refined lube oil was introduced into a 100 ml beaker and then a thermometer inserted. A beaker was placed on a bunsen burner. A flame source was brought at intervals to determine the temperature at which a flash appears on the surface of the sample while the lube oil in the beaker was heated.

Pour point (ASTM D97)

20 ml of the lube oil sample was introduced into a container. The lube oil sample was chilled at specific rate; certain paraffin hydrocarbon (in the form of wax) will begin to solidify and separate out in crystalline form. The temperature at which this occurs is known as cloud point. Further chilling was continued until lube oil stop to flow. The temperature this occurred, is called the pour point temperature.

Specific gravity (ASTM D941-55)

Specific gravity is the ratio of the density of the material to the density of equal volume of water. This was measured using the hydrometer. The density was observed at 60°F and the value recorded.

Metal content

Metal content in re-refined lube oil was determined using the atomic absorption spectrometry (AAS). Sample containing the metal to be analysed was dissolved in water, if insoluble, digesting in the acid dissolved it. The cathode lamp for the element was put in position and the element characteristic wavelength selected using wavelength selector standard solutions of the element to be determined are first prepared and their absorbency measure at selected wavelength.

Viscosity (ASTM D445)

This was obtained with the viscometer. The re-refined samples obtained by various methods. The fresh oil and the used lube oil were heated one after the other to attain a temperature of 100°C. The bulb of the clean viscometer was then filled with the hot oil (at 100°C) to the mark while immersed in a thermostat.

Sulphur content

This test is known or called sulphur analysis. 1 ml of the test sample was introduced into a burette and attached to the spectrophotometer clip. When the position is achieved, the radiation bottom

Table 1. Results of tests using the various refining methods.

Parameter	Fresh lube oil	Used lube oil	Distillation/clay treatment	Acid/clay treatment	Acid treatment method	Activated charcoal/clay treatment
Water content v/v	< 0.20	13.70	0.66	0.40	0.60	0.47
Specific at gravity at 60 °F	0.90	0.91	0.86	0.88	0.86	0.86
KV at 100 °F(Cs)	82.20	61.60	84.10	82.00	84.20	80.20
Viscosity index	92.80	21.10	85.80	88.90	84.40	86.80
Flash point °C	188.00	120.00	168.00	182.00	170.00	178.00
Pour point	-9.00	-35.00	-16.00	-11.00	-15.00	-13.00
Sulphur content	-	0.80	0.046	0.04	0.043	0.042
Iron (ppm)	-	22.50	10.30	2.60	10.50	9.50

is allowed to emit its rays from X ray tubes. The excitation effect is proportional to the concentration of sulphur in the sample.

RESULTS

The results of acid treatment, distillation/clay treatment and activated charcoal/clay treatment with their respective quality test and discussion of these results are given here.

Flash point

The flash points of this oil are 188°C for fresh oil, 100°C for used oil, acid treatment 168°C, 182°C for distillation/clay treatment, 170°C for acid/clay treatment and 178°C for activated charcoal/clay treatment. The decrease in value of flash point for the used oil could be as result of the presence of light ends of oils (Rincon, 2005). In essence, after undergoing combustion and oxidation at high temperature of the combustion engine, the oil breaks down into component parts, which include some light ends.

From Table 1, the pour point of fresh lubricating oil is 188°C, while those obtained using: acid treatment methods, distillation/clay, activated charcoal/clay, are 184,176,172 and 180°C. The decrease in flash point for the used oil, was as a result of distillation with fuel; that is, for an automobile with bad piston rings, the flash point will decrease because of distillation with fuel (Firas and Dumitru, 2006). Hence, the flash point for various recovery methods used here are acceptable concerning the reference standard.

Specific gravity

The specific gravity of the used lube oil is higher than the refined one from the above results.

The results for the fresh and used lubricating oils are 0.8966 and 0.9006 respectively, while those re-refined oil obtained by the various methods were: 0.8595 for distillation, 0.8779 for acid/clay treatment, 0.8564 for acid

treatment and 0.8607 for activated clay respectively. The specific gravity for the used oil was higher than that for the refined oil. The specific gravity of a contaminated oil could be lower or higher than that of its virgin/fresh lube oil depending on the type of contamination (Chevron Lubricating oil FM ISO 100). If the used lube oil was contaminated due to fuel dilution and/or water originating from fuel combustion in the engine and accidental contamination by rain, its specific gravity will be lower than that of its fresh lube oil or the re-refined one.

Viscosity

Viscosity increase can occur due to oxidation or contamination with insoluble matter, from the table, we can see a decrease in kinetic viscosity of the used oil ; this is due to contamination in form of sludge in the used oil. In general, oil is considered unfit for service, if the original viscosity increases or decreases to the next SAE number. Viscosity increase can occur due to oxidation or contamination (Scapin, 2007). Viscosity decrease can be caused by dilution with light fuel. The result of the viscosity test shows that, the used lube oil has lost most of its viscosity due to contamination. However, treatment has restored most of its viscosity. The result shows also that refining using acid/clay method gave the highest viscosity. This can be attributed to the possible conversion of possible contaminants by the acid and removal by the clay from the lube oil. In view of the desirability of the oil to act as a coolant or heat transfer medium, it must be able to retain adequate body at elevated film temperature, yet adequate fluidity elsewhere in the system. This is ensured when the viscosity is above 80. Oil as treated using all four methods meet this specification, but the acid/clay method has an advantage over others.

Metal content

The engine block is made of aluminum, iron and lead, hence during combustion of fuel in the engine chamber, the wear of these metals in parts per million (ppm) are

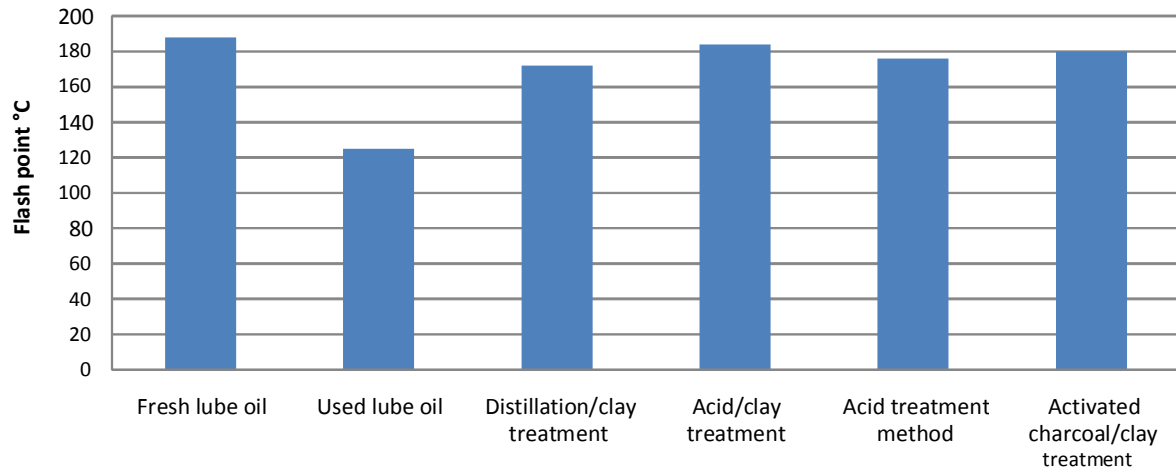


Figure 1. Effect of various refining methods on flash point of used lube oil.

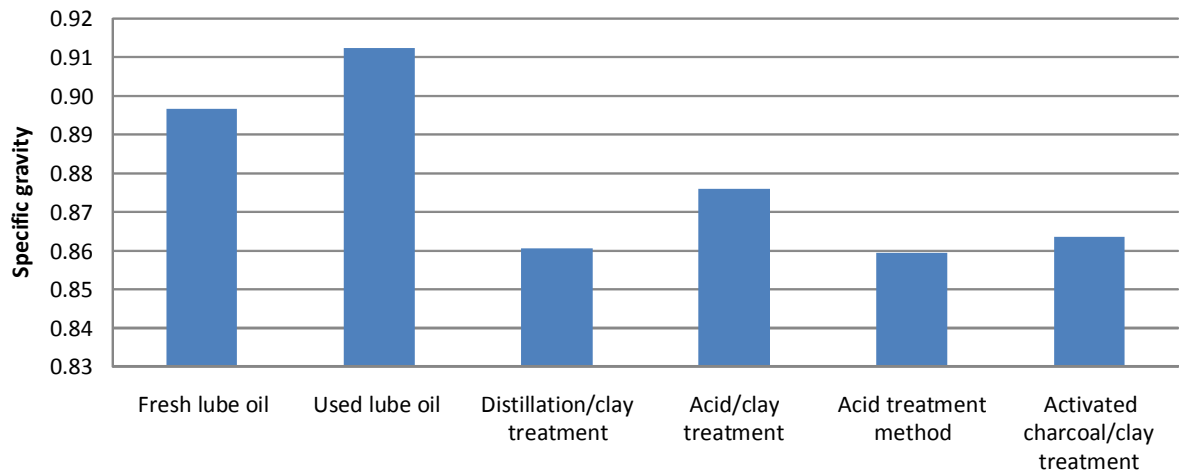


Figure 2. Effect of refining of used lube oil on its specific gravity.

found in the used oil. The wear of these metals is due to the corrosion caused by the presence of water and aided by fuel dilution due to bad piston rings (Art, 2010). One can say that, the recovery methods proved better yield when compared with that of acceptable refined base oil standard of individual metal contents. The result shows that, the acid/clay method had the least metal contents, likely due to conversion of these metals to other harmless products.

Sulphur content

The Figures 1 to 6 shows the values of sulfur content for the used lubricating oil and refined oil by the various methods. The fresh lube oil has an inherent anti-oxidant capacity. The sulphur content of used lube oil are high, this is due to the presence of wear caused between moving parts. Sulfur reacts with the metal to form

compounds of low melting point that are readily sheared without catastrophic wear. Corrosion in engines is caused by mineral acids formed by the oxidation of sulphur compounds in fuel in internal combustion engines with refined oils; those hydrocarbons that were inherently unstable will have been oxidized during use (Rincon, 2005). The function of sulphur content of refined base oil is not clear, more work is required to determine the concentration of sulphur required to meet minimum performance standards.

Pour point

From the results obtained for the used oil, pour point for the used lube oil is high. This is because of the degradation of additive in the lube oil. Pour point especially is of interest when an oil must be under relatively cold condition. Pour point will vary widely

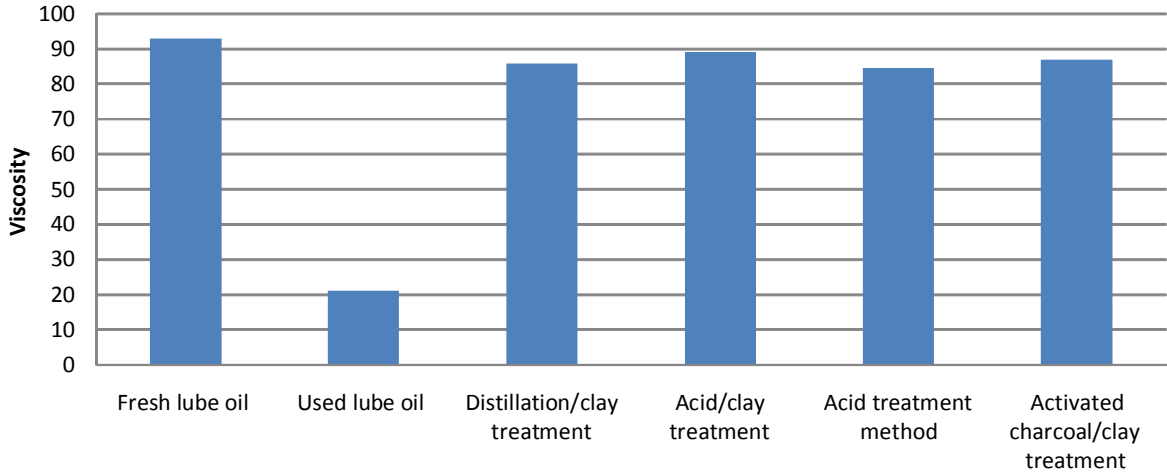


Figure 3. Effect of refining of used lube oil on its viscosity.

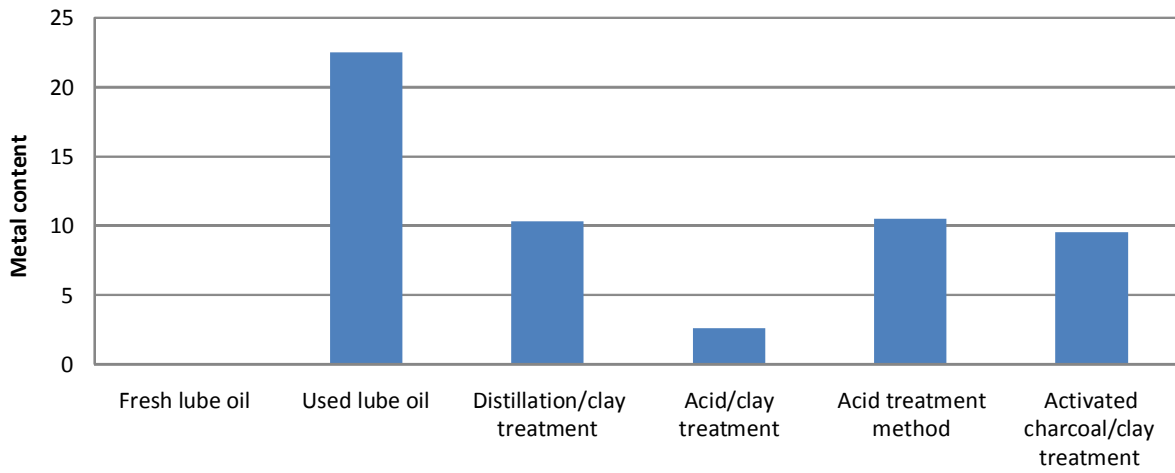


Figure 4. Effect of refining of used lube oil on metal contents.

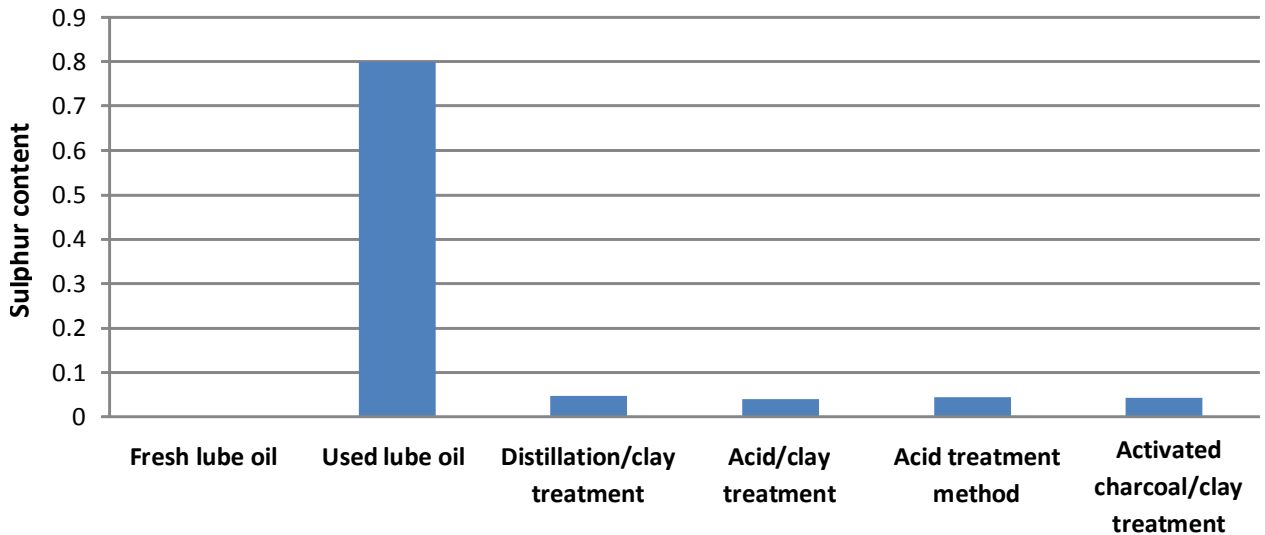


Figure 5. Effect of refining of used lube oil on sulfur contents.

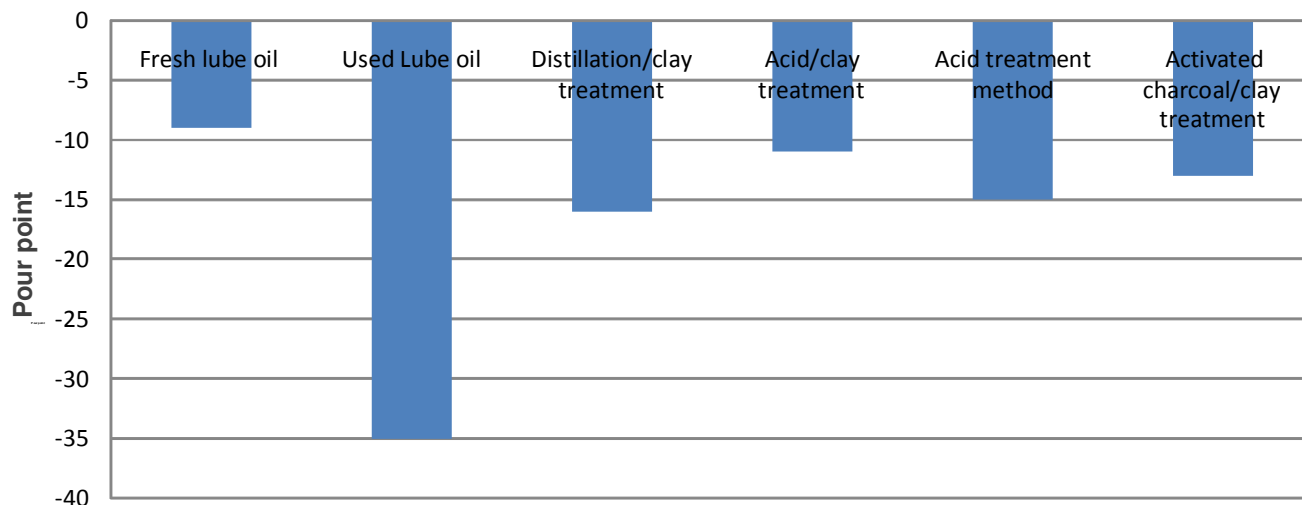


Figure 6. Effect of refining of used lube oil on its pour point.

depending on the base, the source of the lube oil and the method of refining, especially if dewaxing has been done (Firas and Dumitru, 2006; Chevron Lubricating oil FM ISO 100). Here, these recovery methods proved alright when compared with that of fresh lube oil.

Conclusion

From the results presented, it is clear that the four methods effectively removed contaminants from used lubricating base oil and returned the oil to a quality essentially equivalent to oils produced by fresh lube oil stocks. Overall, the refining method using acid/clay proves the best option, judging from the results obtained. It is envisaged that, it will cost less to procure the used lube oil and has proved to yield about 80% while the yield from crude oil is between 5 to 10%. The recycling of used lubrication oil will reduce environmental concern which it has so far posed. It will also reduce the demand for lubricant rich crude which is a finite resource.

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