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RE-REFINING OF USED LUBE OIL, I- BY SOLVENT EXTRACTION AND VACUUM DISTILLATION FOLLOWED BY HYDROTREATING

Eman A. Emam, Abeer M. Shoaib

Department of Refining Engineering and Petrochemicals, Faculty of Petroleum and Mining Engineering, Suez University, Egypt, *emamtah@yahoo.com*

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Abstract

The most important used oil recycling technology is the re-refining. With these processes high quality base oil can be produced. Re-refining of Egyptian local crankcase used lubricating oil by solvent extraction/hydrotreating and vacuum distillation/hydrotreating was investigated. A comparison of its product characteristics with virgin base oil and the Egyptian standard regeneration lubricating oil is introduced. A higher quality of the base oil was obtained using solvent extraction than using vacuum distillation. Also, the re-refined base oil characteristics using solvent extraction have a slight difference, compared to the virgin oil and the Egyptian standard. The best results were obtained by a solvent to oil ratio of 5:1 at 24 hrs settling time. The base oil of total acid number (TAN) 0.2, pour point -7ºC, color 6, carbon residue 0.33%, ash content 0.093%, viscosity index 110 and flash point 194°C was obtained by solvent extraction. The re-refining using vacuum distillation gave the highest oil yield of about 84% compared to solvent extraction (about 78%).

Keywords: re-refining used lube oil; solvent extraction; vacuum distillation; hydrotreating; Ni-Mo/Al_2O_3 catalyst.

1. Introduction

Lubricating oils are widely used in industries to reduce friction and wear by interposing a thin film of oil between metallic surfaces. During normal use, impurities such as water, salt, dirt, metal scrapings, broken down additive components, varnish and other materials can get mixed in with the oil or be generated in it due to thermal degradation or oxidation [1-3]. Therefore, the oil quality gradually decreases to a level that the used oil should be replaced by a new one [4]. Disposing the used oil pollutes environment to a great extent [5]. Due to the increasing necessity of environmental protection and the more and more strict environmental legislation the disposal and recycling of waste oils become very important [6]. As a result, the used oil needs proper management to make it a valuable product [6].

The recycling of used oil has more than a four decade tradition. The idea of recycling of used lubricating oil in the year of 1930 was presented. The recycling of used oil can be accomplished with different methods, which are the reprocessing, reclamation and re-refining [2,7,8]. The most important methods for the recycling of used lubricating oils are re-refining and reclamation [7]. The processes of re-refining of used oil depend greatly on the nature of the oil base stock and on the nature and amount of contaminants in the lubricant resulting from operations.

Used oil has been re-refined using many techniques such as chemical (acid/clay) treatment [2,9], physical treatment by distillation and thin film evaporation and solvent extraction [1]. Furthermore, process waste lube oil can be converted into pyrolysis oil [3,10]. These techniques have different yield and product qualities, construction and operational cost. Since the chemical treatment creates environmental problems, therefore, solvent extraction was proposed as an alternate method [11]. The solvent extraction treatment has received considerable attention in recent years; because it overcomes the problems associated with acid sludge produced from chemical treatment [1]. Solvent could be recovered by distillation [12]. Recently, used oil has been re-

refined by vacuum distillation with chemical treatment or clay treatment, also, vacuum distillation with chemical treatment and hydrofinishing [2,13].

In the last decades, the hydrogenation and hydrocracking technologies modern catalysts have been developed which are able to hydrogenate feeds with high concentration of contaminations (e.g. high metal content refining residues, used engine oils). These catalysts are applied in high amount in so called guard reactor before hydrogenation and/or hydrocracking of residues due to their large pore size [14]. The Co-Mo/Al_2O_3 catalyst can produced the product oils, which had the best ASTM color, acidity, and viscosity index. Ni-Mo/Al_2O_3 catalyst produced the product oils, which had the lowest sulfur content while NiW/Al_2O_3 catalyst produced the product oils that had the best viscosity and flash point [15].

The major aim of this study was re-refined Egyptian local crankcase used lubricating oil to generate base oil by two techniques. The first technique was by solvent extraction followed by hydrotreating which studies the effects of various solvent to oil ratio and settling time on the yield of the refined oil. The second technique was by vacuum distillation followed by hydrotreating. The hydrotreating was carried out by using Ni/Mo catalyst based on silica alumina support. Tests carried out on the used/recycled oil include: flash point, pour point, metal contents, and other characteristics.

2. Experimental

2.1 Characteristic of the used oil

The re-refining of Egyptian local crankcase used oil was investigated. This used lubricating oil was collected by Alexandria Petroleum Company (El MAX) from different places and governorates in Egypt. The specification of used oil was evaluated according to ASTM standard tests and listed in Table 1.

Table 1 Characteristics of used and re-refined oils

Parameter	Used oil	Solvent extraction			Vacuum dist.
		D	E	H	H
TAN, mg KOH/gm	2.9	0.942	0.303	0.203	0.731
Pour point, ºC	-16	-15	-10	-7	-11
Flash point, ºC	128	212	218	194	190
Ash content, wt%	0.93	0.61	0.236	0.093	0.58
Carbon residue, wt%	1.3	2.57	0.97	0.325	0.29
Color	> 8	> 8	> 8	6	6
Water content, wt%	2	0.08	Nil	Nil	Nil
Viscosity at 40ºC, cst.	125.4	138.92	96	75.6	74
Viscosity at 100ºC, cst.	14.8	15.19	11.6	9.9	9.3
Viscosity index	111	111.48	109.28	110	101.5
Specific gravity at 40ºC	0.9	0.8652	0.8652	0.8471	0.8485
Yield, %	-	-	-	78.28	84.31

D- dehydration; E – extraction; H - hydrotreating

2.2 Solvent extraction followed by hydrotreating

The re-refining processes of the used lubricating oil in Egypt did not involve pre-treatment steps before distillation (dehydration), while international studies show complete processes that involve pre-treatment, solvent extraction or vacuum distillation and finishing steps such as clay contacting, hydrotreating and blending. Figure 1 shows the major steps in the two re-refining processes. The solvent extraction steps are as follows:

1. Dehydration (atmospheric distillation): Water and light contaminants were first removed from the used oil. Thus, the used oil was distilled up to 200ºC and furthered fractionated under vacuum (5 mmHg) to eliminate the light hydrocarbons. The residual fraction over 350ºC was obtained.

2. Extraction: This study used methyl ethyl ketone (MEK) as solvent for treatment instead of butyl alcohol and isopropyl alcohol. This choice was due to the difficulties in recovery of this solvent again that results in great lose in solvent which leads to high cost, in addition, the ease of recovery, low boiling point and low cost of the MEK. The solvent was of analytical grade and supplied by E. Merck.

   The dehydrated oil of initial boiling point of 320ºC was subjected to solvent extraction at 25ºC and atmospheric pressure. A mixer settler apparatus was used for extraction and temperature was controlled with the help of thermostatic bath. Dehydrated oil and solvent were stirred for one hour to ensure adequate mixing, and then subjected to sufficient settling. The oil/solvent mixture was separated and was freed from any suspended particles by centrifugation. The solvent was recovered by distillation, as the MEK boiling point is 80ºC, to reuse it again. To determine optimum conditions solvent to oil ratio and settling time were varied.
3. Hydrotreating: Hydrotreating of extracted oil took place by feeding the sample into a trickle bed reactor which serves for laboratory study of heterogeneous catalytic processes under pressure occurring in liquid or gaseous phase. The reactor contains catalyst bed of Ni/Mo that supported by silica alumina base. Commercial grade Ni-Mo catalyst was provided from Albemarle Catalysts Company (KF 841). The process take place at the following operating conditions, temperature: 350ºC, pressure: 50 Kg/cm^2, LHSV: 0.7 and hydrogen to oil ratio: 300 L/L.

   Hydrogen gas stream is supplied to the unit from a hydrogen cylinder having a maximum pressure of 120 Kg/cm^2. The unit was first flushed with nitrogen to remove air, and then kept for 4 hrs under a hydrogen gas pressure of 100 Kg/cm^2 to check any leakage. The catalyst bed was reduced and sulfided. The liquid feed and the hydrogen gas streams are injected under pressure at the top of the reactor, both cross the different zones of the reactor in down-flow direction.

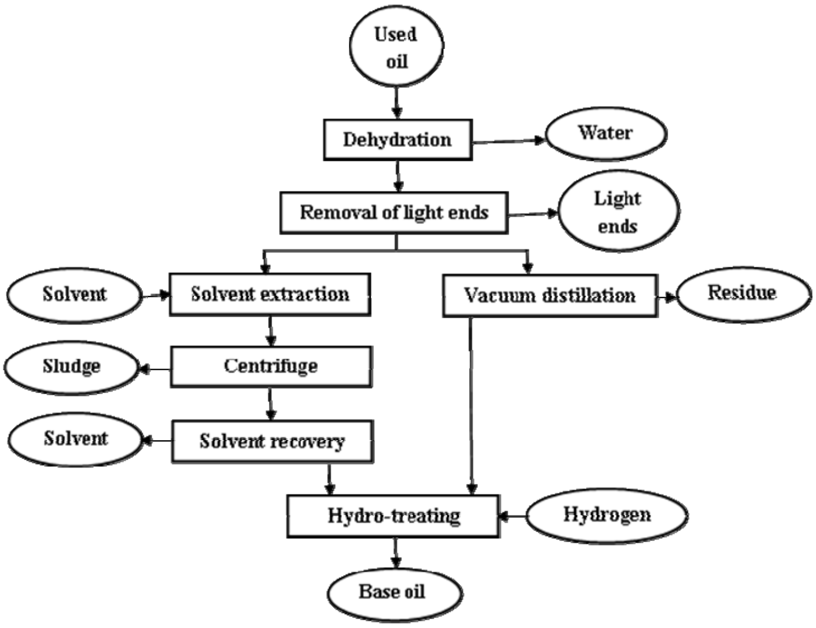

Fig. 1. Major steps in re-refining processes.

2.3 Vacuum distillation followed by hydrotreating

This process combines vacuum distillation and hydrotreating to eliminate most of the polluting substances in used oil. The steps of this process are as follows:

1. Dehydration (atmospheric distillation): This step was discussed in the solvent extraction process.
2. Vacuum distillation: The dehydrated oil obtained is sent directly to a vacuum distillation zone at a temperature of 310ºC under pressure 15 mmHg. The vacuum distillation produces

a residue and at least one fraction of distilled oil, the range of the distillate which sent directly to hydrotreating is from (270 to 320)°C.

3. Hydrotreating: This step in detailed discussed above in solvent extraction process.

2.4 Analysis

ASTM standard methods were used to determine various properties of the used lube oil. Total Acid Number (TAN), specific gravity at 40°C, water content, color, flash point, carbon residue, viscosity index, pour point, ash content, viscosities at 40 and 100°C were determined according to ASTM D974, D1298, D95, D1500, D92, D189, D2270, D97, D874 and D445 respectively. Metal contents were determined using the atomic absorption spectrometer. The hydrocarbon composition was analyzed by distillation gas chromatograph.

3. Results and Discussion

3.1 Solvent extraction followed by hydrotreating

Used oil is a complex mixture of recoverable base oil, additives, water, light hydrocarbons, metals and carbonaceous particles. A good extraction solvent should dissolve base oil and precipitate other substances to form sludge. This process combines extraction with solvent and hydrotreating by removing the foreign substances by solvent and then improving oil quality by hydrotreating. First, the water and light ends are removed and the used oil is separated through MEK extraction. Then the extracted oil is subjected to hydrotreating for purification purposes. The treated oil was analyzed after each step for TAN, ash content, pour point and other characteristics. Table 1 shows the characteristics of the used and treated oil by the various re-refining processes. The metal contents and the hydrocarbon compositions of the treated oil by the various solvent extraction steps are reported in Table 2 and Figure 2, respectively.

Table 2 Metal contents in ppm for different steps of solvent extraction

Metal	Dehydration	Extraction	Hydrotreating
Zn	630	2.31	0.22
Pb	1270	0.569	0.406
Cu	27	Nil	Nil
Mg	300	29.3	22.30
Fe	130	Nil	Nil
Ca	1195	89.14	42.38

Table 3 Yield and ash content at different settling time

Settling time	24 hr	48 hr
Yield, wt%	95.7%	95.7%
Ash content, wt%	0.236	0.189

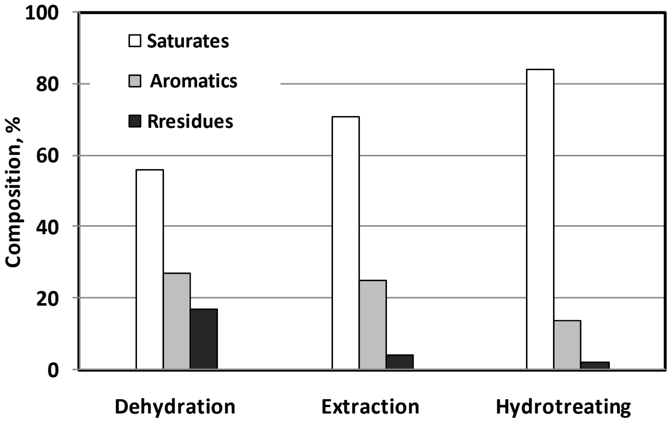

Fig. 2. Composition of the treated oil by the various steps of solvent extraction.

3.1.1 Dehydration step

Water found in lubricating oil in service depends on where the automobile is being used. In normal operating conditions 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. 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. Therefore, the first step of the re-refining of the used oil was dehydration by atmospheric distillation while light hydrocarbons are separated in vacuum distillation. After dehydration process water and light hydrocarbon decrease, however, water decreased from 2 to 0.08 wt%.

3.1.2 Extraction step

The extraction of dehydrated oil by MEK at different solvent to oil ratio was studied. The results of the yield and ash content from the extraction are shown in Figure 3. It is found that the removal of ash content increases with increasing of solvent to oil ratio from 3:1 to 5:1, respectively. The yield and removal of ash content remain independent of solvent to oil ratio greater than 5:1. The capability of a solvent to separate contaminants from used oil is closely related to its solubility parameters. Solvent to oil ratio lower than 5:1 leads to reduce the solvency power and also not to improve the properties of the recycled oil. This means that larger solvent to oil ratio will lead to dissolution of some contaminants especially the ash forming material, which was considered to be undesirable. As a result of the above mentioned facts, the ratio of 5:1 was considered to be the better solvent to oil ratio used for the treatment of used oil. However, critical clarifying ratio for MEK has been reported as 2.6:1 at 35°C [2] with minimum oil remaining in sludge [16]. Perhaps the difference is due to free sedimentation instead of centrifugation and also due to the increase in the temperature of the extraction.

The effect of the settling time was studied. Table 3 reports the extraction by MEK at different settling time with the solvent to oil ratio 5:1. The removal of ash content was slightly increased by increasing settling time from 24 to 48 hrs. However, the increase in settling time has negligible effect on the yield percent.

The results of the extraction of dehydrated oil with solvent to oil ratio 5:1 for settling time 24 hrs are shown in Table 1. The unsaturated, aromatic and heteroatom containing molecules are reduced (Figure 2). The percentage of saturates increase from 56% to 71% due to reduction in the residues percentage so that pour point increased from -15 to -10. In addition, viscosity index, ach content reduced to 109 and 0.236, respectively. Specific gravity of the dehydrated and extracted oil was found to be almost insensitive, as shown in Table 1.

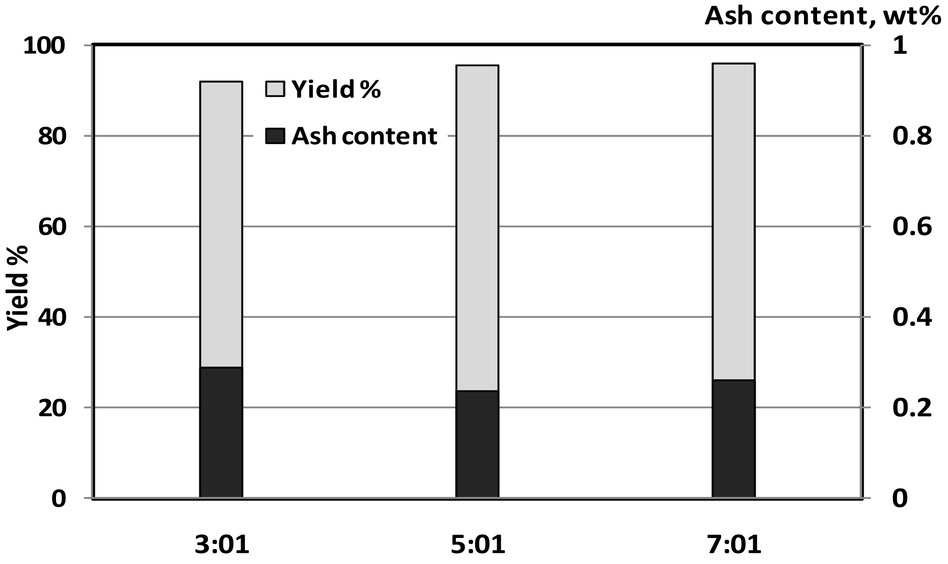

Fig. 3. Yield and ash content at different solvent to oil ratio.

Majority of metal particles coming from the cylinder wall and from the piston get into the engine oil. Such particles are, e.g. iron, copper, magnesium, calcium, etc. Other part of the metals originated from additives that are originally in engine oil [4]. Such particle is e.g. zinc. These metals in parts per million (ppm) are found in the used oil. Also, these metals are found due to the corrosion caused by the presence of water. Table 2 shows that, the extraction step reduced zinc, lead, magnesium, and calcium contents from 630, 1270, 300 and 1195 to 2.31, 0.57, 29.3 and 89.14 ppm, respectively. However, copper and iron were completely removed after the extraction step.

3.1.3 Hydrotreating step

By the knowledge hydrotreating process improves lubricating oils color and color stability and also reduces the level of halogen, sulfur, oxygen, nitrogen and metals compounds. Reduction in metallic content is due to effect of de-metallization bed (alumina). Also, a lot of the aromatics and other unsaturates (which were not eliminated by previous steps) are saturated to an acceptable low level. Saturates are increased to about 84% (Figure 2). In all steps before hydrotreating, the removal of color was negligible. The hydrotreated oil clearly appeared under a suitable treatment for the removal of color. Color was improved from 8 to approximately 6 (Table 1). In addition, used oil was found to have a TAN of 2.9 mg KOH/gm while the dehydration and extracted oil steps reduced this value to 0.942 and 0.303 mg KOH/gm, respectively. However, the hydrotreated oil had a TAN value of 0.203 mg KOH/gm.

The decrease in value of flash point for the used oil could be as a result of the presence of light ends of oils. 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 [17]. The flash point of the re-refined oil was facilitated by the removal of the light ends. The flash points are 128°C, 212°C, 218°C and 194°C for used oil, dehydrated oil, extracted oil, and hydrotreated oil, respectively.

3.2 Vacuum distillation followed by hydrotreating process

The vacuum distillation process for used oil re-refining consists of three steps. In the first step water and light ends are reduced. After this step the dehydrated oil is treated by vacuum distillation. The final step is the hydrotreating of the oil after the vacuum distillation treatment. Characteristics of the re-refined base-oil after the final step of vacuum distillation process (hydrotreating step) are shown in Table 1. On comparing properties of used and re-refined oil (Table 1) it is clear that all characteristics were varied after treating by vacuum distillation followed by hydrotreating. The specific gravity of the re-refined oil was changed from 0.9 to 0.8485 and the kinematic viscosity was changed from 14.8 to 9.3 cst. at 100ºC. TAN is also reduced significantly from 2.9 to 0.731 mg KOH/gm, indicating that organic and inorganic acids, esters, phenolic compounds, lactones; resins etc. have been reduced. The pour point was changed from -16 to -11ºC. The saturated compounds were increased from 56% to 78% due to hydrotreating of oxidation product and other unsaturated hydrocarbon, also color will be improved. The metal contents of the re-refined oil showed lower value than used oil. In addition, the iron and copper content were completely removed after hydrotreating (Figure 4). The yield of the base oil was found to be about 84%.

3.3 Comparison of solvent extraction and vacuum distillation

The performance characteristics of the used oil are varying considerably than those of virgin and the Egyptian standard regeneration lubricating oils [18]. The re-refined base oil properties are comparable with those of the virgin base oil, the Egyptian standard regeneration lubricating oil and the used oil as shown in Figure 5. Figure 4 compares the metal contents of re-refined oil by the solvent extraction and vacuum distillation. Significant differences are observed with respect to the ash content, pour point, and other characteristics, as well as the metal contents.

Pour point is very important to users of lubricants in low temperature environment. As the lube oil is used, the long aliphatic chains attached to the aromatic ring is separated and cracked as a result of oxidation. The oxidation products, such as aldhydes and ketones have a low pour point, however, the pour point of the used oil is -16ºC lower than the virgin oil (-8ºC) and the Egyptian standard oil (-3ºC). By treatment the oxidation products are removed or the long chains may be reformed as in the hydrotreating. So the pour point increases to -7 and -11 by solvent extraction and vacuum distillation, respectively. The increasing pour point by solvent extraction could be due to the removal of oxidation products and contaminants by solvent, in addition, the increasing of the saturated compounds. The saturated and aromatic compounds concentrations in the re-refined oil are about 84 and 14% by using solvent extraction instead of 78 and 20% by vacuum distillation, respectively.

Petroleum products contain acidic components present as additives or as degradation products. Total acid number (TAN) is used as a guide in the quality control of lubricating oil and also as a measure of lubricant degradation in service [6]. Figure 5 shows that, TAN in the base oil from vacuum distillation was found to be more than three times that from solvent extraction.

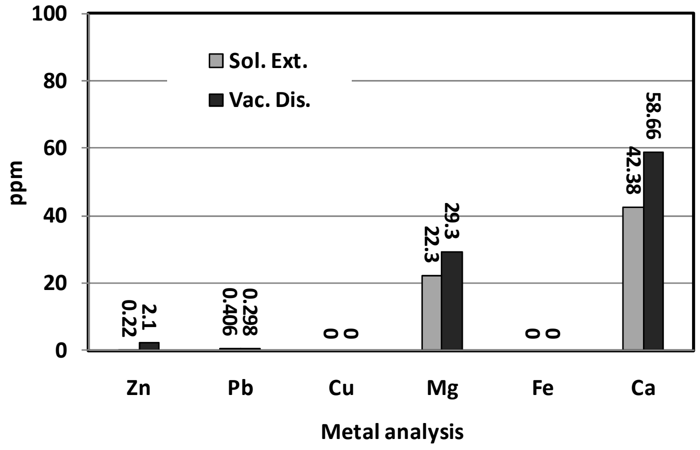

Fig. 4. Comparison of the metal contents of re-refined oils.

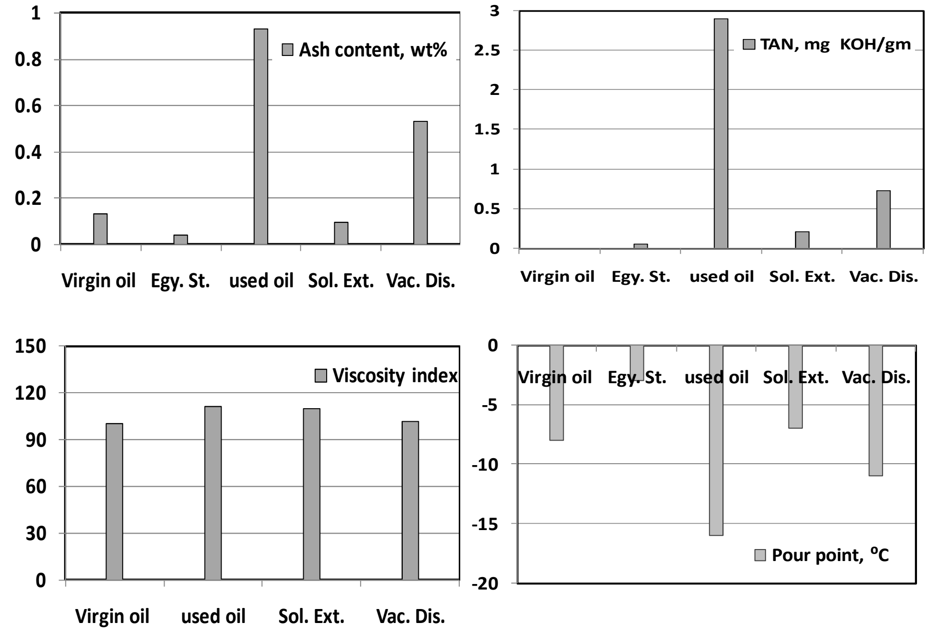

Fig. 5. Comparison between the properties of re-refined oil with the virgin, Egyptian standard [18] and used oils.

Viscosity is the most important consideration of choosing lubricants. The viscosity index (VI) refers to the changing degree of viscosity dependent on temperature. The increasing of viscosity can occur due to oxidation or contamination with insoluble matter [17]. From Table 1, it is very surprising that the re-refined oils have the lowest viscosity, much lower than the used oil. This could be attributed to the re-refined processes described above were very efficient in reducing the contaminants in the used oil including metals and other contaminants (Figure 4). The result shows also that treating using solvent extraction process gave the higher viscosity index than vacuum distillation and virgin oil (Figure 5). In addition, a higher viscosity index, no finishing process should be additionally required to improve it.

Both the re-refining processes results showed that high quantity of magnesium and calcium in the re-refined oil is achieved as compared to other types of metals, as shown in Figure 4. In addition, solvent extraction gave the best results of calcium and magnesium contents. The large amount of magnesium content in the used lubricant oil is mostly contributed by the additives added for the performance improvement of the lubricant oil. However, the vacuum distillation process is more effective in removing lead. The result for lead is 0.406 ppm using solvent extraction and 0.298 ppm by vacuum distillation. However, copper and iron of re-refined oil from the two processes are nil showing that completes removal is achieved.

The result shows also that re-refining using vacuum distillation gave the highest oil yield of about 84%. The decrease of oil yield by solvent extraction (about 78%) can be attributed to oil trapped in the oil sludge during the sedimentation step.

On comparing characteristics of re-refined base oil to virgin, the Egyptian standard and used oils, it is clear that solvent extraction and vacuum distillation are good techniques for the removal of contaminants from used oil which enhances desired properties for quality lubricating oil. In addition, Figure 5 shows that the solvent extraction qualifies first with respect to pour point, ash content, and TAN. With the addition of specific chemical additives, the properties of the lubricating oil are enhanced. Various types of additives are blended with base oil according to its grade and specific duty.

4. Conclusions

This study was carried out on Egyptian local crankcase used lubricating oil collected by Alexandria Petroleum Company (El MAX) from different places and governorates in Egypt. The two re-refining processes were studied, namely: solvent extraction/hydrotreating and vacuum distillation/hydrotreating. The results were compared with each other and with those of virgin base oil and the Egyptian standard regeneration lubricating oil. From the results presented, it is clear that the two processes effectively re-refined the used lubricating oil with 78 and 84 yield% using solvent extraction and vacuum distillation, respectively. The most excellent quality of the base oil re-refinery by solvent extraction was obtained using solvent to oil ratio 5:1 with settling time 24 hrs, while, the oil compositions were consisting of 84% of saturates, 14% of aromatics and 2% of residue. Also, it can be carried out at ambient temperature with cheap and low boiling point solvent MEK. There is slight difference in quality between the re-refine base oil using solvent extraction and the base virgin and the Egyptian standard oils. With the addition of specific chemical additives, the properties of the re-refine oil are enhanced.

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