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Re-refining of Used Lube Oil, II- by Solvent/Clay and Acid/Clay-Percolation Processes

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ABSTRACT

Used oils are lubricating oils which have become unsuitable for their proposed use. They may be recycled through the use of re-refining process to achieve useful products. This study compares two different re-refining processes. A laboratory scale setup of solvent extraction/clay and acid/clay-percolation processes were established to re-refine used oil collected from different sources. A comparison of its product characteristics with virgin base oil and with Egyptian standard regeneration lubricating oil characteristics is introduced. The results showed that, pour point increased from -15ºC for feed oil to -2ºC for acid/clay-percolation process and -6ºC for solvent/clay process. This is compared with -8ºC for virgin base oil. Sulfur content was found about 0.42wt% for acid/clay-percolation and 0.81 wt% for solvent/clay. In general, a best quality of the re-refined base oil using acid/clay-percolation was obtained and nearly meets the Egyptian standards. On the other hand, a higher yield of about 83% using solvent extraction/clay treatment was achieved.

Keywords: *Re-refining used oil; Base oil; Solvent extraction; Clay-percolation; Acid treatment*

1. INTRODUCTION

As With increasing new industries, increase in number of vehicles and mechanization of agriculture, and the volume of used lubricating oil produced each year is also increasing. Generated used oil can be considered as a source or as a resource of pollution. The used oil contains water, salt, broken down additive components, varnish, gum and other materials (Durrani et al., 2011; Kamal and Khan, 2009; Ogbeide, 2010). 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, aldehydes, phenolic compounds, alcohols, acidic compounds, non-stable products of hydrocarbons. In addition, used oil absorbs nitrogen oxides and the acidic fuel combustion exhaust gas. These compounds besides dust, fuel, lubricating oil additives degradation products, and fuel additives regularly decrease the lubricating oil performance. Moreover, the viscosity increases by production of an asphalt-like sludge, which a metallic scrapings act as catalysts at the high operating temperature and oxygen vicinity (Bridjanian and Sattarin, 2006; Rahmanet al., 2008). This used oil needs proper management to make it a valuable product by minimizing the quality of oil being improperly disposed off and reducing the waste oils environmental burden. Therefore, recycling of used oil justifies the interest in elimination of pollution.

The recycling of used oil has more than a four decade tradition. The idea of recycling of used oil was presented in the year of 1930. Initially the used oil was burned to produce energy, and later this oil was re-blended to engine oil after treatment. Recycle of used oil has been carried out by several methods (Gorman 2005; Josiah and Ikiensikimama, 2010; Kamal and Khan, 2009).

Recycling technology is the most important used oil re-refining. During re-refining the mechanical, physical and chemical contaminations are removed with the following processes: distillation, acidic refining (Abdel-Jabbar et al., 2010; Kamal and Khan, 2009), solvent refining (Durrani et al., 2011; Ogbeide 2010), clay treatment, hydrogenation (Kamal and Khan, 2009; Jhanani and Joseph, 2011), or combinations of the formers. These processes have different yield and product properties, construction and operational cost.

Solvent extraction followed by adsorption has been found to be one of the competitive processes for recycling of used lubricating oil. Solvent chosen should have maximum solubility for base oil and minimum for additives and carbonaceous matter. Propane and ethane have also been used as extracting solvents giving low yield 72-80% (Rincon et al., 2007). Solvent could be recovered by distillation.

Sulfuric acid has been used to remove asphaltenic material. The product is then clay treated (Josiah and Ikiensikimama, 2010; Rahman et al., 2008). The sludge could be used as fuel which leads to the production of acidic gases. Use of acid could be avoided by treating used oil with natural polymers (Kamal and Khan, 2009). Recently, used oil has been re-refined by thin film distillation under high vacuum followed by clay treatment or hydro-treatment (Kamal and Khan, 2009; Jhanani and Joseph, 2011).

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Natural clay is used as adsorbent in the treatment of used oil. Clay has been activated and dried up. There are basically two clay treatment methods. These are contact by mixing treatment and percolation or filtration through a bed of adsorbent (Olugboji and Ogunwole, 2008).

This study has been aimed to re-refine Egyptian local crankcase used oil using two processes, searching for higher quality and yield. The re-refining processes were solvent extraction followed with clay treatment and acid treatment followed with activated clay-percolation technique. A comparison of its product characteristics with virgin base oil and with Egyptian standard regeneration lubricating oil characteristics is investigated.

2. EXPERIMENTAL

A laboratory scale setup was established for re-refining used oil. Figures 1 and 2 shows the major steps in the processes of re-refining. Egyptian local crankcase used oil was re-refined. This used lubricating oil was collected by Alexandria Petroleum Company (El MAX) from different places and governorates in Egypt. Collected oils were then mixed together to represent a complete spectrum of used lube oil.

The re-refining processes of the used lubricating oil in Egypt did not involve pre-treatment steps before dehydration, while international studies show complete processes that involve pre-treatment, solvent extraction or other techniques followed with finishing steps such as clay contacting, hydrotreating and blending.

The first step of the re-refining involved removal of water from the used oil by atmospheric distillation. Thus, the used oil was distilled up to 200^{o}C and furthered fractionated under vacuum (5mmHg) to eliminate the light hydrocarbons. The residual fraction over 350^{o}C was obtained. The dehydrated oil (feed oil) was collected and sent to the next steps for further treatment. The next steps involved the solvent extraction followed with clay treatment or acid treatment followed with clay-percolation. The characteristics of the used and feed oils were listed in Table 1.

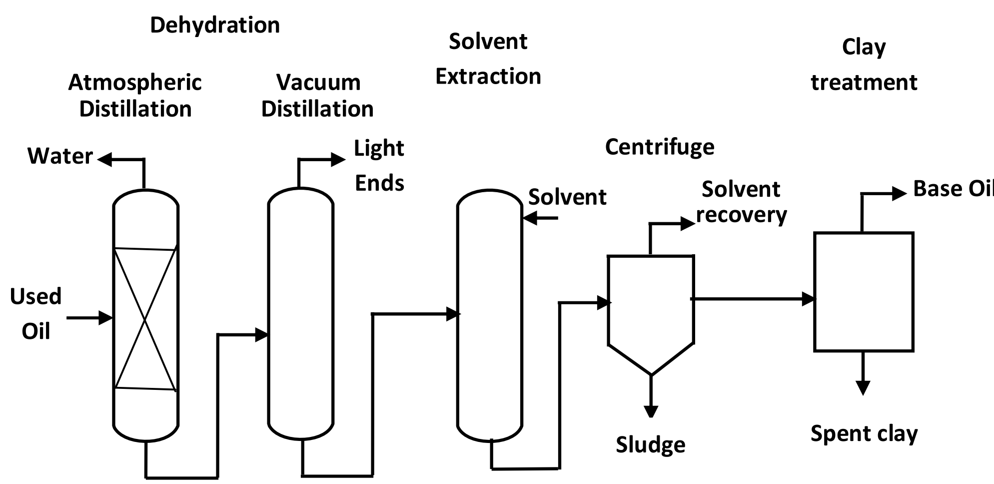

Fig 1: Major steps in solvent extraction/clay re-refining process.

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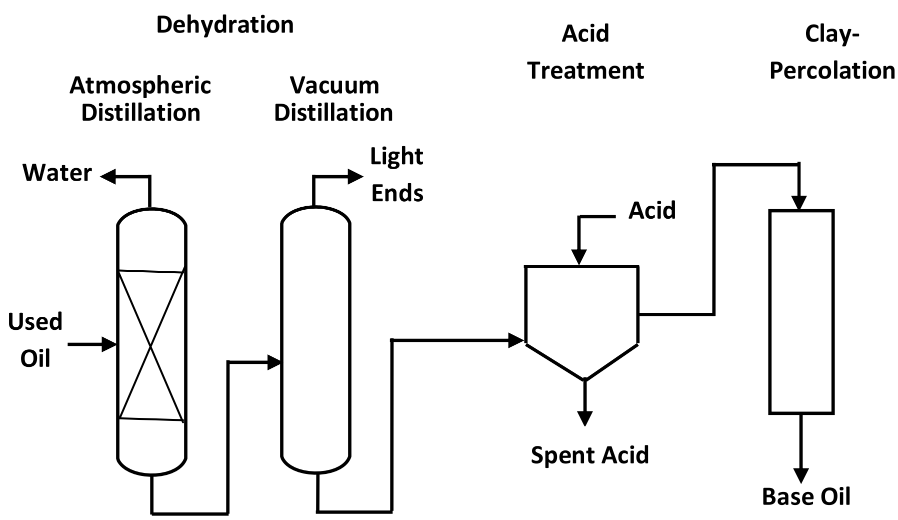

Fig 2: Major steps in acid treatment/clay-percolation re-refining process.

The process of solvent extraction followed with clay treatment of feed oil (dehydrated oil) in the next stage was applied. Firstly, solvent extraction study used methyl ethyl ketone (MEK) as solvent for treatment. This solvent is easily of recovery, low boiling point and low cost of the MEK. The solvent was of analytical grade and supplied by E. Merck. The feed oil was mixed to solvent at 25 °C and atmospheric pressure. Solvent to oil ratio was 5:1. A mixer settler apparatus was used for extraction and temperature was controlled with the help of thermostatic bath. The oil/solvent mixture was stirred for one hour to ensure adequate mixing, and then subjected to sufficient settling for 24 hours. The mixture was separated and was freed from any suspended particles by centrifugation. The Solvent was recovered by distillation, as the MEK boiling point is 80°C, to reuse it again.

At the clay treatment step, 100 ml of extracted oil was mixed with a solvent of petroleum ether with a ratio 1 to 2, respectively, and then mixed with a measured amount of the clay (20 % w/w). The clay sample was taken from the Eastern Desert of Egypt near the Red Sea Coast. The mixture was performed at the room temperature of 30 ± 2°C on a magnetic stirrer with constant stirring. The mixing time was one hour. The treated oil was separated by settling and then filtrated to remove clay and other solids. The solvent was separated from treated oil by distillation.

Table 1: Characteristics of used and feed oils.

Parameter	ASTM	Used oil	Feed oil (dehydrated oil)
TAN, mg KOH/gm	D974	2.9	0.922
Pour point, °C	D97	-16	-15
Flash point, °C	D92	128	212
Ash content, wt%	D874	0.93	0.61
Carbon residue, wt%	D189	1.3	2.57
Color	D1500	> 8	> 8
Water content, wt%	D95	2	0.08
Viscosity at 40°C, cst.	D445	125.4	138.92
Viscosity at 100°C, cst	D445	14.8	15.19

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Viscosity index	D2270	111	111.48
Specific gravity at 40ºC	D1298	0.9	0.8652
Sulfur content, wt%	D129	0.97	-
Saturated content %	-	-	56
Aromatics content %	-	-	27
Residues %	-	-	17

At acid treatment, feed oil was treated with 98% concentrated sulfuric acid with a ratio 4:1, respectively. The mixture was then stirred for one hour at 50°C. The mixture was then allowed to cool and kept undisturbed for 24 hours for deasphalting and settling of acid sludge from acid treated oil. After sludge removal, the treated oil was washed with ethyl alcohol absolute to extract the soluble acid still remained.

The next step of acid treatment was the clay-percolation, an adsorption process would take place. Clay was firstly activated at 120ºC for 2 hours. Activated clay is used to improve color and oxidation stability of the treated oil by acid. Percolation technique was carried out via a continuous process. The treated oil by acid passed through adsorbent of activated clay in a double jacket long glass column.

For each process, re-refined base-oil was collected and analyzed. ASTM standard methods were used to determine various properties of the base-oil (as listed in Table 1). Metal contents were determined using the atomic absorption spectrometer. The hydrocarbon composition was analyzed by distillation gas chromatograph.

3. RESULTS AND DISCUSSION

Two different sets of processes were used to study re-refining used lube oil. Solvent extraction by MEK followed with further treatment by clay and acid treatment followed with the clay-percolation. The treated oil was analyzed for pour point, ash content, water content, viscosity index, total acid number (TAN), specific gravity, sulfur content, metal content and hydrocarbon composition. These properties were compared to each other and with their values in the virgin base oil and also with Egyptian standard regeneration lubricating oil characteristics. These characteristics of the treated oil are shown in Table 2 and Figure 3. The hydrocarbon compositions of the treated oil by the various processes are illustrated in Figure 4.

Figure 3 is comparing some of the re-refined oils characteristics produced from the two processes with the virgin base oil. Petroleum products contain acidic constituents present as additives or as degradation products. Total acid number (TAN) is the quantity of base expressed in milligram of potassium hydroxide per gram of sample. Acid number is used as a guide in the quality control of lubricating oil and also as a measure of lubricant degradation in service. Here, feed oil was found to have a TAN of 0.922 mg KOH/gm while re-refined base-oils have about 0.055 and 0.052mg KOH/gm with solvent/clay and acid/clay-percolation, respectively. These results indicate those organic and inorganic acids, esters, phenolic compounds, lactones; resins etc. have been reduced more successfully using acid/clay-percolation process. Specification of TAN for lube oils varies depending on its grade and end-use.

Table 2: Characteristics of treated oils.

Parameter	Solvent/Clay	Acid/Clay-percolation
Sulfur wt.%	0.81	0.42
Water content, wt%	Nil	Nil
Specific gravity at 40ºC	0.6991	0.8202
Metal content, ppm		
Fe	Nil	Nil
Cu	Nil	1.048
Zn	117.8	52
Yield, wt%	83.05	63.76

As the lubricant 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 aldehydes and ketones have a low pour point so as we may notice the pour point of the feed oil is low (-15ºC) and lower than the virgin base oil (-8ºC). By treatment the oxidation products are removed, so the pour point value increases again. From Figure 3, pour point of the re-refined base-oils was found to be sensitive with the re-refining processes. However, the pour point of the acid/clay-percolation is -2ºC and of the solvent/clay is -6ºC. It may be attributed to the higher removal of the oxidation products and contaminants using acid/clay-percolation process.

Ash-content of the product oil was low. After acid/clay-percolation process, ash content of the re-refined base-oil was significantly reduced to 0.12wt% (Figure 3) lower than its value in the virgin base oil of about 0.13wt%. Whereas, ash content with solvent/clay process was 0.17wt %.

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Viscosity is the most important consideration of choosing lubricating oils. The strength of the oil film is approximately proportional to its viscosity, so the higher viscosity indicates the stronger strength of the oil film. Increasing viscosity of used oil can occur due to oxidation or contamination. Viscosity decrease can be caused by dilution with light fuel. The viscosity index (VI) refers to the changing degree of viscosity dependent on temperature: the higher VI means a lower viscosity change in the temperature change, and vice versa. Figure 3 shows that, a higher viscosity index of the feed oil, no finishing process shall be additionally required to improve it, making it more suitable for recovery and reuse with a relatively smaller operating cost. Thus, the VI of the re-refined base oils is higher than the feed and the virgin values. However, the result shows that the re-refining using acid/clay-percolation gave the highest VI.

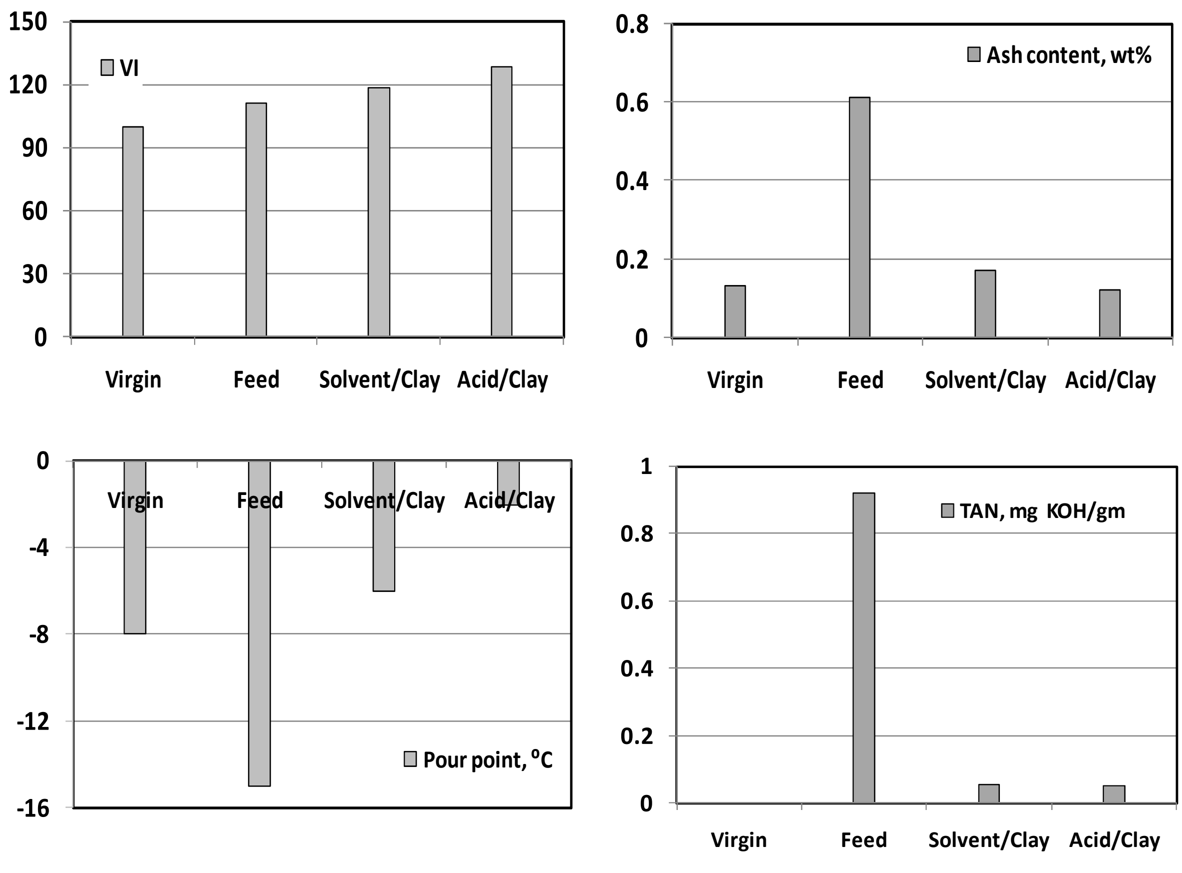

Fig 3: Comparison between the properties of re-refined base oil with the virgin and feed oil.

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 found in the used oil. In addition, 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. The best re-refining process proved better yield when compared to that of acceptable refined base oil standard of individual metal contents. The metal content of the treated oils after solvent/clay and acid/clay-percolation are shown in Table 2.

The treated oils showed complete removal of contaminated iron. Acid/clay-percolation process results showed that high quantity of zinc is adsorbed in the activated clay-percolation, compared to the other process. The large amount of zinc content in the used lubricant oil is mostly contributed by the additives added for the performance improvement of the lubricant oil (for example, zinc dithiophosphates). The result for copper is nil and 1.05 ppm with solvent/clay and acid/clay-percolation, respectively.

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Table 2 shows the values of sulfur content for the re-refined base oils by the two processes. The sulfur content of used oil 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 damage wear. Corrosion in engines is caused by mineral acids formed by the oxidation of sulfur compounds in fuel in internal combustion engines with lubricating oils; those hydrocarbons that were inherently unstable will have been oxidized during use. Sulfur content was found about 0.42wt % for acid/clay-percolation and 0.81 wt % for solvent/clay.

The specific gravity of the feed oil is higher than the re-refined oils (see Tables 1 and 2) and lower than the virgin base oil (0.89). The results for the feed and re-refined oils with solvent/clay and acid/clay-percolation are 0.8652, 0.6991 and 0.8202, respectively. The specific gravity of contaminated oil could be lower or higher than that of its virgin base oil depending on the type of contamination. If the used 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.

From Figure 4, the feed oil has not more than 56% of saturated compounds and the rest is aromatics and residues compounds. After re-refining processes, the saturation compounds increased to 76% and 84% with solvent/clay and acid/clay-percolation, respectively. The increasing of the saturated compounds using acid/clay-percolation may be attributed to that the most of the aromatic hydrocarbons are left behind in the clay-percolation.

Yield is a very important factor as it reflects the effectiveness of the process and has direct relation to the process cost as high yield means more available material to sell and it increases the motivation for production but it offset the quality as high yield mostly contributes to low quality. Yield of the base-oil was found to be 83 % and 63.8% with solvent/clay and acid/clay-percolation, respectively (Table 2). The lower yield with acid/clay-percolation process may be referring to removal of a high amount of contaminants, sludge, and metals.

The re-refining process produced sludge in the following steps: dehydration, solvent extraction or acid treatment and clay treatment. If disposed to the environment, separated sludge can cause severe pollution as they are concentrated forms of contaminants. However, these sludges can be used as a modifier for bituminous materials. They can also be used for the preparation of carbon rods as they are rich in carbon content. Moreover, the sludge is completely combustible with net heating value amounting to 4,000 kcal/kg (Rahman, et al., 2008). If burned, use of appropriate burners and methods for pollution abatement is necessary. Furthermore, it was concluded that treatment of acid sludge with different salt formulations provides a potentially lowest cost source of gilsonite varnish for news ink and also helps in reducing the environmental problem created by re-refining used oil (El-Adly, et al., 1997).

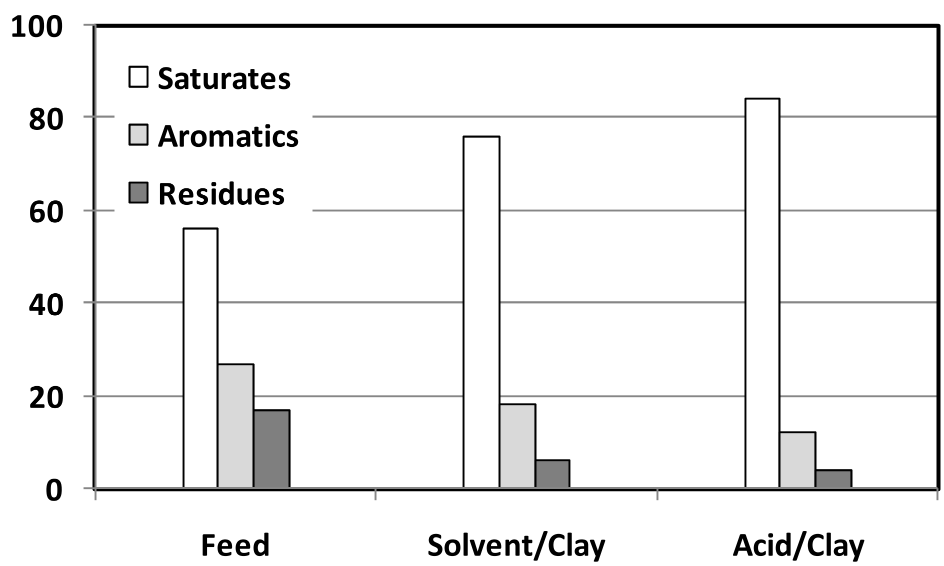

Fig 4: Composition of the feed and re-refined base oils.

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By comparing the characteristics of the re-refined base oils produced from the two processes (see Table 2 and Figures 3) with the Egyptian standard regeneration lubricating oil characteristics as shown in Table 3. The characteristics of re-refined base oil produced by acid/clay-percolation process nearly meet the Egyptian standards except for the ash content which need more treatment. But, solvent/clay process requires more treating to meet the Egyptian standards. However, its yield is the highest; so, the performance of re-refined oil could be increased by adding more additives.

From the above results (Table 2 and Figures 3&4), it can be seen that the acid/clay-percolation process has the best performance in treating the used oil and gave the best characteristics of the treated oil. It may be explained that, the lubricating oil during usage leading to the formation of oxidative products/organic acids, unsaturated, condensed aromatics and mercaptans, as phaltenes and petroleum resins. The removal of these compounds is accomplished with sulfuric acid. Sulfuric acid is a poly functional mineral acid which can act both as a sulphonating and an oxidizing agent. Also it can act as a catalyst for some polymerization reaction of unsaturated hydrocarbons hence treatment of the used oil with sulfuric acid results sulphonation and oxidation of the degraded products. In addition, in the clay-percolation step, the remaining contaminants were removed by using thermally activation clay, which proves even more selective and give high surface area, high porosity particles.

Table 3: Egyptian Standard regeneration lubricating oils characteristics*

Test	Unit	Kinematic viscosity at 100□C			ASTM
		9.3-12.5	12.5-16.3	16.3-21.9	
Flash point by Pensky Martin Closed-Cup (min)	□C	185	190	195	D93
Flash point by Cleveland Open-Cup (min)	□C	200	205	210	D92
Pour point (max)	□C	-3	-3	-3	D97
Water content (max)	vol%	0.01	0.01	0.01	D1744
Conradson carbon residue (max)	wt%	0.35	0.45	0.55	D189
Inorganic acids and soluble alkaline	-	Nil	Nil	Nil	D182
Ash content (max)	wt%	0.04	0.04	0.04	D874
Color by ASTM (max)	-	2	3.5	4	D1500
Sulfur content (max)	wt%	0.35	0.4	0.5	D129
Total acidity (max)(mgKOH/gm oil)	-	0.05	0.05	0.05	D974

* Egyptian Organization for standardization & Quality (EOS), 2005

4. CONCLUSION

The effect of the re-refining Egyptian local crankcase used oil by using solvent/clay and acid/clay-percolation processes were studied and compared with the virgin base oil and the Egyptian standard regeneration lubricating oil characteristics. The processes of re-refining of used oil are performed using natural clay. The result shows that the acid/clay-percolation process gave lower characteristics of the re-refined base oil than solvent/clay process. This process also decreases the zinc content in re-refined base oil. After re-refining processes, the saturation compounds increased to 76% and 84% with solvent/clay and acid/clay-percolation, respectively. Maximum yield of 83% was obtained with solvent/clay process. It is clear that acid/clay-percolation process is a good technique for the removal of impurities from used oil which enhances desired characteristics for quality base oil. The characteristics of the re-refined base oil as specific gravity, pour point, and other from acid/clay-percolation process nearly meet the Egyptian standards.

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