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Used lubricating oils re-refining by solvent extraction

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Abstract

The objective of this work is to investigate the re-refining of used lubricating oils using solvent extraction process Experiments were carried out on used oils collected from several service stations. Used oils were subjected to solvent extraction of base oil using different classes of solvents including alcohols (i.e. methanol, 1- propanol, butyl alcohol and iso-butanol), ketones (i.e. acetone and methyl ethyl ketone) and hydrocarbon solvent (i.e. Hexane) to pre-select suitable solvents. Bench scale study was carried out to investigate the effect of different variables including mixing time, mixing speed, settling time and temperature. Extraction processes were carried out using butyl alcohol, 1-propanol, and acetone. The results obtained indicate that extraction with butyl alcohol gives the highest extraction yield of 93.4% with high impurities at room temperature, followed by 1-propanol where the extraction yield was 90.7% but at higher mixing time, mixing speed and temperature. An extraction yield of 51% was obtained by acetone. The extracted base oils were analyzed to determine the effect of solvent on the metallic and sulfur content. It was found that the metallic content of the extracted base oil by acetone is the lowest followed by butyl alcohol. On the other hand, the sulfur content of the extracted oil by butyl alcohol was lower than that using acetone.

Keywords

Used Lubricating Oils, Waste Lubricating oils, Re-Refining ,Recycling, Solvent Extraction

1. Introduction

Lubricants are fluids filled into engines, gearboxes and hydraulic systems that are used to prevent over-heating and damage between two solid surfaces in contact with each other and therefore are an important component of an engine to enable it to perform optimally [1].

In Egypt the Egyptian General Petroleum Co-operation (EGPC) study revealed that approximately 300,000 tons of engine oil lubricants are used locally each year for automotive and industrial purposes and estimated that the actual amount of waste oil that could be collected annually is 150,000 tons. "Recycling this quantity of waste oil should produce approximately 120,000 tons [2].

The present work concentrates on a specific type of waste oil, spent lubricants which can come from the use in engines as lubrication.

One of the more common and significant sources arises from the use of engine lubricants in automobiles. Waste oil generated from automobile usage, is the material studied in this work due to its constant generation from routine oil changes, as well as contamination from dirt, water, salts, metals, incomplete products of combustion, or other materials. Additives to lubricating oil may also break down under use, adding contamination [3].

The basics of this pretreatment is the use of a solvent to selectively extract the base oil components from the waste lubricant oil in a process that would be quite similar to the commonly used in crude oil refining to separate out asphaltenes for producing heavy neutral base oil (bright stock)[4].

2. Experimental Procedure

2.1. Material

2.1.1. Used Oils

In this study, only used crankcase lubricating oils were used as test samples. The samples were collected from different service stations and mixed in a single container. Used motor oil was allowed to homogenize and settle in a barrel so that free water and any settable suspended solids could be removed. Their specifications were listed in table (1).

Table 1. *Specifications of Used oils*

Test	Results
Kinematic Viscosity @ 40 ^{o}C (C.P.)	146.28
Kinematic Viscosity @ 100 ^{o}C (C.P.)	15.76
Viscosity Index	109
Sulfur Content (ppm)	1
Ash Content (ppm)	1.05
Sulfated Ash Content (ppm)	9.9
Water Content (ppm)	0
Metallic Content: (ppm)	
Ca	990
Zn	550
Fe	83

2.1.2. Solvent

Analytical grade solvent including alcohols such as butyl alcohol, iso-butyl, methyl alcohol, 1-propanol, 2-propanol, ketons such as methylethylketone (MEK) and acetone and hydrocarbon solvents such as hexane were used in this study.

3. Determination of Water Content

The water content in the used oil samples were determined to decide whether the samples need hydration or not. A test sample was analyzed by TGA instrument Model (TGA-50Shimadzu-Japan) to indicate the water content [5].

4. Methodology of Solvent Extraction

4.1. Centrifugal Tube Technique

The extraction performance of these solvents was evaluated at different solvent to oil ratios. Curves were determined for the percentage extraction yield as the mass of oil, expressed in grams.

A six previously weighed glass centrifugal tubes such as those used in ASTM method D-96 [6] are filled with mixture of 10 gm of used oil sample (W_{oil}) and solvent ($W_{sol.}$) at specified ratio.

- The samples are stirred by an electrical stirrer at 1200 r.p.m for 15 min. to miscibilize oil and solvent.
- The tubes are introduced in the centrifuge for 10 min. at a centrifugal speed of 750 r.p.m
- The solvent and base oil mixture was separated from the wet sludge.
- The wet sludge was then washed by 7 cm^3 of n-hexane and 28 cm^3 of 2-propanol as described by Reis and Jernimo [7]. The washing process is anticipated to remove about 95% of interstitial oil content present in the sludge phase.
- Washed sludge was placed in a dryer for 15 min. at about 100°C to evaporate excess solvents.
- The dry sludge was then reported as (W_d) and the percentage extraction yield was calculated.

4.2. Soxhlet Technique

2 gm of used oils were placed on a sintered glass, which was held in a wire mesh. Then the samples were set into an extraction tube and condenser was put on the top of soxhlet extractor. 200 ml solvent was placed to the reboiler (500 ml measuring flask) and start heating for 3 hours. The extracted sludge in the sintered glass was dried in a dryer who has been kept at a temperature above the boiling point of solvent for 1 hour. Weight the dried sludge and calculate the percentage extraction yield [8].

5. Study the Factors Affecting Solvent Extraction of Used Oil

Several factors have been varied to study their effect on extraction of used oil solvent extraction. These factors are:
1- Type of solvent
2- Mixing time
3- Mixing speed
4-Temperature

5.1. Type of Solvent

The used oil samples with various solvents to oil weight ratios were placed in a centrifuge tubes and mixed for 25 minutes at 25 ^{o}C, then centrifuged, washed, dried and weighted.

5.2. Effect of Mixing time

The used oil samples with various solvent to oil weight ratios were placed in a centrifuge tubes and mixed for 5, 15 , 25 minutes at 25 ^{o}C , then centrifuged, washed, dried and weighted.

5.3. Effect of Mixing speed

The used oil samples with various solvent to oil weight ratios were placed in a centrifuge tubes and mixed by stirrer at speed of 400,800, and 1200 r.p.m., then centrifuged, washed, dried and weighted.

5.4. Effect of Temperature

The used oil samples with various solvent to oil weight ratios were placed in a centrifuge tubes and mixed for 15 minutes at temperatures of 25, 40, and 60 ^{o}C then centrifuged, washed, dried and weighted.

6. Preparation of Extracted Base Oil Samples

200 gm of used oil samples were placed in 500 ml beakers, and then the solvent was added in proportions of 4:1, 6:1, 7:1 and 9:1. The mixture was mixed for 15 minutes, then allowed to settle for 24 hour to ensure adequate extraction .The base oil and solvent mixture was separated from sludge phase. The extracted solvent and base oil mixture was placed in a Dean and Stark distillation apparatus, and then heated at 110 ^{o}C until the solvent evaporated. The evaporated solvents were received in a flask and the base oils were collected to determine their properties. The properties were determined according to ASTM standard.

7. Results and Discussion

7.1. Thermo-Gravimetric Analysis (TGA)

TGA of used oil in figure (1) shows that, based on this weight behavior, the process can clearly be broken up into three distinct zones.

Zone (1) in which there is no significant weight loss occurred over a temperature range. This indicates that the amount of water is very small and can be neglected.

Zone (2) characterized by a more rapid rate of weight loss. This zone occurred at a temperature between 209 ^{o}C to 466 ^{o}C. It is clear that the sample loses the most significant amount of its weight in this region (93%) and it is believed that the major process involved is the loss of the volatile hydrocarbons (probably paraffinic) found in the sample.

Zone (3) shows that, the sample losing the remaining weigh between 460 ^{o}C to 560 ^{o}C.This works out to a much slower rate than in the previous zone. It is believed that in this region, there is a transition from a liquid to solid.

There is no amount of water observed using Dean and Stark distillation apparatus until the temperature reached to 120 ^{o}C. This is to insure that the amount of water can be neglected.
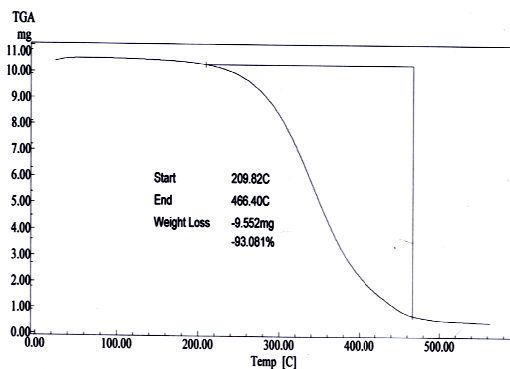

Fig. 1. Thermo-gravimetric analysis of used oil

7.2. Pre-Selection of Solvent

Figure (2), shows that as the solvent to used oil ratio

increases the extraction yield increases at room temperature .Alcohols such as methyl alcohol, 1-propanol, butyl alcohol and iso-butyl alcohol have a high removal performance compared with ketones such as acetone. This result agree with Burrel's [7] classification of solvents (which based on their capacity to form hydrogen bond). Thus, alcohols have a high capacity, ketones have a moderate capacity and hydrocarbon solvents have a low capacity.
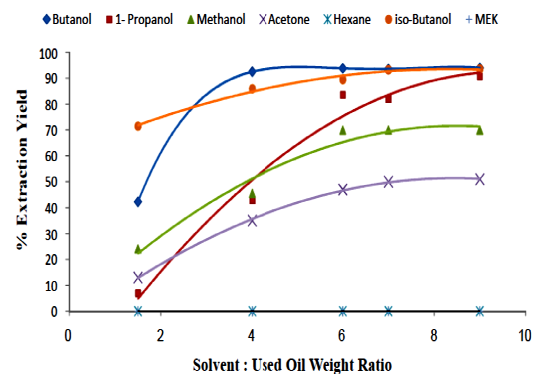

Fig. 2. Evaluation of extraction yield with several solvents using centrifugal tube technique

Hydrocarbon solvents such as hexane when mixed with used oils, the liquid hydrocarbons at room temperature keep stable the solution of macromolecular and other additives as well as the dispersion of carbonaceous and other particles. No destabilization is observed after centrifugation time or many days of gravity settling, no particles are seen by direct observation for solvent to oil ratio from 1 to 15 and no sludge settles at the bottom of the test tubes.

Methyl ethyl ketone (MEK) when mixed with used oils at room temperature takes the same behavior as hexane where no destabilization is observed after centrifugation time and no sludge settles at the bottom of the test tubes.

Soxhlet technique was used to insure the results of the centrifuge tube technique, Figure (3), shows that the extraction yields of solvents are close to the results of centrifuge tube method after 2 hours of heating.
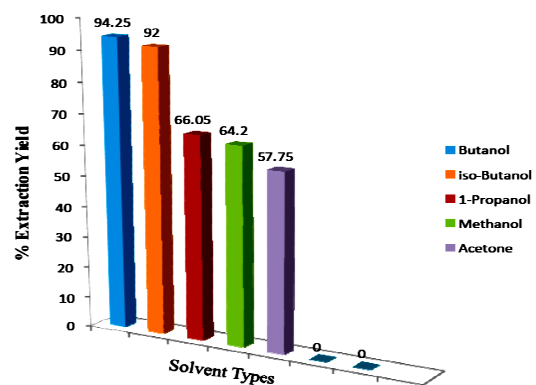

Fig. 3. Evaluation of extraction yield with several solvents using centrifugal tube technique

7.3. Effect of Mixing Time

In figure (4-a), the percent of the extraction yield slightly increases with increasing mixing time at the same solvent to oil ratio. The yield increases with increasing solvent to oil ratio up to point at which they stabilize at ratio 6:1 for all mixing times. These results agree with Brownawell et al.[9] in that, there were only 2 layers, in which case the viscosity index improvers of the used oil will come out with the sludge layer. The three layer separation appears to occur most often if the viscosity index in the poly-isobutylene type.

In figure (4-b), the percent of extraction yield increases with mixing time at the same solvent to oil ratio. The maximum yield (90.7 %) was obtained at mixing time of 25 minutes and solvent to oil weight ratio of 9:1.

In figure (4-c), shows the percent extraction yield increase with increasing mixing time for the same solvent to oil ratio .The maximum extraction yield (51%) obtained at mixing time 25 minutes and solvent to oil ratio 9:1. The Extraction yield at 25 minutes with acetone is lower than that in case of butyl alcohol and 1-propanol at room temperature. This result agrees with Burrell's classification in that the ketones have a moderate capacity [7].

7.4. Effect of Mixing Speed

The effect of mixing speed was studied at 400, 800, 1200 r.p.m. The results of these experiments are presented in figure (5-a). It can be observed that, for the same solvent to oil ratio there is a slight difference in the extraction yield between all mixing speeds, this means that the butyl alcohol gives a high extraction yield at low mixing speed and this may be related to the high capacity of butyl alcohol to form hydrogen bond.

It can be observed that in figure (5-b), as the mixing speed increases the extraction yield increases for the same solvent to oil weight ratio. At ratios 7:1 to 9:1 the extraction yield slightly increases with the mixing speed this is related to the stabilization occurring.
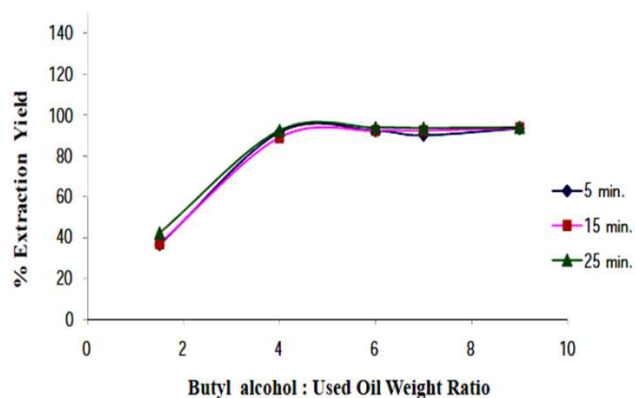
In figure (5-c), the extraction yields increases as mixing speed increases at the same acetone to used oil ratio. The maximum yield obtained at 1200 r.p.m. for ratio 9:1.
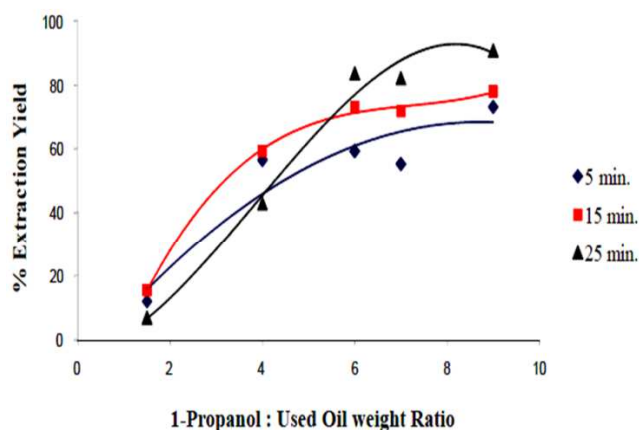
7.5. Effect of Temperature

Figure (6-a), shows the effect of extraction temperature on the percent extraction yield for the system of butyl alcohol / used oil. As seen in the figure, as the extraction temperature increases the percent extraction yield increases for the same solvent to oil ratio. However, this will not assist in optimizing this process based on the extraction temperature. This is because the optimum temperature should result in, simultaneously, maximum sludge removal and minimum oil losses.

In figure (6-b), the extraction yields slightly increases with increasing temperature probably due to the combination of the following factors: on one side, the
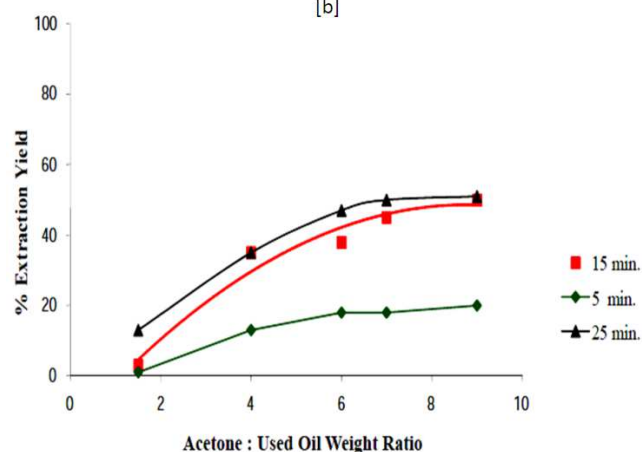
solubility of the base oil components in the organic solvent increases with temperature and, on the other side, the amount of base oil retained by impurities separated from the waste oil decreases with increasing temperature. Furthermore, the increasing yield observed could also be due to an increase in the solubility of waste oil impurities with increasing temperature.

[a]

[b]

[c]

Fig. 4. *Effect of solvent to used oil ratio on the extraction of base oil at different mixing times using butyl alcohol, 1-propanol and Acetone*
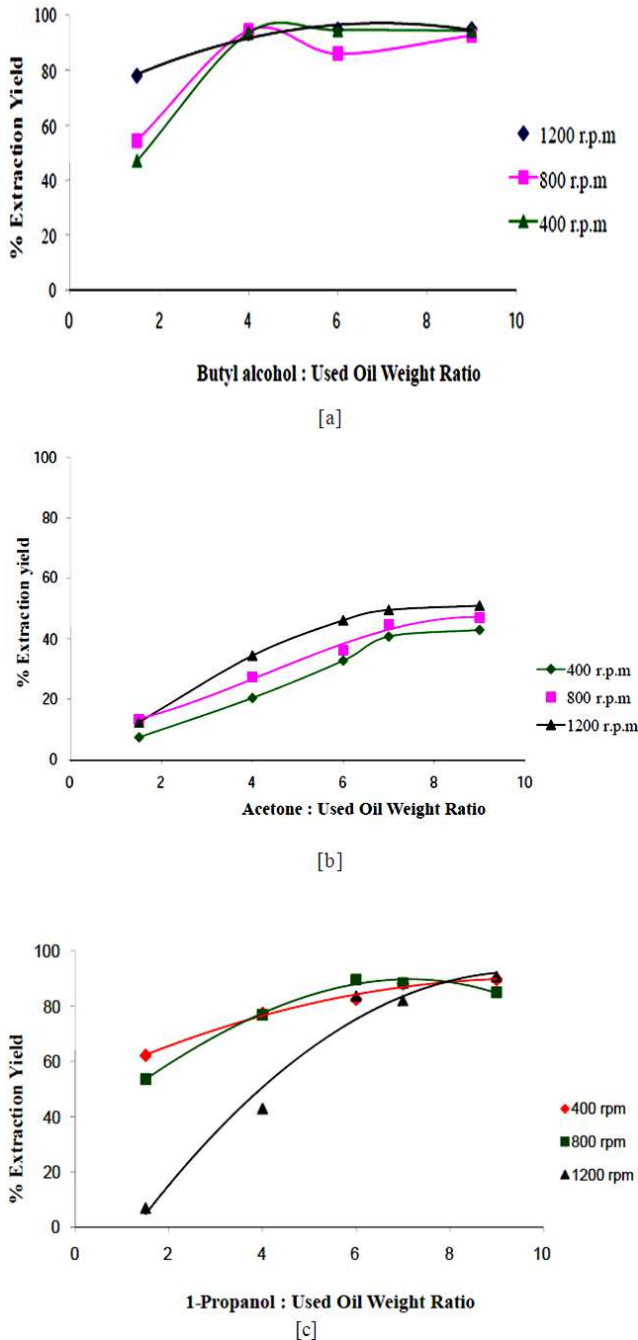
[a]

[b]

[c]

Fig. 5. Effect of solvent to used oil ratio on the extraction of base oil at different mixing speed using butyl alcohol, 1-propanol and Acetone

Figure (6-c), shows that the extraction yield increases as temperature increases for the same acetone to oil weight ratio. The maximum yield obtained at temperature of 60 $^{\circ}$C. It can be observed that the extraction yield at temperature 40 $^{\circ}$C is lower than that at temperature 25 $^{\circ}$C (room temperature).
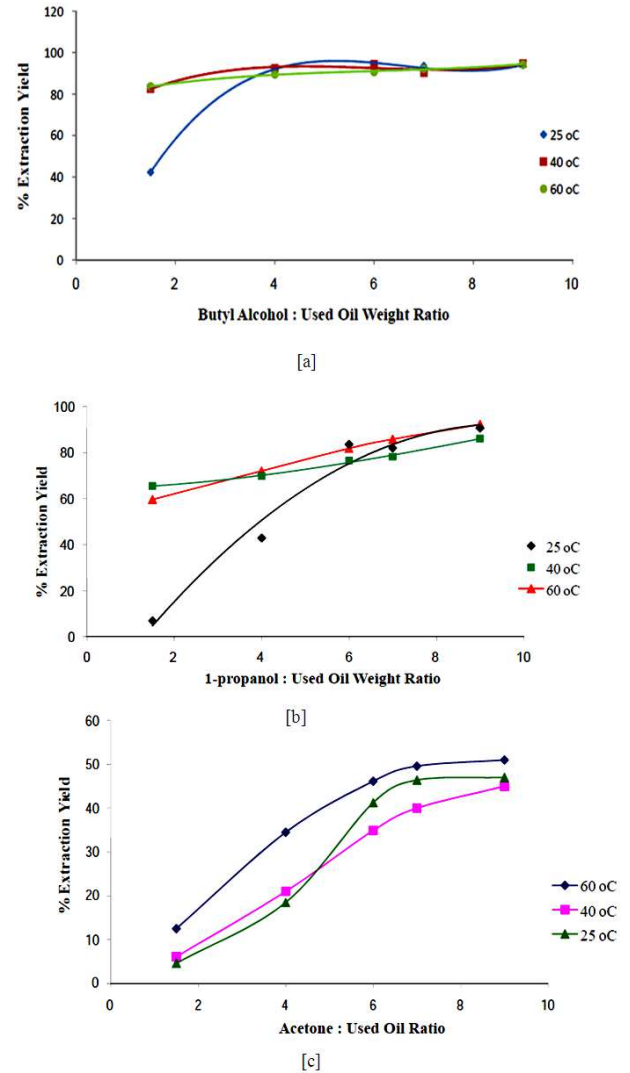

[a]

[b]

[c]

Fig. 6. Effect of solvent to used oil ratio on the extraction of base oil at different temperatures using butyl alcohol, 1-propanol and Acetone

7.6. The Properties of Extracted Base Oils

7.6.1. Percent Ash Content

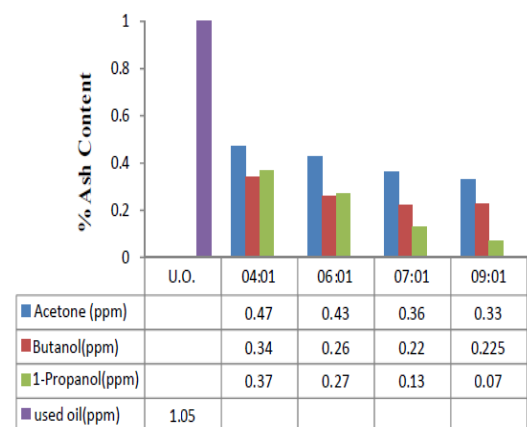|	U.O.	04:01	06:01	07:01	09:01
Acetone (ppm)		0.47	0.43	0.36	0.33
Butanol(ppm)		0.34	0.26	0.22	0.225
1-Propanol(ppm)		0.37	0.27	0.13	0.07
used oil(ppm)	1.05				

Fig. 7. Ash content of the extracted base oil

The ash content of the extracted base oil sample was determined according to ASTM D482[10].Knowledge of the amount of ash-forming material present in a product can provide information as to whether or not the product is suitable for use in a given application. Ash can result from oil or water-soluble metallic compounds or from extraneous solids such as dirt and rust. As shown in figure (7), it can be observed that the property of ash content for the extracted oil using polar solvents was improved. It was found that the ash content reduced from 1.05 ppm in the used oil to 0.07 ppm in the extracted base oil using 1-propanol. The ash content using butyl alcohol is lower than using 1-propanol and acetone for ratio 4:1 and 6:1, the ash content using 1-propanol is lower than using butyl alcohol and acetone for ratio 7:1 and 9:1.

7.6.2. Sulfated Ash Content

The sulfated ash content in the extracted base oil sample was determined according to ASTM D874 [11].The sulfated ash can be used to indicate the concentration of known metal-containing additives in new oils. When phosphorus is absent, barium, calcium, magnesium, sodium and potassium are converted to their sulfates and tin (stannic) and zinc to their oxides. Sulfur and chlorine do not interfere, but when phosphorus is present with metals, it remains partially or wholly in the sulfated ash as metal phosphate. As shows in figure (8), the sulfated ash content of the base oil extracted by three solvents were improved. It was found that the sulfated ash content reduced from 9.9 ppm in the used oil to 0.1 ppm in the extracted base oil using 1-propanol at ratio 9:1. The base oil extracted by1-propanol has the lowest sulfated ash content followed by butyl alcohol and acetone.
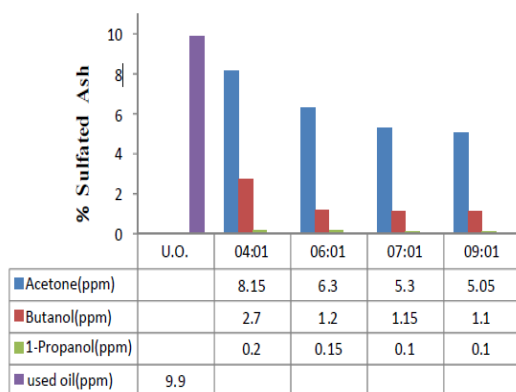
	U.O.	04:01	06:01	07:01	09:01
Acetone(ppm)		8.15	6.3	5.3	5.05
Butanol(ppm)		2.7	1.2	1.15	1.1
1-Propanol(ppm)		0.2	0.15	0.1	0.1
used oil(ppm)	9.9				

Fig. 8. Sulfated Ash content of the extracted base oil

7.6.3. Metallic content

The oil sample (2 g) was treated with concentrated sulphuric acid (2 g) and heated on a hot plate until dry in a crucible. The crucible was transferred to a muffle furnace and ashed at 550°C until all traces of carbon were removed. This was indicated by the absence of a charcoal colour and took about 30 minutes. After cooling the sample was treated with concentrated hydrochloric acid (6 ml) and

filtered through a Whatman no. 541 filter paper. The solution was then made up to 25 ml with distilled water [12]. The solution was analyzed by an atomic absorption instrument and the reading compared with counts from prepared calibrated sample to determine the iron, calcium and zinc content.

As shows in figure (9), the metallic content of the extracted base oil by butyl alcohol, 1- propanol and acetone at solvent to used oil ratio 9:1 was compared with the metallic content in used oil at room temperature.

It can be observed that the percent metallic content obtained by acetone is the lowest followed by 1-propanol and butyl alcohol for calcium, zinc and iron. Although butyl alcohol has a maximum extraction yield at low solvent to oil ratio but the metal content in the extracted base oil is the highest compared with 1-propanol and acetone. butyl alcohol reduces the calcium content in the base oil from 990 ppm to 437 ppm about 55% and the zinc content from 550ppm to 150 ppm about 72 % and iron content from 83 ppm to 43 ppm about 48%.On the other hand, the calcium content in the extracted base oil obtained using acetone reduced to 160 ppm about 83%, zinc content 139 ppm about 74% and iron content to 33 ppm about 60%.
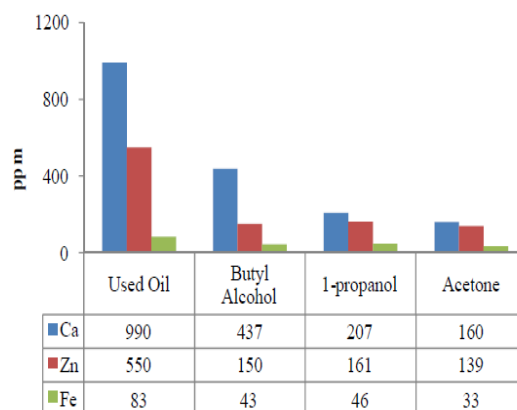
	Used Oil	Butyl Alcohol	1-propanol	Acetone
Ca	990	437	207	160
Zn	550	150	161	139
Fe	83	43	46	33

Fig. 9. Comparison between metallic content in used oil and extracted base oil

8. Conclusion

The base oil yields obtained by extraction of waste oil with polar solvents increase with increasing solvent/oil ratio up to a point at which they stabilize. This is due to the combined effect of factors such as the system viscosity which is affected by the extraction temperature, the detergent dispersant additive concentration, and the difference between the solubility parameters of the system components. Increasing the temperature increases the solubility of base oil in the solvent.

Only butyl alcohol gives the highest yield at lower mixing time, mixing speed, settling time and temperature followed by 1-propanol and acetone, this is reflect the high performance of alcohols.

Stabilization with ketones occurs at a lower ratio due to

their smaller viscosities and solubility parameters. Thus, the higher polarity of alcohols may lead to base oil with a higher level of impurities, as indicated in the metallic content of the extracted base oil.

For both alcohols and ketones the extraction yields increase with increasing molecular weight of the solvent because the difference between the solubility parameters of solute and solvent decreases in this way.

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