

Rerefining of Waste Lube Oil via Solvent Extraction Followed by Catalytic Hydrotreatment

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WITH increased time of usage, lubricating oil loses its lubrication properties and thus must be evacuated and a fresh one replaced. Recovery of waste oil is environment friendly and economic. The waste lube oil was treated by N-methyl-2-pyrrolidone (NMP) + 1% KOH at different conditions as temperatures from 50 to 70 °C and solvent feed ratio from 1/1 to 7/1. The best conditions which produce good quality raffinate with high yield at 70 °C and solvent feed ratio 5/1. The fresh catalyst NiMo/Al₂O₃ that consists of NiO = 5.2 wt.% , MoO₃ = 23 wt.%, Al₂O₃ balance was applied for re-refining of the best raffinate at different reaction temperatures range from 320 to 410 °C, hydrogen pressure ranges from 30 to 50 bars and liquid hour space velocity (LHSV) ranges from 0.3 to 0.7 h⁻¹. The best conditions of hydrotreating to produce the high quality lube oil are (temperature = 350 °C, pressure = 50 bar and LHSV = 0.5 h⁻¹).

The catalytic tests carried out using both spent and rejuvenated catalyst (using 4 % oxalic + Fe(NO₃)₃ at continuous modes) under the constant temperature, hydrogen pressure and liquid hour space velocity (350 °C, 50 bar, 0.5 h⁻¹) respectively, in order to compare the hydrodesulphurization (HDS) activity of fresh, rejuvenate and spent catalyst. The result indicated that oxalic acid treatment improved the equilibrium HDS activity of the catalyst (nearly close to the equilibrium of fresh), and also improved the quality of waste lube oil.

Keywords: Refining, Used lubricating oil, Solvent extraction and Hydrotreatment.

Lubricating oils are the most valuable constituents in crude oil. Lubricating oil constitutes about 2% of petroleum derivatives and is one of the few that is not totally consumed during its use⁽¹⁾. Lubricating oils are used to reduce friction and wear by interposing a film of material between rubbing surfaces⁽²⁾. Lubricants contain about 90% base oil and less than 10% additives. The Environmental Protection Agency's definition of waste oil is as follows: waste oil is any oil that has been refined from crude oil or any synthetic oil that has been used and a result of such use is contaminated by physical or chemical impurities⁽³⁾. Regeneration of waste oil can be beneficial by: (i) Reducing environmental pollution; (ii) Saving foreign exchange for importing virgin lube oils; (iii) Conserving of mineral resources.

Waste oil can be a very valuable resource, if managed properly. Average crude oils have 3-8 % base-oil, whereas lube crudes typically have 12-16 % base-oil. This compares with 65-75 % recoverable base-oil content in used automotive oils, which if burnt or dumped would mean the loss of a valuable natural resource. Re-refining of waste oil is energy efficient; less energy (about one third) is used to produce a gallon of base stock from waste oil than to produce the same gallon from crude oil. It is also environment friendly⁽⁴⁾. Regeneration of waste oil and associated product markets should be patronized by the government⁽⁵⁾.

Among the alternative processes practiced for recycling used lubricating oils during recent years, solvent extraction process has received considerable attention⁽⁶⁻⁸⁾. This process replaces successfully the classic acid-clay treatment whereby a useful organic sludge is produced instead of the toxic acidic sludge⁽⁹⁾. When solvents are added to the waste oil they dissolve the oil and flocculate contaminants like metals, ash, and others^(10, 11).

The advantage of NMP over other commonly used solvents is: non toxic nature, high solvent power, the easy recovery from solute and high selectivity for aromatic hydrocarbon. NMP can be used for re-refining of waste lube oil with lower sludge, carbonaceous particles and polymer content⁽¹²⁾. The addition of potassium hydroxide will increase into solvent, the sludge sedimentation rate where it easily destabilizes the dispersion and increases sludge removal from waste lube oil^(2, 13). Mild hydrotreating is the key to successful re-refining of used lubricating oils removal; the process produces oils of superior color and with acceptable viscosity. Furthermore, the process provides an operational simplicity, economic feasibility, and environmental attractiveness. This kind of treatment avoids the bleaching clay process, and consequently its disadvantages.

In this work hydrotreatment coupled with solvent extraction. The hydrotreating process has many advantages: Production of a high viscosity index lube oil with a good and stable color and well oxidation resistance; yet has low or no discards⁽¹⁴⁾.

Experimental

Feedstock

Waste lubricating oil is kindly supplied from Alexandria Petroleum Company. The characteristics are indicated in Table 1.

Solvent extraction process

A mixture of solvent (NMP, KOH, 3 gm/L) and dehydrated used lubricating oil was subjected to a jacketed mixer settler apparatus for 60 min at variable conditions. The sludge was allowed to settle down, two phases were separated upper refined oil layer and bottom extract layer {(mixture of N-methyl 2-pyrrolidone (NMP) and oil)}. The NMP solvent dissolved in raffinate phase was separated by distillation. To determine optimum condition solvent – oil ratio and temperature were varied.

TABLE 1. Properties of waste lube oil (WLO) feedstock.

Properties	Value
Refractive index, 70 °C	1.4733
TAN, mg KOH/ gm	0.942
Density, 70 °C	0.8652
Flash point, °C	218
Ash content Wt%	0.61
Carbon residue Wt%	2.57
Pentane insoluble	6.64
Pour point, °C	-12
Kinematic viscosity, cSt,40 °C	136.5
Kinematic viscosity, cSt,100 °C	14.46
Viscosity index	105
Sulphur content, wt%	0.75
Color	>8
Asphaltene, wt%	5
Iron, ppm	24.11
Zinc, ppm	44.93
Calcium, ppm	84.4
ASTM distillation	ASTMD86
IBP	180
4ml	205
10ml	230
12ml	255
14ml	270
20ml	295
Hydrocarbon, wt%	
Saturate ,wt %	56%
Aromatic , wt%	36
Resin ,wt%	8

Extraction variables

A. Extraction temperature : The extraction temperature was 50 °C, 60 °C and 70 °C and the settling temperature was 50 °C, 60 °C and 70 °C, respectively for one hour at constant solvent feed ratio of 1:1 by weight.

B. Solvent feed ratio : Extraction processes were carried out at various solvent to feed ratios (1:1 to 7:1) at constant extraction temperature of 70 °C and settling two hours.

C. Oxalic acid leaching reagent : 4 % oxalic acid solution is prepared with 5% H₂O₂ and Fe (NO₃)₃ as oxidizing agent for the leaching experiments.

- Take 10 gm of the spent catalyst and add the required concentration of the oxidized oxalic acid (500 ml) in 1 L flask.

- Heat for 60 min at 100 °C with continuous stirring. Finally, after cooling, by filtration, the oxalic acid solution which contains the metal leaching, is reduced to one – third of its original volume. The solid (unfiltered catalyst) is dried in atmosphere, heated at 110 °C and calcined at 450 °C for 4 hr.

The promoter was made of hydrogen peroxide (H₂O₂); addition was in batch mode only but the promoter (ferric nitrate) addition was varied in two different ways (continuous and batch modes).

In the continuous addition mode, oxalic acid solution was pumped through the catalyst bed and ferric nitrate (promoter) solution was added to the oxalic acid reagent dropwise continuously throughout the run.

In the batch addition experiments, all of the ferric nitrate solution was mixed with the oxalic acid reagent in a single batch at the start of the experiment and the reagent mixture was pumped and recycled through the catalyst bed. The total amount of reagents used and their concentrations were the same in both cases.

Catalyst

a- Fresh catalyst (Cat: C20 – 7 – 05 TRX) was supplied from Alexandria Petroleum Company and used as hydrotreated catalyst for waste lube oil (that consists of [(NiO = 5.2 wt %), (MoO₃ = 23 wt %) and (Al₂O₃ balance)]).

b- Spent catalyst, which has been used in re-refining of waste lube oil after 5 years (life time), at Alexandria Petroleum Company. The chemical and physical characteristics of the fresh and spent catalysts are illustrated in Table 2.

TABLE 2. Characteristics of fresh and spent catalysts.

Characteristics	Fresh NiMo/Al ₂ O ₃	Spent NiMoP/Al ₂ O ₃
<i>Chemical compositions (wt%)</i>		
Mo	15.01	9.58
Ni	3.56	2.55
Al	34.74	33.91
P	-	10.55
Ni	-	4.12
Others	0.55	0.91
<i>Physical characteristics</i>		
Surface area, m ² /g	186.2	103.6
Pore volume, cc/g	0.4196	0.266
Pore radius, Å ⁰	37.13	34.54

Catalytic activity test

Catalyst performance tests were carried out in a down flow, high pressure microreactor unit (cata-test unit). The unit consists of a stainless steel reactor (internal diameter 19 mm, external diameter 27 mm, length 50 cm), it is divided into three zones, each of them is heated and separately temperature controlled. 100 ml of the catalyst are charged in the middle zone of the reactor.

The catalytic activity experiments are carried out under the operating conditions illustrated in Table 3.

The most important properties of feedstock, raffinate of extraction and products of hydrotreatment are measured using the standard methods indicated in Table 4.

TABLE 3. Catalytic activity operating conditions.

Conditions	Description
Reaction temperature , °C	320, 350, 380, 410
Total hydrogen pressure, bar	30, 50, 70
LHSV, h ⁻¹	0.3, 0.5, 0.7
H ₂ /Feed ratio, L/L	300
Catalyst volume, ml	100
Charge stock	Extracted lube oil
Catalyst type	Fresh

TABLE 4. Standard method (ASTM).

Refractive index	ASTM-D1747
Density	Mataller Toled-DE40
Kinematic viscosity	ASTM-D445
Viscosity index	ASTM-D2270-98
Sulphur content, X-ray sulfur spectrophotometer	ASTM-D4294
Pour point	ASTM-D97
Ash content	ASTM-D482
Flash point	ASTM-D92
Carbon residue	ASTM-D527
Color	ASTM-D156

Results and Discussion

A dehydrated waste lube oil of an initial boiling point (180 °C) was conducted from Alexandria Petroleum Company. The physico-chemical characteristics and hydrocarbon component analysis are presented in Table 1. The given data show that the waste lube oil has lower oxidation stability owing to its high total acid number (0.942 mg KOH/gm). Waste lube oil is of high aromatic content reaches to 36 wt, %

as well as a sulphur compound content of 0.75 wt%. These undesirable constituents are the main reason behind the low oxidation stability. Waste lube oil has high ash content and carbon residue of 0.61 wt. % and 2.57 wt. % respectively which is considered to reflect oil additive residues and other sources such as wearing and solid residues which leave more residue deposits when evaporated after being subjected to the heat of an engine. Waste lube oil had high percent of different metals as shown in Table 1, such as iron, calcium and zinc also found in waste oil as a result of the virgin oil additives, which were used to improve the properties of the final oil. The viscosity index of the waste oil was found to be 105, which is due to the degradation of the majority of the viscosity index improver through usage; however some of this improver remains unchanged. The waste oil had a low flash point of 218 °C due to the decomposition of some of the base oil to light products. Dark and opaque color is attributed mainly to the presence of carbonaceous materials, the different additive types, condensable and oxidizable hydrocarbons and non-hydrocarbons as oxygen, nitrogen, metals and sulphur compounds.

Various techniques have been used in this study to regenerate the waste lube oil. These treatments are:

- *Solvent treatment (physical refining) which removes undesirable materials.
- *Hydrotreatment, which converts the undesirable materials to desirable one.

Solvent treatment (Extraction)

Extraction has been carried out for the studied hydrated waste lube oil in this work by using N-methyl 2-pyrrolidone.

Oxidation products have a boiling temperature range similar to that of the base oil and represent a problem since they cannot be separated by distillation ⁽¹⁵⁾.

To overcome this problem, very low quantities of strong base (KOH, 3gm/L) have been added to the solvent. It has caused the elimination of the major part of the oxidation products and metallic compounds. Removal of the oxidation compounds occurs due to the effect of KOH which neutralizes the acid compounds and induces their saponification and subsequent precipitation. The (-OH) group of the potassium hydroxide breaks the hydrogen bonds between the polar impurities and the dispersant detergent additives of the waste oil.

Extraction variables had been studied in order to control the degree of extraction and the selectivity of the process. These are extraction temperature and solvent feed ratio.

Extraction temperature

Extraction temperature is considered as one of the most effective extraction variables. The dissolving action of the solvent increases with temperature up to complete miscibility; hence the solvent selectivity is greatly influenced. The extraction temperature is governed by solvent stability and the initial boiling point of feedstock.

Extraction was carried out using NMP associated with KOH 3gm/l at constant solvent feed ratio of 1:1 by weight and at different temperatures from 50 °C to 70 °C to optimize the temperature which can give the highest yield with the best quality of raffinate (refined product).

The effect of extraction temperature on the yield and sulphur of the raffinates is shown graphically in Fig.1. The yield of lub oil, sulphur content, total acid number (TAN), refractive index and density content decrease as extraction temperature increased as shown in Fig. 1 (a, b and c) and the decrease may be attributed to the removal of highly polar aromatic components by the extraction stage⁽¹⁶⁾.

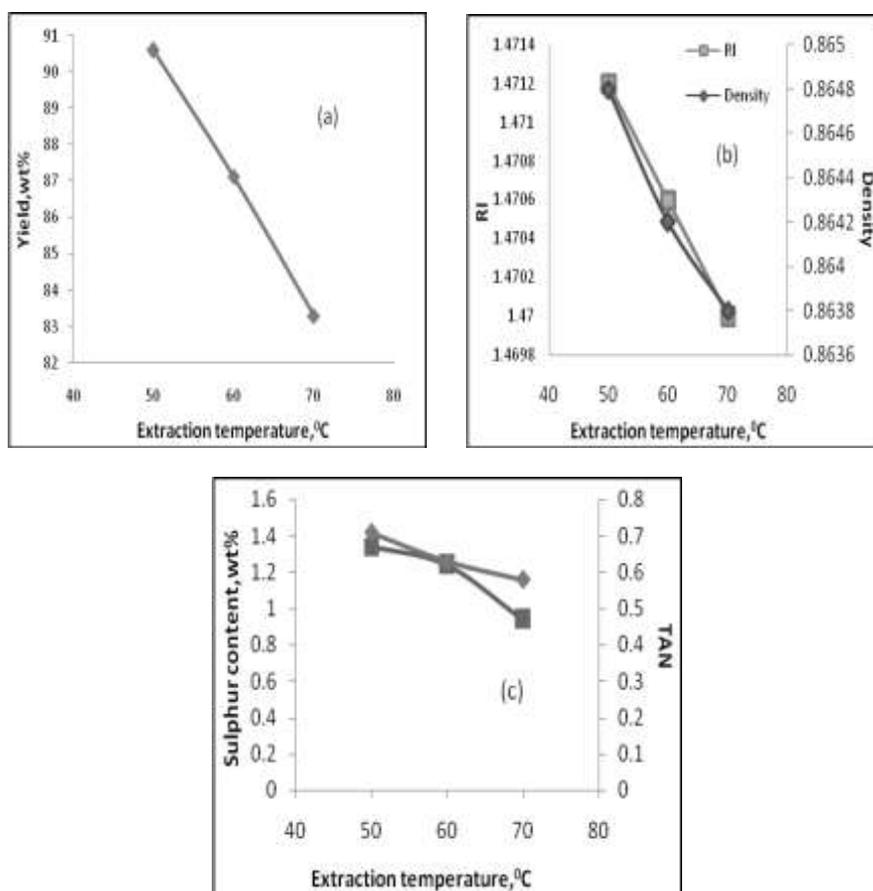


Fig. 1. Effect of extraction temperature on (a) yield, (b) density, refractive index and (c) total acid number, sulphur content.

Figure 2 shows that the inflation of the extraction temperature had increased the viscosity index of the raffinate sharply up to 60 °C while slightly increased at 70 °C.

The refining effectiveness number (REN) is considered to be a good measure of the attainable refining effect, *i.e.* the lower is REN the better is the solvent efficiency. Taking the viscosity index change as the refining performance parameter and by applying this to the present investigation (Fig. 2, a and b), it can be observed that the most suitable extraction temperature is 70 °C at which $REN=3.34$ ⁽¹⁷⁾.

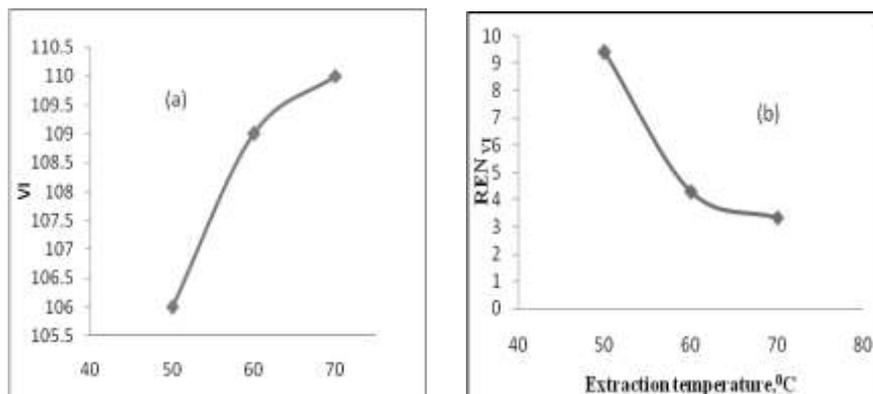


Fig. 2. Effect of extraction temperature on (a) viscosity index and (b) refining effectiveness number .

Solvent feed ratio

Extraction has been carried out at various solvent feed ratios and extraction temperature of 70 °C to determine the optimum solvent ratio.

Solvent feed ratio has an obvious effect upon the yield and characteristics of the raffinates. The low yield of the raffinate was accompanied by better quality of the product. The yield of raffinate decreases by increasing the solvent-to-feed ratio due to the increase of the solvent power (Fig. 3a).

The decrease in carbon residue, contents of sulphur and ash and pentane insoluble by increasing solvent feed ratio may be attributed to the removal of the more aromatic components by the extraction process (Fig. 4a, 5b and 3c).

The decrease of the refractive index, density and the sulphur content with increasing solvent feed ratio confirms the prior findings (Fig. 5a & 5b).

The increase of the solvent feed ratio improves the raffinate quality in term of increasing the viscosity index of the raffinates (Fig. 3b). Also, increasing percentage of removal of acids, ash and pentane insoluble component with increasing solvent feed ratio, (Fig. 4b), confirms the improvement of quality of raffinate.

The oxidation products of the organic and organo metallic compounds results from the oxidation of additive contaminants which lead to the increase in total acidity of the waste oil decreasing by increasing solvent feed ratio (Fig.4b). This may be due to the increasing of solvent efficiency.

The data of refining effectiveness number (REN) show that the solvent feed ratio of 5/1 equal to 1.83 will be quite adequate for extraction of waste oil as in Fig. 5c.

The best raffinate (at S/F 5/1 & temp, 70 °C) was used as a starting base material for producing lube oil via catalytic hydrogenation, with using fresh NiMo\Al₂O₃ catalyst.

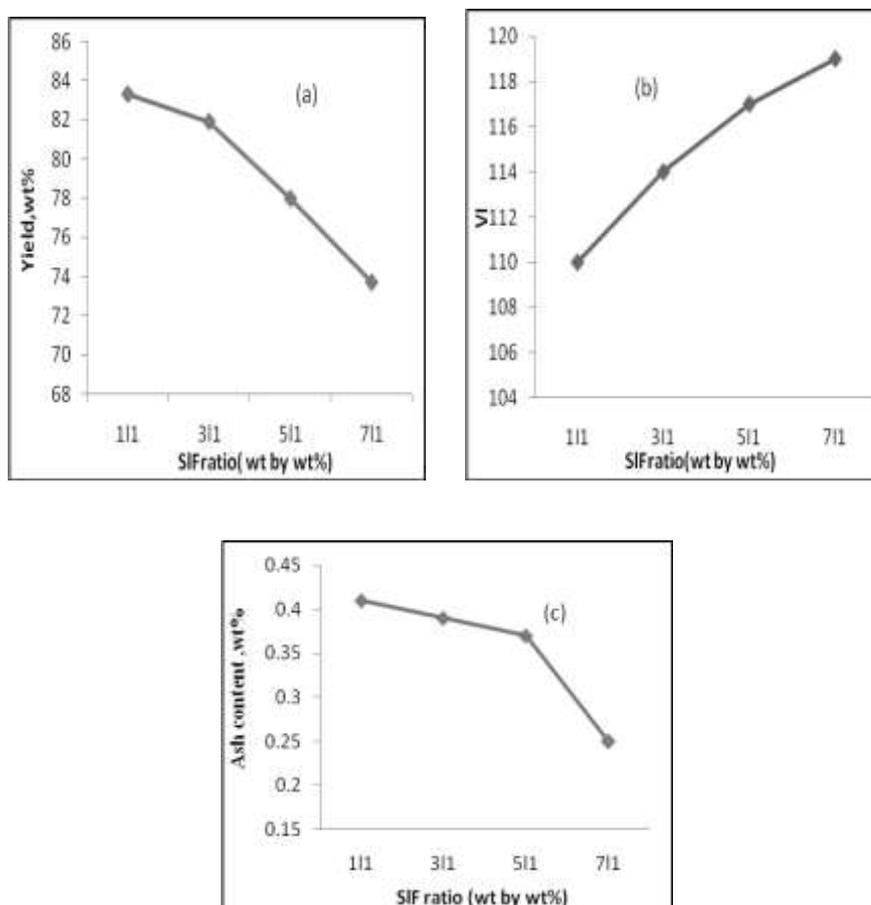


Fig. 3. Effect of solvent feed ratio on yield, viscosity index and ash content.

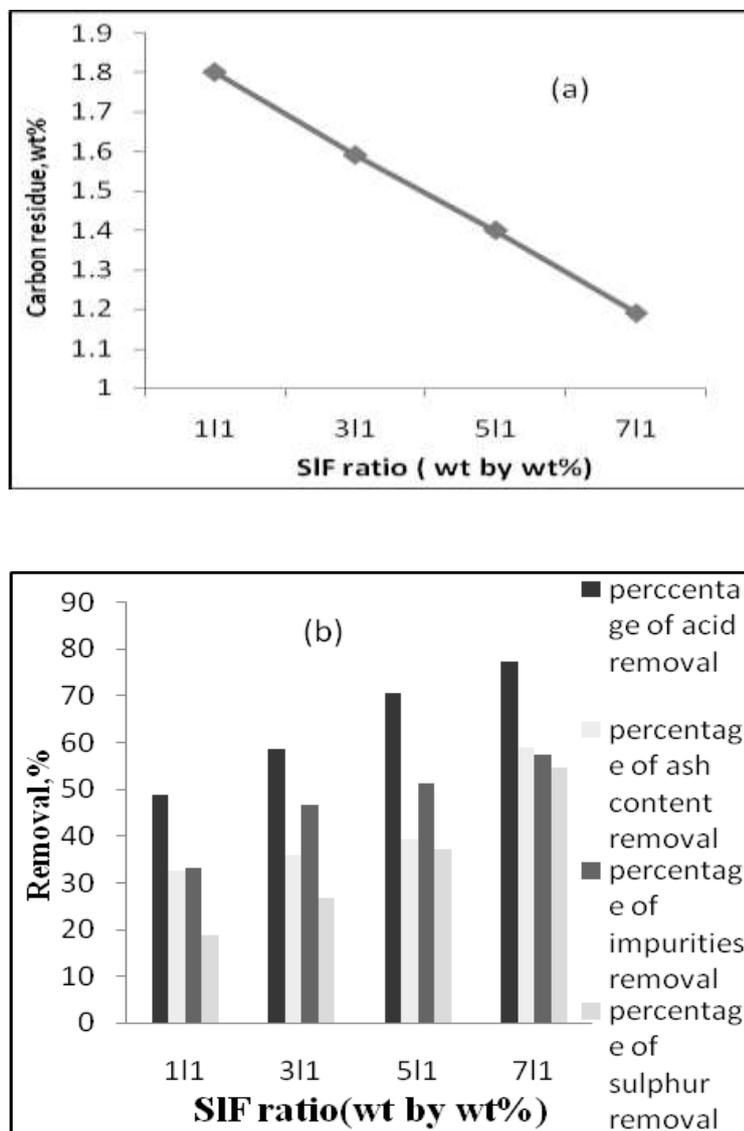


Fig. 4. Effect of solvent feed ratio on (a) carbon residue (b) removal of acids, ash, impurities and sulphur.

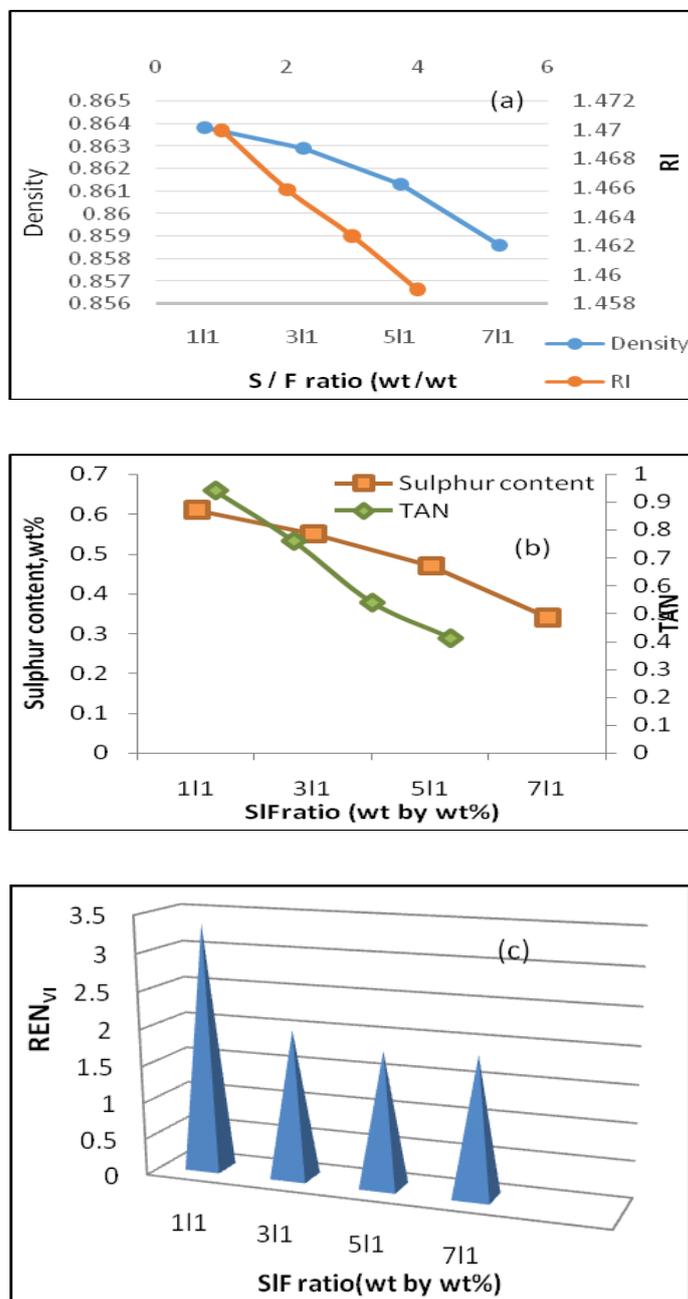


Fig. 5. Effect of solvent feed ratio on (a) density, refractive index (b) total acid number, sulphur (c) refining effectiveness number.

Hydrotreating treatment

Effect of operating conditions on hydrotreating of waste lube oil

The hydrotreating process of the base stock was carried out in a dynamic phase at different reaction temperature (320 °C–410 °C), hydrogen pressure (30 – 70 bar) and liquid hourly space velocity (0.3 – 0.7 h⁻¹).

1. *Effect of reaction temperature* : The results of Fig. 6 and 7 represent the effect of reaction temperature on the yield and product quality. It was shown that the yield of treated waste lube oil was clearly affected by reaction temperature, *i.e.* decreased as the reaction temperature increased, also the total acid number decreased from 2.5 at 320 °C to 0.1687 at 410 °C.

As the reaction temperature increased the aromatic content decreased from 33.5% at 320°C to 19.3 % at 410°C, at the same time. On the other hand, the total saturate content increased from 60 % at 320°C to 78 % at 410°C, this is due to the increase in hydrogenation activity.

Resin was decreased from 7.4 to 2.7 wt.% with increasing reaction temperature. This can be attributed to the decomposition of resin which is present in the feed to coke reported⁽¹⁸⁾.

The partial hydrogenation of cyclic and, heterocyclic aromatics, followed by splitting of sulphur and oxygen bonds had liberated the sulphur as H₂S and removed the oxygen from the organo metallic oxygenated and acid components. A drop in the value of sulphur content and total acid number is in agreement with this interpretation. The splitting of sulphur and oxygen bond lead to the removal of about 65.62 and 88.2% of the total sulphur and from 73.46 to 97.98 of the total acid number respectively at 320 °C and 410 °C.

Viscosity index was improved and increased from 128 at 320 °C to 130 at 410 °C. The color of the oil became lighter by increasing reaction temperature, and the amount of pentane insoluble compounds decreased by increasing temperature from 320°C to 410°C. Generally the quality of the treated waste lube oil was improved by increasing temperature.

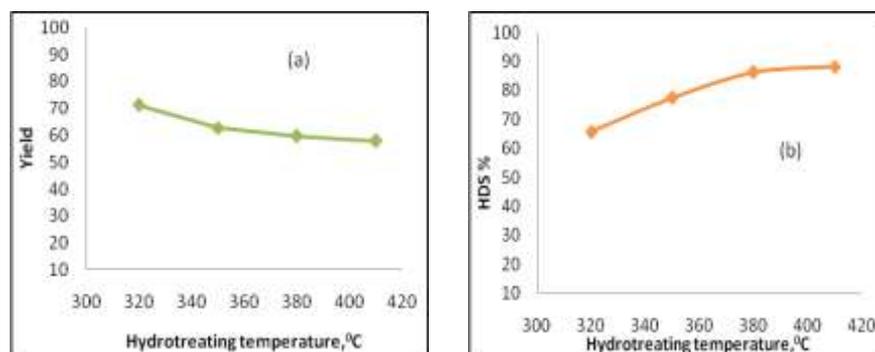


Fig. 6. Effect of hydrotreating temperature on (a) yield, (b) HDS.

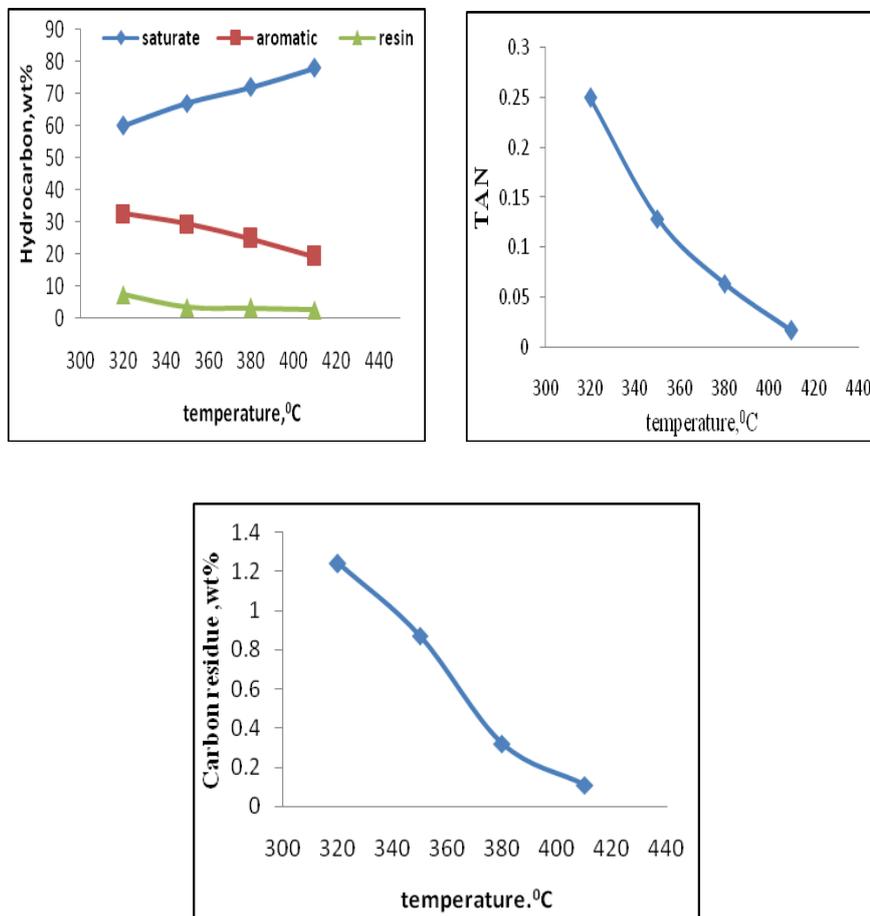


Fig. 7. Effect of hydrotreating temperature on (a) hydrocarbon (b) total acid number and (c) carbon residue.

2. *Effect of hydrogen pressure* : The results represented in Fig. 8 show that as the total hydrogen pressure increased from 30 to 70 bar, a great change in the yield and quality characteristics of lube oils was observed, HDS increased from 61.4% to 84.2% and aromatic content was decreased from 33.5% to 25.5 % at 30 to 70 bar; this can be attributed to the increase of hydrogenation activity of the catalyst with increasing the total hydrogen pressure in addition to the increase of the saturation activity and reduction of coke formation⁽¹⁸⁾.

3. *Effect of liquid hourly space velocity* : The effect of liquid hourly space velocity on the quality characteristics of the raffinate was studied at 350 °C and at hydrogen pressure of 50 bars which is represented through Fig. 9 and 10.

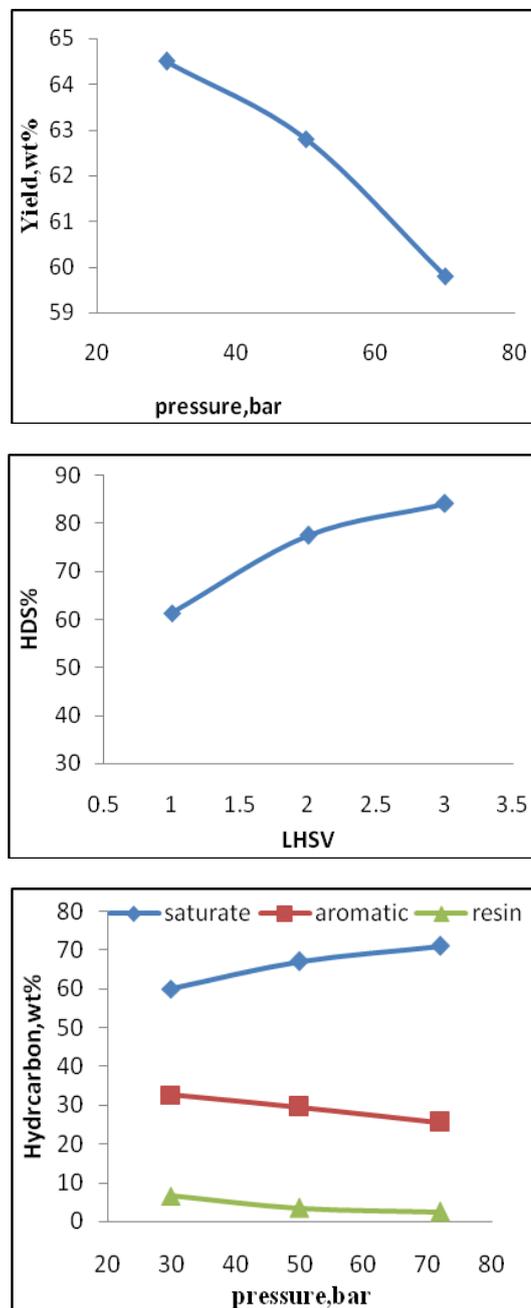


Fig. 8. Effect of hydrotreating pressure on (a) and (c) hydrocarbon.

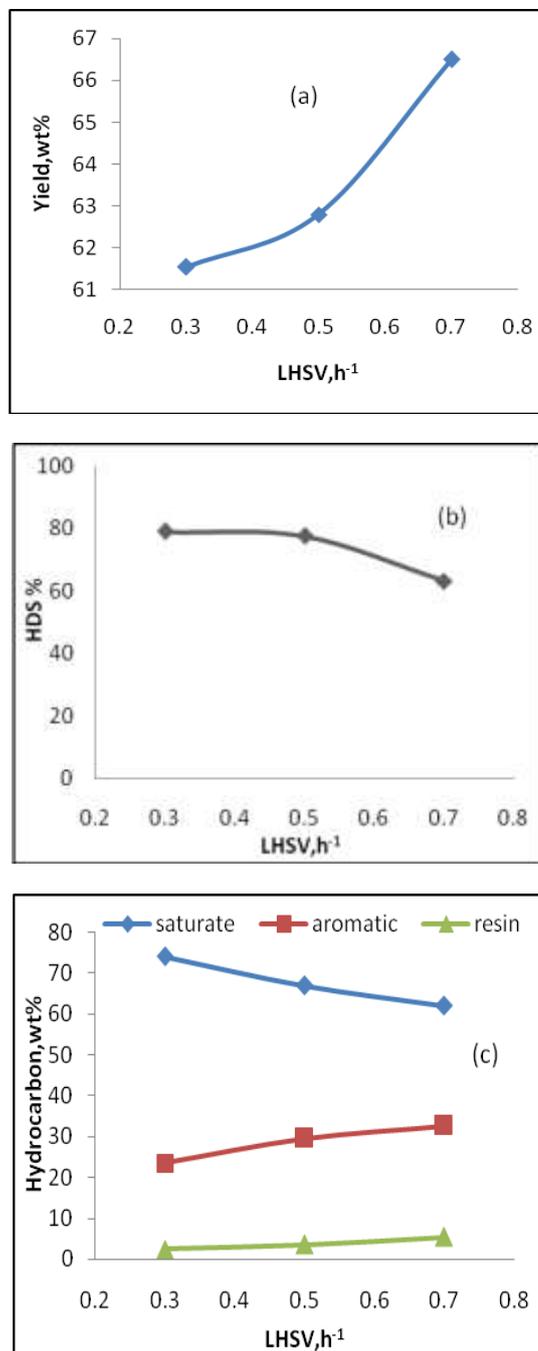


Fig. 9. Effect of hydrotreating LHSV on (a) yield (b) HDS, (c) hydrocarbon structure.

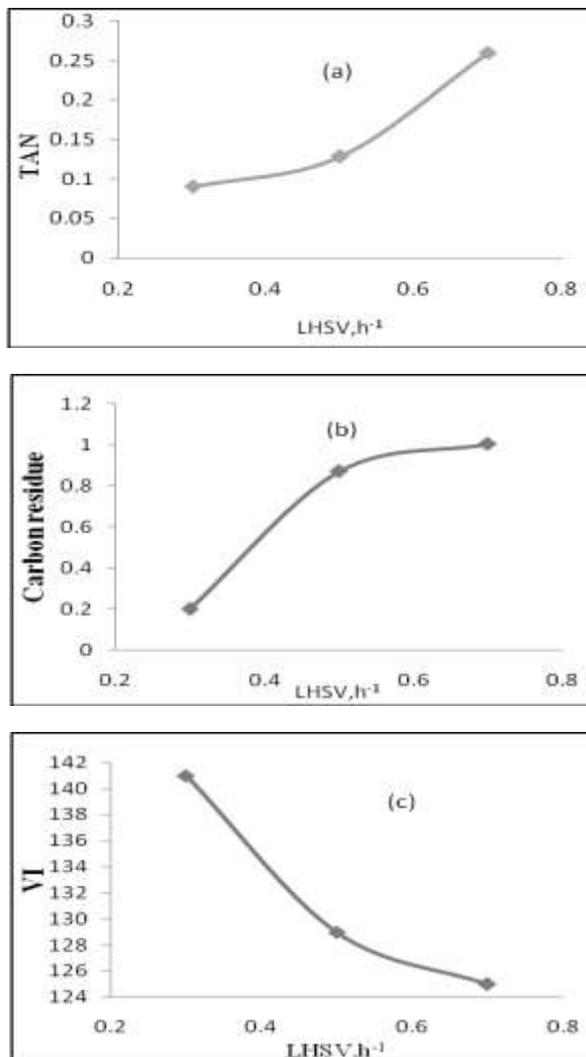


Fig. 10. Effect of LHSV on (a) total acid number, (b) carbon residue and (c) viscosity index.

Evidently, by increasing liquid hour space velocity from 0.3 to 0.7, the hydrotreatment activity of the catalyst decreased due to the decrease in contact time between the reacting waste lube oil molecules and the active sites of the catalyst. It was found that the yield, density, refractive index and total aromatic content increased while saturate and HDS activity of the catalyst was decreased. This can reflect that no improvement in the quality of waste lube oil was attained by increasing LHSV.

Hydrodesulphurization activity of spent and rejuvenated catalyst

Table 5 shows the catalytic testes carried out using both spent and rejuvenated catalyst (using 4 % oxalic + $\text{Fe}(\text{NO}_3)_3$ at continuous modes) under the constant temperature, hydrogen pressure and liquid hour space velocity (350°C , 50 bar, 0.5 h^{-1}) respectively. The data indicate that the activity of catalyst is further decreased after 5 years due to carbonaceous and metallic deposition on the catalyst. It means that the surface area of the catalyst decreased with increasing these contaminants, *i.e.* pore plugging due to long operation ⁽¹⁹⁾.

Table 5 shows the catalytic test results HDS activity by the rejuvenated catalyst increased to be 65.33 more than the spent, and aromatic content decrease from 32 to 30.5wt % and saturate increase from 63.5 to 65.5 wt % indicating that the improvements in treated catalysts activity may be attributed to the formation of more Ni Mo S active phase. This phase is a result of the sulphiding of the β -NiMoO₄ compound formed during the reoxidation treatment ⁽²⁰⁾.

Oxalic acid treatment improved the equilibrium HDS activity of the catalyst (nearly close to the equilibrium of fresh), the oxidized 4%oxalic acid solution solvent approached the activity of the spent catalyst about 85 % from the fresh catalyst ⁽²¹⁾.

TABLE 5. Hydrotreating of waste lube oil using fresh, spent and rejuvenated catalysts.

Catalyst Characteristics:	Fresh	Spent	Rejuvenated
Yield, wt%	80.6	90.4	85.4
Yield, wt%(from WLO)	62.8	70.5	66.6
Density, 70°C	0.8654	0.866	0.863
Viscosity index	129	120	124
Sulphur content, wt %	0.17	0.3	0.26
HDS %	77.33	60	65.33
Refractive index, 70°C	1.4576	1.4599	1.45798
Pour point, $^\circ\text{C}$	3	-3	0
Carbon residue	0.87	1.16	0.98
TAN, mg KOH/ gm	0.1285	0.2275	0.1456
ASTM color, unit	2.5	5	3.5
Hydrocarbon,wt%			
Saturate	67	63.5	65.5
Aromatic	29.5	32	30.5
Resin	3.5	4.5	3.5

Conclusions

The used lube oil contains impurities such as metals, aromatic and carbonaceous materials that have carcinogenic effect and pollute environment. Solvent extraction process is used to regenerate used lube oil using NMP& KOH 3g/l at different temperatures range from 50 to 70⁰C, and solvent to feed ratio range from 1/1 to 7/1.

The physico - chemical properties were determined to select the optimum condition that gives good yield high quality. The results indicate that the best solvent to feed ratio and temperature is 5/1 and 70⁰C, respectively. The best raffinate was used as starting base material for producing lube oil via catalytic hydrogenation, using freshly NiMo\Al₂O₃ catalyst.

The best conditions of hydrotreating to produce the high quality lube oil are (temperature=350⁰C, pressure=50 bar and LHSV=0.5h⁻¹).

The optimum condition of hydrotreating applied to the extracted waste lube oil with rejuvenated and spent catalyst to compare (HDS) activity and the quality of product.

The result indicated the improvement of the quality of waste lube oil and HDS activity nearly approaches to that the fresh of the same type.

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إعادة تدوير الزيوت المستعملة باستخدام المذيبات والمعالجة الحفزية بالهيدروجين

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مع زيادة وقت الاستخدام لزيوت التشحيم تفقد خصائصها، وبالتالي لابد من استبدالها بزيوت تزييت اخر غير مستعمل.

تمت معالجة زيوت التشحيم بواسطة KOH % 1 (NMP) + 1 N- Methyl-2-pyrrolidone عند درجات حرارة من 50-70 درجة مئوية ونسبة تغذية المذيب الى الزيت المستخدم من 1/1 إلى 7/1.

وجد ان أفضل الظروف التي تنتج منتج ذات جودة عالية مع ارتفاع العائد كانت عند 70 درجة مئوية ونسبة تغذية المذيب الى الزيت 5/1.

استخدم الحفاز NiMo / AL₂O₃ عند درجات حرارة من 320-410 درجة مئوية وسرعة مرور السائل على سطح الحفاز من 0.3-0.7 مم في الدقيقة وضغط هيدروجيني من 30-50 بار فوجد ان احسن معالجة للزيت المستخدم كانت عند سرعة مرور السائل على سطح الحفاز 0.5 مم في الدقيقة.

تمت المعالجة الحفزية عند درجة حرارة 350 درجة مئوية و سرعة مرور السائل على سطح الحفاز 0.5 مم في الدقيقة وضغط 50 بار باستخدام حفاز مستخدم وحفاز معالج باستخدام 4% حمض اوكساليك و نترات الحديد للمقارنة في ازالة الكبريت باستخدام الحفاز النشط والحفاز المعالج.

أوضحت النتائج ان الحفاز المعالج بحمض الاوكساليك كان الاكثر نشاطا في ازالة الكبريت من الزيت المستخدم وتحسين خواصه.