

Treatment of Waste Generator Oils by Using Various Methods

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Abstract

In general, lubricating oils consist base oil and chemical additives, which are working to prolong the time of use, improve the performance of oil in severe conditions, and keep the machine clean. These oils lose ability to lubricate during use because of exposure to internal and external pollutants, which requires replacement oil and disposal of used oil, which is one of the dangerous pollutants to the environment. The current research aims to purify and re-refine used lubricating oil using different processing methods, which include (vacuum distillation, acid / bentonite, distillation / bentonite, and acid/distillation treatments).

Physical properties were studied for the treated oils, which include viscosity at 40 °C, specific gravity at 20 °C, flash point, pour point, and ash content in accordance with the American Standard Test Materials. Also chemical properties of the treated oils were studied which includes the total acid number and FTIR spectroscopy. The results showed that all treatment methods were worked to improve the physical properties of oils as compared with the used oils, but the best results were obtained using (acid/ bentonite) treatment method as compared with the specifications of the fresh oil. FTIR analysis of treated oils showed that different results in the removal of pollutants, which include carbon particles, water and organometallic compounds such as compounds of nitrogen, sulfur and oxygen, but it was found that (acid/ bentonite) treatment is the best method as compared with the spectrum of the fresh oil.

Keywords: Recycling, Waste Oil, Methods and Treatment.

معالجة زيوت المولدات المستهلكة باستخدام طرائق متنوعة

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وزارة العلوم والتكنولوجيا / دائرة بحوث المواد

بغداد-العراق

الخلاصة

تتكون زيوت التزييت بشكل عام من زيت اساس ومضافات كيميائية تعمل على اطالة زمن الاستعمال وتحسين اداء الزيت بظروف قاسية وبقاء الماكينة أنظف. تفقد هذه الزيوت قدرتها على التزييت خلال الاستخدام نتيجة لتعرضها للملوثات الداخلية والخارجية مما يتطلب تبديلها بزيت جديد والتخلص من الزيت المستهلك الذي يعتبر من الملوثات الخطيرة للبيئة. يهدف البحث الحالي الى تنقية واعادة تصفية زيوت التزييت المستعملة باستخدام طرائق معالجة مختلفة والتي تشمل طريقة التقطير الفراغي وطريقة حامض / بنتونايت، وطريقة التقطير / بنتونايت، وطريقة الحامض / التقطير. تم دراسة الخواص الفيزيائية للزيوت المعالجة والتي تشمل اللزوجة بدرجة ٤٠ م ° والكثافة النوعية بدرجة ٢٠ م ° ونقطة الوميض ونقطة الانسكاب ومحتوى الرماد طبقا للمواصفات الامريكية القياسية على التوالي . و دراسة الخواص الكيميائية للزيوت المعالجة والتي تشمل الرقم الحامضي الكلي وكذلك امتصاصية الاشعة تحت الحمراء بمقياس فورييه. لقد اظهرت نتائج البحث ان طرائق المعالجة المختلفة عملت على تحسين الخواص الفيزيائية للزيوت المعالجة بالمقارنة مع الزيوت المستعملة بنسب متفاوتة ولكن أفضل النتائج تم الحصول عليها باستخدام طريقة المعالجة (حامض/ بنتونايت) بالمقارنة مع المواصفات الفيزيائية للزيت الجديد. اظهرت امتصاصية الاشعة تحت الحمراء للزيوت المعالجة كفاءة متفاوتة في ازالة الملوثات والتي تشمل الدقائق الكربونية والماء والمركبات العضوية الفلزية مثل مركبات النترجين والكبريت والاكسجين ولكن وجد ان طريقة المعالجة (حامض/ بنتونايت) هي الافضل عند مقارنتها مع طيف الاشعة تحت الحمراء للزيت الجديد.

الكلمات المفتاحية: تدوير، الزيوت المستهلكة، طرائق المعالجة

Introduction

Petroleum lubricating oils consist of complex mixtures of hydrocarbon molecules which they have carbon atoms range from (20-34)(*Concawe, 1985*). Lubricating oils are used to protect rubbing surfaces and promote easier motion of connected parts and serves as a medium to remove high build up of temperature from the moving surfaces. With the increasing of surface temperature the oil undergo degradation leading to change in properties such as: viscosity, specific gravity, and then dirt and metal parts are deposited into the lubricating oils(*Durrani et al., 2011*).

Waste lubricating oil made up primarily of hydrocarbon fraction and destroyed additives and it also contain physical and chemical impurities which formed during the incomplete combustion of organic matter and heavy metal particles that introduced through wear process (*Calgary, 2004*). With increased time of usage, the lubricating oil loses its lubricating properties as a result of over-reduction of desired properties, and thus must be evacuated and a fresh one replaced(*Rahman et al., 2008*).

The demand of generator oil in Iraq is increasing day by day because of the large use of small and big electrical power generator engines.

Huge economic benefits and environmental protection are gained from recycling and regeneration of waste lubricating oil which is now a subject of pressing national interest in some countries. Waste lubricating oil can be recycled to make new lubricants or industrial fuels(*Etebu et al., 2011*; *Anwar et al., 2012*).

In the recycling process, a number of stages are applied depending on the original source of used oil, the level of contamination and the sophistication of

the technology utilized (*Thrash, 1991*; *Jhanani and Joseph, 2011*).

In general, there are four main points for all waste oil regeneration technologies which include:

1-Removing of water and fuel

In this, moisture and fuel can be removed according to difference between their physical properties and lubricating oil such as boiling point, specific gravity, and solubility.

2-Removing of asphaltic compounds

Solid foreign matters such as metal powder resulted from mechanical wear and destroyed additives are found in waste lubricating oil. Deasphalt process can be occurred by physical treatment such as solvent extraction and distillation or chemical treatment such as acid treatment.

3-Fractionation

Usually, a petroleum product is mixture of diversified organic compounds, so the foreign matter can be removed by fractionation.

4-Finishing

Clay or hydro treatment is used to remove some foreign matters like chlorine, nitrogen, oxygen, and sulfur compounds (*Mynin et al., 2004*).

This study has been aimed to re-refine waste generator lubricating oil using four treatments which include; vacuum distillation, acid/bentonite, distillation/bentonite, and acid/distillation and also study the physical and chemical properties of treated oils such as specific gravity, viscosity, flash point, pour point, ash content, and total acid number (TAN).

The main goal of this research is to study the changes of FTIR absorption spectra of used, fresh, and treated oil by different treatments to evaluate the efficiency of treatment methods.

Materials and Methods

a-Lube oil The tested sample of fresh generator oil was obtained from Shell company and applied in electrical power generator type 400 kv Perkin company for(150 hr as recommended by the supplied company). At the end of the 150 hr , the oil was drained and collected from electric power generator machine for analysis as shown in table (1).

Table(1) Used and Fresh Generator Oils Specification

Property	Fresh Generator oil	Used Generator oil	Testing Method ASTM
Specific gravity at 25°C	0.881	0.898	D941-5
Viscosity at 40°C ,cst	145	95	D445
Flash point , °C	217	179	D92
Pour point ,°C	-17	-13	D97
Total acid Number mg KOH /g	1.613	2.983	D644
Ash Content ,wt%	0.8597	1.174	D482-03

b-Sulphuric Acid Technical (Fisher chemicals)

c-Sodium Hydroxide (Fluka company)

d- Iraqi bentonite

The Iraqi bentonite sample used in this work was obtained from (State Company of Geological Survey and Mining), it's chemical composition are listed in table(2).

Apparatus and Equipment

There are many laboratory glassware and equipment used in this work such as picnometer , Rotational viscometer (Brookfield Type), open cup flash point tester(Koehler Instrument)

,pour point tester (Koehler Instruments), distillation ,filtering equipment ,separating equipment ,and centrifuge.

Table (2) Chemical Composition of Iraqi Bentonite

Material	Percentage Weight (%)	Material	Percentage weight (%)
SiO ₂	54.07	MgO	3.20
Fe ₂ O ₃	5.59	K ₂ O	0.57
CaO	5.65	L.O.I.	12.40
SO ₃	1.10	O.M	7.19
Na ₂ O	0.87	Moisture	0.47
Cl	0.92	C.E.C.	76.59
Al ₂ O ₃	15.05	Total C.	0.93
TiO ₂	0.79	Mon	77.00

L.O.I; Lost on ignition, O.M ; Organic Matter, C.E.C.; Cation exchange capacity, Mon;Montmorillonite

FTIR Analysis

The FTIR spectra of the oil samples were recorded on Shimadzu FTIR model by placing a small drop of the compound on one of the KBr plates. Place the second plate on top and make a quarter turn to obtain a nice even film. Place the plates into the sample holder and run a spectrum.

Experimental Procedures

The collected waste generator oil was poured into beaker and allowed to settle for 24 hour to allow the contaminants such as water ,dirt, metal chip ,and wear particles to settle at the bottom of the beaker. The upper layer of the mixture was decanted into another beaker and filtered using filter paper and vacuum pump to increase the rate of filtration.

Distillation Treatment

The first step of the re-refining involved removal of water from filtered used oil by atmospheric distillation .Thus ,the used oil was distilled up to 200 °C under vacuum pressure (5mmHg) to remove light hydrocarbons

.The residual fraction ranging (270-350°C) was obtained leaving a very dark and waxy residue in the distillation flask.

Acid / Bentonite Treatment

The filtered oil was treated with sulphuric acid (10 % v/v) for (30- 40 minutes) at 40-45°C with continuous stirring. The mixture was allowed to cool and settle overnight. The oil was separated by decantation. Sodium hydroxide solution (5% w/v) and bentonite(5g) were added to the oil and mixing was done by mechanical stirrer for about 1hr at 70-80°C with continuous stirring .The mixture was allowed to cool and separate into two phases .The oil was decanted and filtered with filter paper and further filtered by centrifugation for 1hr at 2000 rpm.

Distillation / Bentonite Treatment

The first step of the re-refining involved removal of water from filtered used oil by atmospheric distillation .Thus ,the used oil was distilled up to 200°C under vacuum pressure (5mmHg) to remove light hydrocarbons .The residue was cooled at room temperature and treated with bentonite (5gm) for each 100ml of treated oil then mixed by mechanical stirrer for about 1hr at 70-80 °C, the sample was filtered and subjected to further filtration by centrifugation for 1hr at 2000rpm.

Acid/Distillation Treatment

The filtered oil was treated with sulphuric acid (10 % v/v) for (30- 40 minutes) at (40-45 °C) with continuous stirring. The mixture was allowed to cool and settle overnight .The oil (top layer) was separated by decantation. Sodium hydroxide solution (5% w/v) was added to neutralize the residue of acid .The mixture was allowed to separate into two phases .The oil was decanted and filtered with filter paper

and further filtered by centrifugation for 1hr at 2000 rpm. The treated oil was poured into the vacuum distillation flask. The oil was distilled under vacuum pressure (5mmHg) and the hydrocarbon fraction was obtained at temperature rangin (270-350 °C) leaving a very dark and waxy residue in the distillation flask.

Results and Discussion

Four treatment methods were used to study the re-refining process of waste lubricating oil which include: vacuum distillation, acid / bentonite, distillation / bentonite, and acid/distillation (fig 1.).

The treated oil was analyzed for physical and chemical properties. The physical properties include viscosity, specific gravity, pour point, flash point, and ash content ,while the chemical properties include total acid number and FTIR spectroscopy.

The experimental results of specification of used generator oils after treatments with their respective quality test are listed in table (3).

Table(3) Used Generator Oil Specification after Treatment by Various Methods

Treatment method	Distillation Treatment	Acid/Bentonite Treatment	Distillation / Bentonite Treatment	Acid/Distillation Treatment
Parameter				
Specific gravity at 25°C	0.846	0.894	0.875	0.784
Viscosity at 40°C ,cSt	34	136	118	10
Flash point , °C	200	200	165	145
Pour point ,°C	-13	-16	-8	-20
Total acid Number mg KOH /g	0.437	1.361	0.868	1.264
Ash Content ,wt%	0	1.077	1.009	0

1-Physical properties a-Specific Gravity

From table (1) and Fig (1) ,it can be seen that the specific gravity of used generator oil is higher than that of fresh oil. This is may be due to the presence of contaminate in used generator oil as a result of used it with operating conditions. Fig (2) shows that the specific gravity values changed with change the rotes of treatment of generator oil. This is attributed to that there are different type of contaminates in the oil after each treatment (Udonne, 2011).

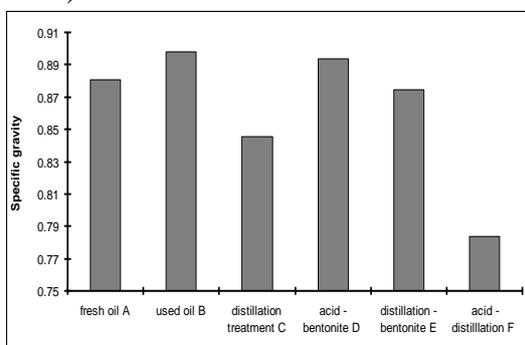


Figure (1) The Effect of Treatment Methods of Using Generator Oil on its Specific Gravity

b-Viscosity

As shown in table (1)and fig(2),the viscosity of fresh generator oil is greater than that of used generator oil as a result of the exposed of the used generator oil to the oxidation and contamination with soluble materials(Tran *et al.*,1991). Viscosity decrease can be caused by dilution with light fuel. Figure (3) shows an improvement in oil viscosity and gives the highest value with the treatment by method –D.

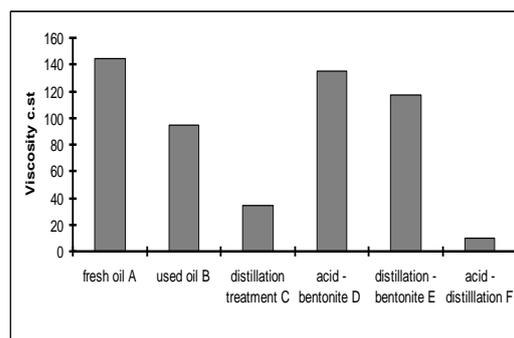


Figure (2) The Effect of Treatment Methods of Using Generator Oil on its Viscosity

c-Flash Point

From fig(3),the flash point of used generator oil was lower than of the fresh oil because the used oil was contaminated with fuel or light hydrocarbon fractions that resulted from combustion and degradation .As comparison of the treatment methods ,it was found that the best result of flash point was obtained with acid/ bentonite and vacuum distillation methods ,this means that the latest methods were effective for removing light hydrocarbon fraction and fuel(Friday *et al.*, 2008).

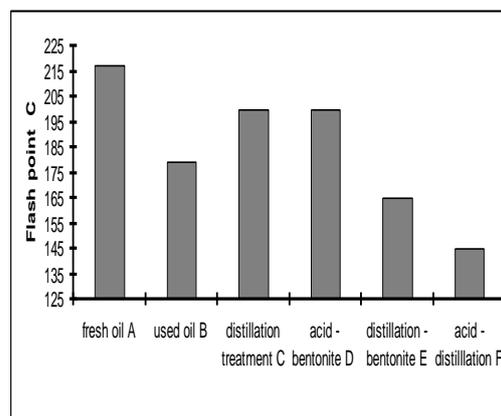


Figure (3) The Effect of Treatment of Using Generator Oil on its Flash Point

d-Pour Point

Pour point especially is of interest when oil must be used under relatively cold condition. From figure (5) and table (1),the pour point of the used generator

oil is lower than of the fresh oil because of the degradation of additive that occurred during use. As comparison the flash point of the treated oil by different treatment methods, it was found that the acid/ distillation is the best method for treating used oil, this means that the latest method is effective for removing wax and heavy hydrocarbon fractions (Udonne, 2011).

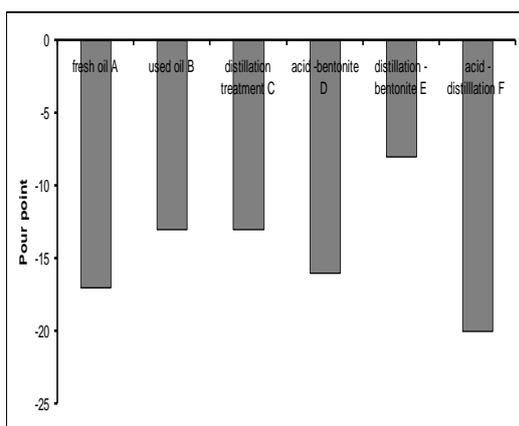


Figure (4) The Effect of Treatment Methods of Using Generator Oil on its Pour Point

e-Ash Content

Figure(5) shows the ash content of used oil is high because of the presence of metals in lubricating oil that come from various sources such as wear, contamination and additives. Wear metals result from friction or corrosion of the engine components, for example, pistons, bearings, etc. during operation. Contamination can come from dirt, leaks or residual metal pieces. Detergent additives, anti-oxidants, anti-wear agents, etc., are added to improve lubricity and to reduce engine wear (Burrows *et al.*, 1965). The results of the treatments show that the best results was obtained by method C which can reduce the value of ash to zero because the additives and other sources of ash remained with the residue at the bottom of distillation flask.

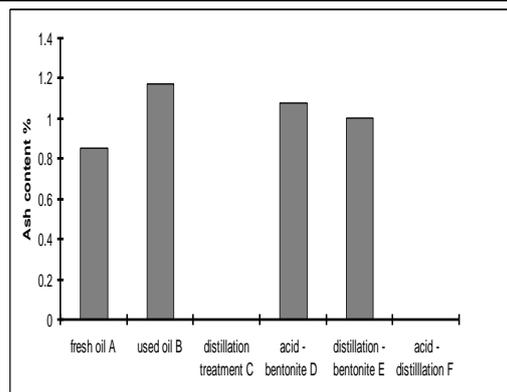


Figure (5) The Effect of Treatment Methods of Using Generator Oil on its Ash Content

2- Chemical properties

a-Total Acid Number (TAN)

Total acid Number (TAN) is the quantity of acid or acid-like derivatives in the lubricant. The TAN of a new oil is not necessarily nil since oil additives can be acidic in nature. From figure (6), it is observe that the acid number of used generator oil has high value. The increases in TAN usually related to oil oxidation or contamination with an acidic product (Udonne, 2011). The best low values of the TAN obtained with the methods of treatments C and E.

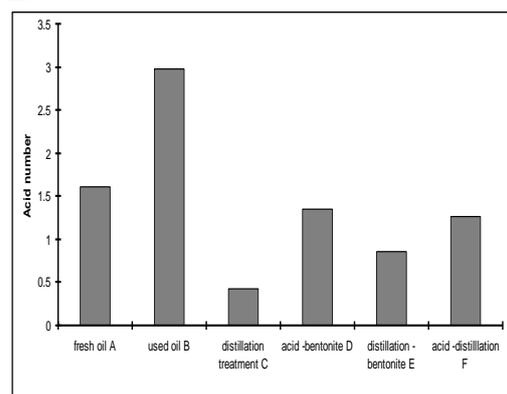


Figure (6) The Effect of Treatment Methods of Using Generator Oil on its Acid Number

b-FTIR Analysis

The spectra of used and fresh generator oil are shown in figures (7) and (8) respectively.

The absorbance that appeared around the region 3600cm^{-1} to 3895cm^{-1} is due to vibration changes in the molecules of

the oil ; these peaks are as a result of presence of impurities such as metals, sand stones etc. Similarly, the region 3400cm^{-1} shows the presence of O-H bonds, thus depicting the presence of water as an impurity in used oil.

The spectrophotometric plots for figures 7 and 8 gave similar characteristics with that from the fresh oil in terms of prominent peaks at around vibrating frequencies 2840cm^{-1} to 3000cm^{-1} ; this region indicates the presence of alkanes with Sp -hybridization and C-H absorption. Other prominent peaks were seen around 1400cm^{-1} this due to deforming of C-H bonds (Usman, and Kayode-Sote, 2011).

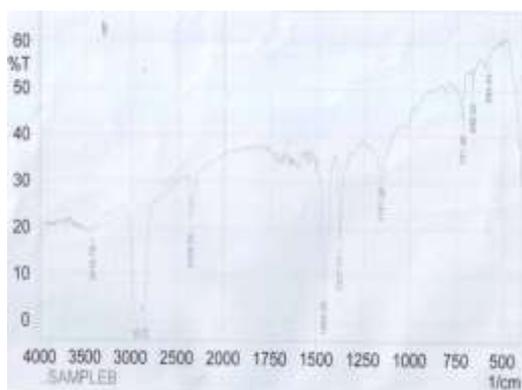


Figure (7) FTIR Spectrum of Used Generator Oil

The spectra of used oil show general response in the carbonyl group region of between 1800 to 1670cm^{-1} related to oxidation products of oil (George and McIntyre, 1987).

In all lubricating systems, organic compounds exposed to high temperature and pressures in the presence of oxygen will partially oxidize and by-products produced such as ketones, esters, aldehydes, carbonates, and carboxylic acids. Some of these compounds are dissolved by the oil or remain suspended in oil.

The spectra of used oil show characteristic absorbance of between 1650 to 1600cm^{-1} related to nitration

products of oil which formed when organic compounds exposed to high temperature and pressures in the presence of nitrogen and oxygen to form nitrogen oxides such as NO , NO_2 , and N_2O_4 . Sulphate by-products such as SO_2 and SO_3 are formed by oxidation of these sulphur compounds, and these compounds show characteristic infrared absorbance between 1180 and 1120cm^{-1} .

The FTIR analysis of soot is measured by taking the absorbance intensity at 2000cm^{-1} . Soot particles are formed when a rich fuel air mixture is burned (Robinson and Hons 2000).

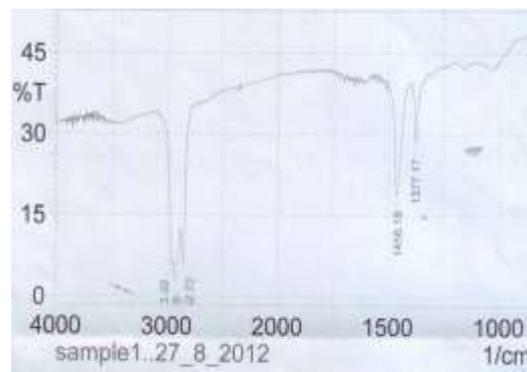


Figure (8) FTIR Spectrum of Fresh Generator Oil

Figure (9) shows the FTIR spectrum of treated oil by distillation method which shows the presence of water and that is agreed with the low viscosity value. The soot absorbance intensity was very weak and this agreed with ash content. Sulphation by-products absorbance intensity was very weak and this means this method was effective to remove the sulphation products, and the nitration and oxidation by-products absorbance intensity were strong and this means this method was effectiveness to remove the nitration and oxidation products.

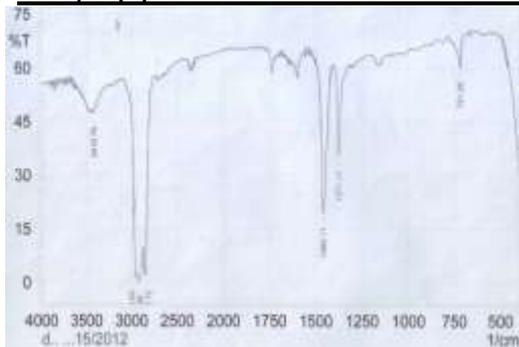


Figure (9) FTIR Spectrum of Treated Generator Oil by Distillation Method

Figure (10) shows the FTIR spectrum of treated oil by acid/bentonite method which show the absorbance intensity of water was very weak and that is agreed with the high viscosity value, the soot absorbance intensity was strong and this agreed with high ash content. Sulphation by-products absorbance intensity was very weak and this means this method was effective to remove the sulphation products, and the nitration and oxidation by-products absorbance intensity were very weak and this means this method was effective to remove the nitration and oxidation products.

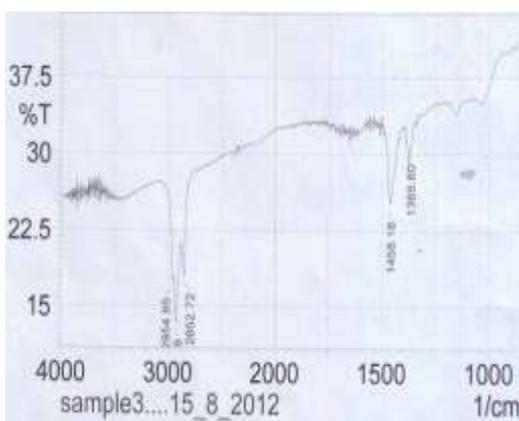


Figure (10) FTIR Spectrum of Treated Generator Oil by Acid/Bentonite Method

Figure (11) shows the FTIR spectrum of treated oil by distillation/acid method which show the absorbance intensity of water was strong and that is agreed with the viscosity value. The soot absorbance intensity was strong and this agreed with ash content.

Sulphation by-products absorbance intensity was strong and this means this method was effectiveness to remove the sulphation products and the oxidation by-products absorbance intensity were very weak and this means this method was effective to remove oxidation products while the nitration by-products absorbance intensity were strong and this means this method was effectiveness to remove nitration products.

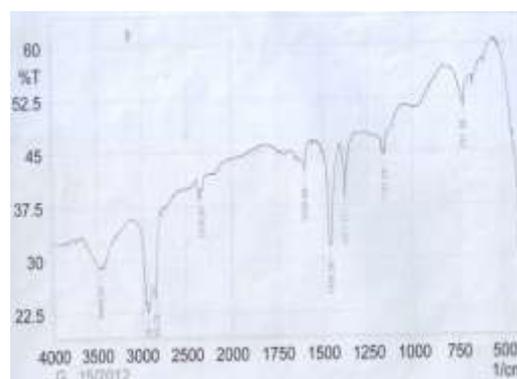


Figure (11) FTIR Spectrum of Treated Generator Oil by Distillation/Acid Method

Figure (12) shows the FTIR spectrum of treated oil by distillation/bentonite method which show the absorbance intensity of water was very strong and that is agreed with the high viscosity value, the soot absorbance intensity was weak, the oxidation by-products absorbance intensity were very weak and this means this method was effective to remove oxidation products. The nitration by-products absorbance intensity were strong and this means this method was effectiveness to remove nitration products and sulphation by-products absorbance intensity was strong and this means this method was effectiveness to remove the sulphation products.

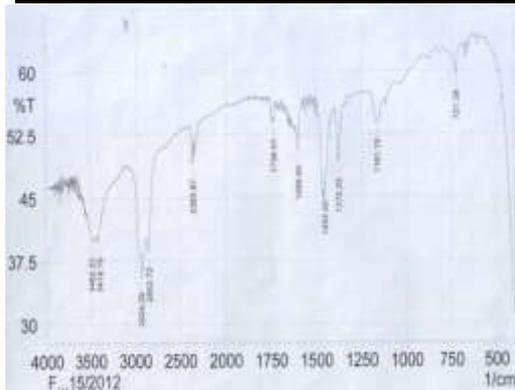


Figure (12) FTIR Spectrum of Treated Generator Oil by Distillation / Bentonite Method

Conclusion

In this work, different processing methods, which include (vacuum distillation, acid / bentonite, distillation / bentonite, and acid/distillation treatments were applied to purify and re-refine waste lubricating oil.

The results of physical properties which include viscosity, specific gravity, flash point, pour point, and ash content show that the acid/bentonite is good technique for removal the impurities from used lubricant oil which enhances desired characteristics for quality of fresh oil. As treatment methods changed, the absorbance of infrared of lubricating oil also changed. It can be deduced that, the FTIR spectroscopy of the treated oil by acid / bentonite method gave the closest in terms of structure to fresh oil, although there are some impurities still in the oil.

From FTIR spectroscopy, it was established that FTIR analysis provides good information about chemical composition that lead to the condition of the lubricating generator oil.

According to the analysis of treated used oil, there was good results for removing impurities and recycling used oil

,but there were some considerations should be studied when select the treatment method including the yield, bright stocks utilities, overall energy, and hazardous chemicals.

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