THE EFFECT OF FULLER'S EARTH AND DIFFERENT ACID SOLVENTS ON USED ENGINE OIL THROUGH ACID-CLAY TREATMENT FOR RENEWABLE ENERGY

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ABSTRACT

In this study, the fuller's earth (FE) and different acid solvents on used engine oil (UEO) using acid-clay treatment were investigated. The reclamation efficiency of different acids paired with FE was measured through several analyses. All the UEO samples showed positive water content. The treated oils' density was improved to 0.718 g/ml compared to UEO of 0.855 g/ml. The FT-IR did not enhance components due to alkene, aldehyde, and methane with similar wavelengths to untreated EO. Copper (Cu) and lead (Pb) content in treated EO were not detected.

Keywords: *Used engine oil, fuller's earth, acid-clay treatment, adsorption*

INTRODUCTION

Today, numerous industrial and automotive sectors generate large amounts of used engine oil (UEO) globally. Due to the increasing number of vehicles, the volume of the UEO produced each year is increasing. However, engine oil (EO) performance deteriorates over time as the additives are changed chemically, and the EO is contaminated with various unwanted pollutants. EO efficiency deteriorates due to varying physical and chemical interactions of foreign matter that consists of filling, metal powder, oxidation product, and other degrading additives [1].

The improper disposal of UEO due to the rapid growth of automotive and machinery industries has raised concern to many as the waste is classified as hazardous. This contributes to severe environmental pollution if improperly disposed of, such as uncontrolled dumping and landfilling. Moreover, UEO management is a growing concern to many nations, especially in industrial and urban areas. Commonly, the UEO is dumped on the ground, down the sewers, or sent to landfills where it either ends up flowing into the ground or floating on water surfaces [2].

Somehow, the idea of UEO recycling is a great effort, and it has been a four decades tradition since it was first presented in the 1930s. Initially, the UEO has undergone combustion for energy production, and then it was re-blended with EO after treatment. In short, the evolution of recycling technology is crucial for re-refining the UEO to remove the physical, mechanical, and chemical contaminations through the process such as distillation, hydrogenation, acidic refining, solvent refining, or combinations of the formers [3].

The previous studies understood that acid-clay is the standard effective method to reclaim used oil (UO) in removing the contaminants [1]-[4]. Several research papers use activated carbon (AC) to treat the UEO by replacing clay with adsorbents [5],[6]. UEO was recovered using various types of adsorbents such as date palm kernels powder, bentonite, and eggshell powder [6]. However, to date, the use of acid solvents paired with adsorbents on UEO recovery still lacks in much of the published literature. Meanwhile, the fuller's earth (FE) is a sedimentary clay with high magnesium oxide content commonly used in bleaching, refining edible oils, and clarifying petroleum. FE is preferred due to its high adsorption capacity and low purchasing cost. It decolorises the oil by tint reduction to a light shade without altering oil's chemical properties [7]. As a natural adsorbent, it can remove heavy metals in wastewater and extract resin and sulfur-containing compounds, unsaturated and polycyclic material, organic residues of sulphuric acid, and oil solvents of UEO [2],[7]-[8].

Therefore, the present work aimed to reclaim the UEO using different acid solvents, namely HCl, H_2SO_4, and H_3PO_4 paired with FE through acid-clay treatment. Other acid solvents were used to study its performance in FE clay, whereas the FE clay was used as a bleaching material that could improve the appearance of UEO. The reclamation efficiency of each sample of different acids was measured through several analyses such as water content, density, sludge formation, Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible (UV-Vis) spectroscopy, and atomic absorption spectroscopy (AAS). This study also aimed to compare acid-clay treatment's effectiveness to recover the UEO and make it reusable. This unique approach meets the arising of environmental predicament due to improper disposal of UEO.

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METHODOLOGY

Materials

In this study, virgin engine oil (VEO) of PERODUA Genuine Oil 5W-30 API SM, UEO of the same brand (sample II), and unknown brands of UEO samples from three different vehicles (Sample I, III, and IV) were collected from local car service centers. Each sample was analysed for water content. Sample II underwent different acid treatment, namely HCl, H_2SO_4, and H_3PO_4, followed by FE's clay treatment (Sample A, B, and C). FE was bought online from EvaChem with a decolouring ability of 98.6%, a particle size of 200 mesh, moisture of 8.25%, and oil retention of 3.56%. The treated EO of each sample obtained was then analysed for density, sludge formation, and chemical properties. The analyses were then compared with the VEO and the untreated UEO of the same brand to determine the acid-clay method's effect in reclaiming the oil. Initially, 37% of HCl from LAB-SCAN that has been diluted to 5%, 10%, and 15%; 98% of H_2SO_4 from LAB-SCAN that has been diluted to 5%, 10%, and 15%; 85% of H_3PO_4 from SYSTERM that has been diluted to 5%, 10%, and 15%. Bruker FT-IR spectrometer, Shimadzu UV mini 1240 UV-vis spectrophotometer and Hitachi Z-5000 polarized AA were used for characterisations.

Experimental Procedure

In the acid treatment, 50 ml of UEO was measured and placed on a regulator hot plate maintained around 40-45°C. Then, 5 ml of 5% HCl was introduced simultaneously with stirring of the mixture for 10 min. At the end of this acid treatment, the acidic oil was allowed to settle for 24 hours for the sediment at the beaker's bottom could be formed and decanted. Then the mixtures were centrifuged at 1000 rpm to separate base oil from sludge for one hour [9]. These steps were then repeated with 10% and 15% concentration of HCl and repeated with different acids, namely H_2SO_4 and H_3PO_4, at 5%, 10%, and 15% concentration. Once the acid treatment was completed, the clay treatment of FE was then conducted on a 15% concentration of acidic oil samples. The samples were subjected to bleaching, where the dark colour and smell were removed. The acidic oils were placed on a regulator hot plate and maintained at 110°C. 4g of FE was introduced into it, and the mixture was stirred continuously for 15 min [10].

After the clay treatment was done, each bleached oil sample went through neutralisation with a 5 ml solution of 10% sodium hydroxide (NaOH) for 10 min [10]. Each of the oil samples was allowed to settle for 24 hours and decanted to another beaker to discard the residue at the bottom. Lastly, the sedimented oil then went through filtration using filter paper, and the filtrate collected was studied in terms of properties and efficiency of the acid-clay treatment.

Characterisation of UEO

Water content

The presence of water content in the UEO samples was determined by conducting a few steps. Firstly, all the untreated UEO samples were pre-treated to remove contaminants such as small debris using a vacuum filter. An electronic balance weighed empty beakers of 100 ml. After weighing, 100 ml of the UEO were measured by a measuring cylinder and poured into each beaker. The mass of each beaker containing UEO was recorded. The samples were then heated in the oven at a temperature of 140°C for evaporating the water, as mentioned by Hamawand et al. [11]. After one hour of heating, the samples were cooled down to room temperature and weighed again. Then, the final mass was recorded, and the mass of the UEO after dehydration was calculated.

Sludge formation

After acid was added to the UEO, it was left for sedimentation for 24 hours, centrifuged to separate the sludge's oil. Two layers were formed after the centrifuge, where the bottom layer was the sludge while the top was the sludge-free oil. The sludge-free oil was then separated, and leftover sludge was heated in the oven at 140°C for 1 hour 30 minutes to solidify the sludge produced [11]. After heating, the mass of sludge produced was weighed and recorded.

Density

Density was determined by calculating the ratio of the substance's mass to the mass of the same volume of water [11]. The density was recorded of each sample of VEO, untreated UEO, and treated EO samples, namely sample A, B, and C. Sample A was the 15% HCl and FE treated; Sample B was the 15% H_2SO_4 and FE treated; and Sample C was the 15% H_3PO_4 and FE treated.

FT-IR Analysis

The characterisation of liquid samples of VEO, UEO, and treated EO were conducted using a Bruker FT-IR spectrometer. One drop of each solution was placed on the plate simultaneously to be analysed. The FT-IR result among these was compared to see the difference in molecular compounds.

UV-Vis analysis

Once the reclamation process was completed, each oil sample's UV-Vis spectrum was recorded with a wavelength range of 190-1100 nm and equipped with quartz cells having a path length of 10 mm. The optical absorption of the samples was recorded over a wavelength range of 360-600 nm.

AAS analysis

The metal content of different metals found in the treated UEO was obtained by AAS using Hitachi Z-5000 Polarised AAS. Sets of

organometallic standards of metal, namely copper (Cu), iron (Fe), and lead (Pb) at 2.5 ppm, 5 ppm, and 10 ppm were prepared, and metal concentrations were determined by introducing the test solutions of EO samples into the flame of the AAS and after that recorded the responses. Metal concentrations were determined from the calibration curve that was obtained from standard solutions [12].

RESULTS AND DISCUSSION

Water Content

Water content is one of the unavoidable contaminants present in the EO. Its presence is the result of absorbing moisture directly from the air, condensation of humid air entering the oil compartment, corroded or leaky heat exchanger, fuel combustion, oxidation, and free water entry during oil changes. Figure 1 shows the water content level results, and it was understood that all the UEO samples contain water. All four samples showed positive water content in it with an average of 17.39%. This indicates that the water content varies depending on various factors such as grade of EOs, usage of EO, leaking of air coolers, leaking of engine cooling system, and atmospheric condensation.

Sludge Formation

The sludge collected was black, rigid, and compacted in a small quantity at the bottom of the tube after the centrifugation process. Figure 2 shows the bar chart of the mass of sludge produced. As shown in Figure 2, it was understood that the higher the acid concentration, the heavier the mass of sludge produced. This shows that 15% of the HCl acid concentration produced more sludge than the rest of the acid solvents. However, the sludge produced from 10% and 15% of H_2SO_4 was insignificant, and the sludge produced from 10% and 15% H_3PO_4 remained the same. The results obtained almost satisfy the review provided by Hamawand et al. [11].

Density

As Hamawand et al. [11] mentioned, UEO density increases with increasing amounts of oxidation products and solid contaminants such as metal formed while the EO is in use. Figure 3 shows the density comparison of the VEO, untreated EOs, and treated EOs of samples A, B, and C. As shown in Figure 3, the untreated UEO is higher than the VEO and treated EOs. The average densities of recovered oils were between 0.718 g/ml to 0.755 g/ml—sample C gave out the closest VEO density. Thus, from the data taken,

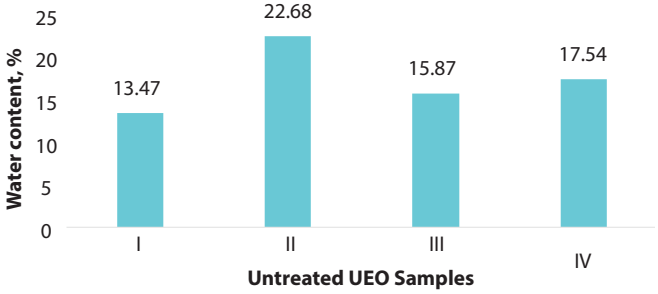

Figure 1 Water content removed in UEO

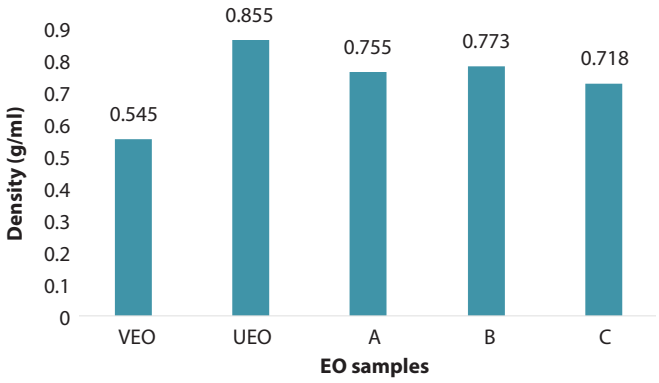

Figure 3 Comparison of density in samples

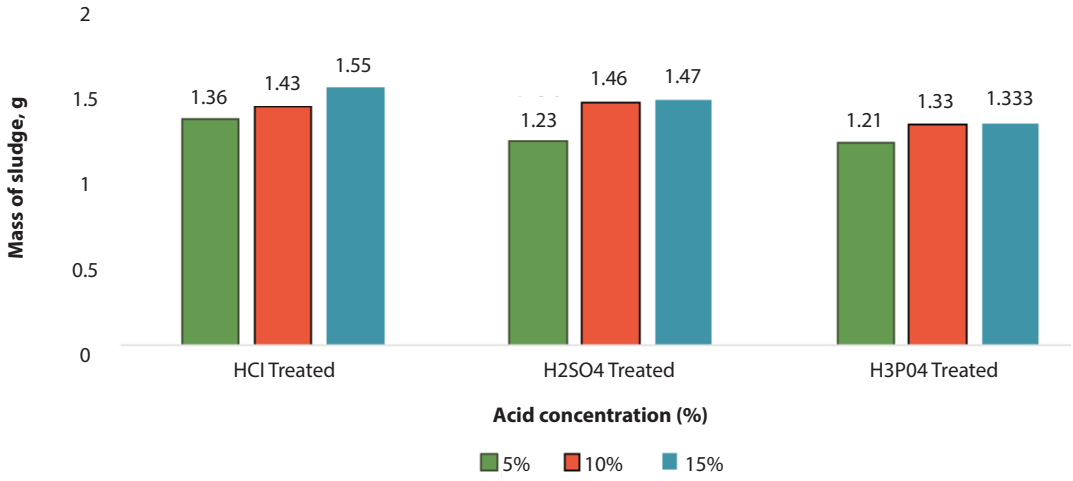

Figure 2 Mass of sludge produced

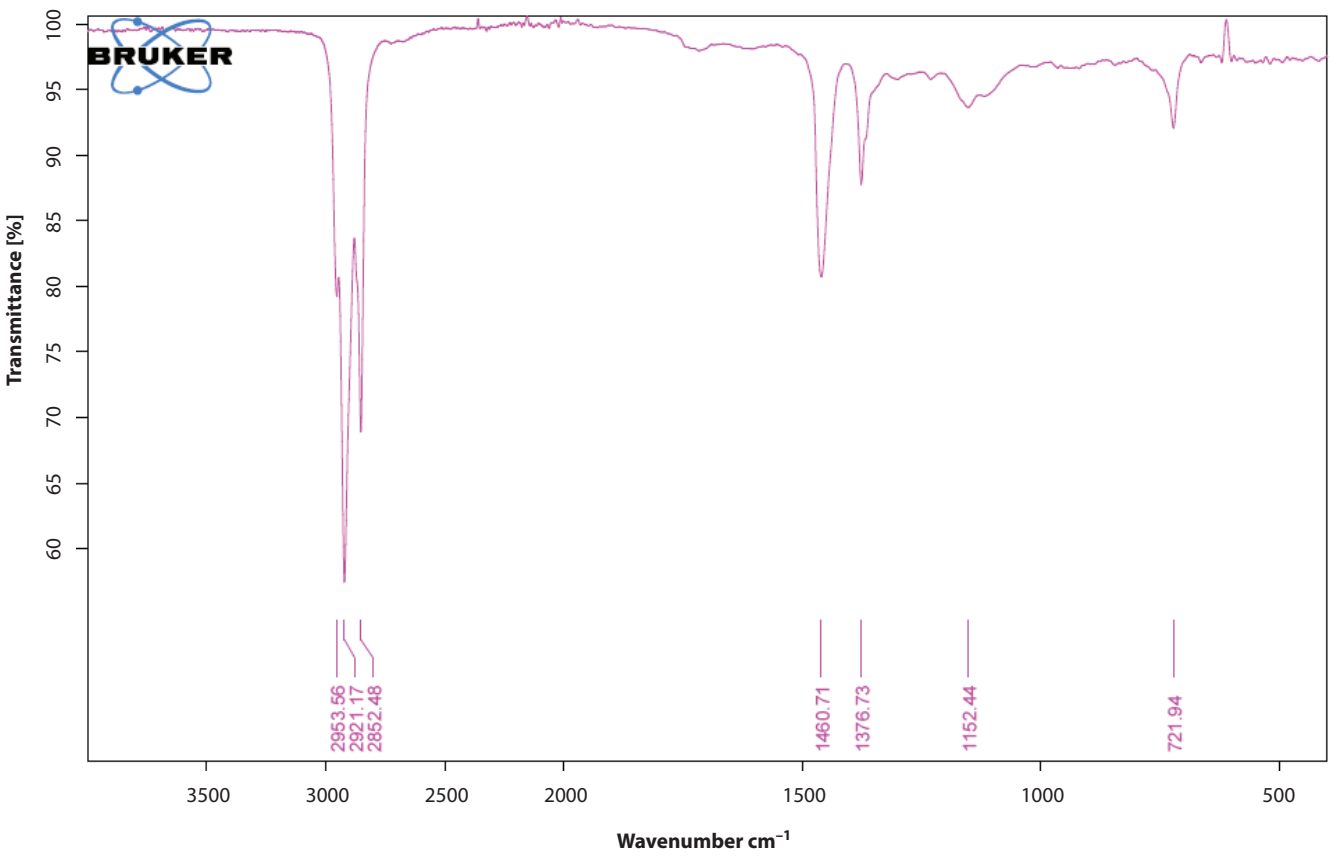

Figure 4 Spectrum of VEO

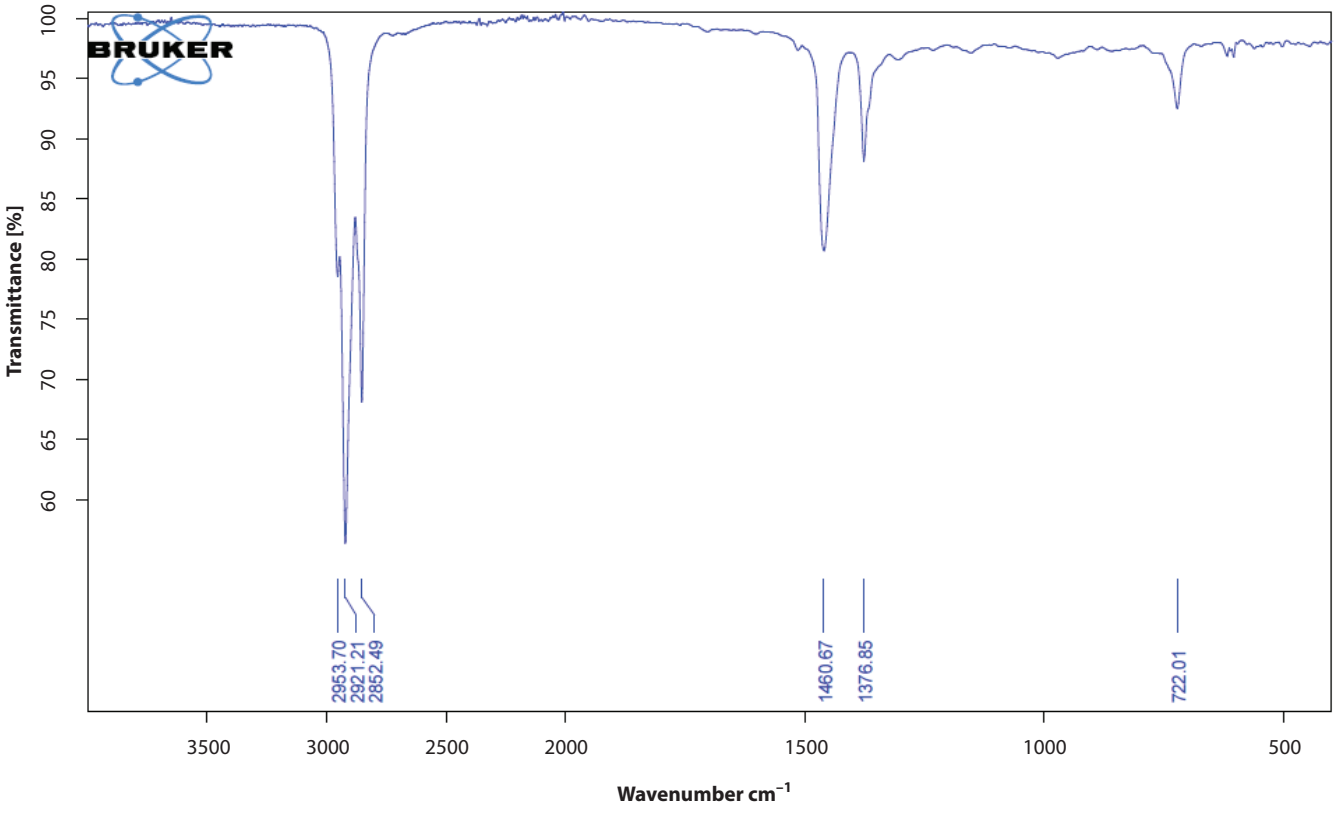

Figure 5 Spectrum of UEO

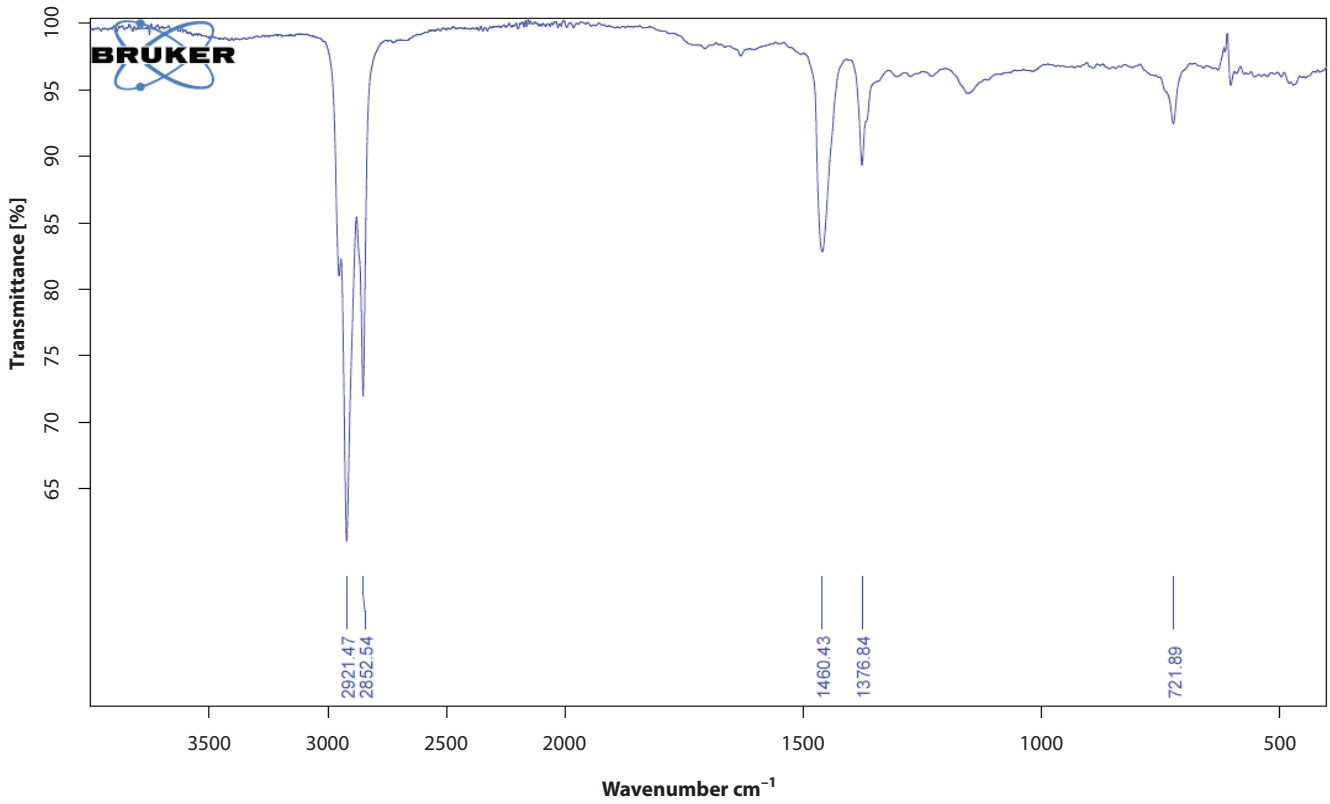

Figure 6 Spectrum of sample A

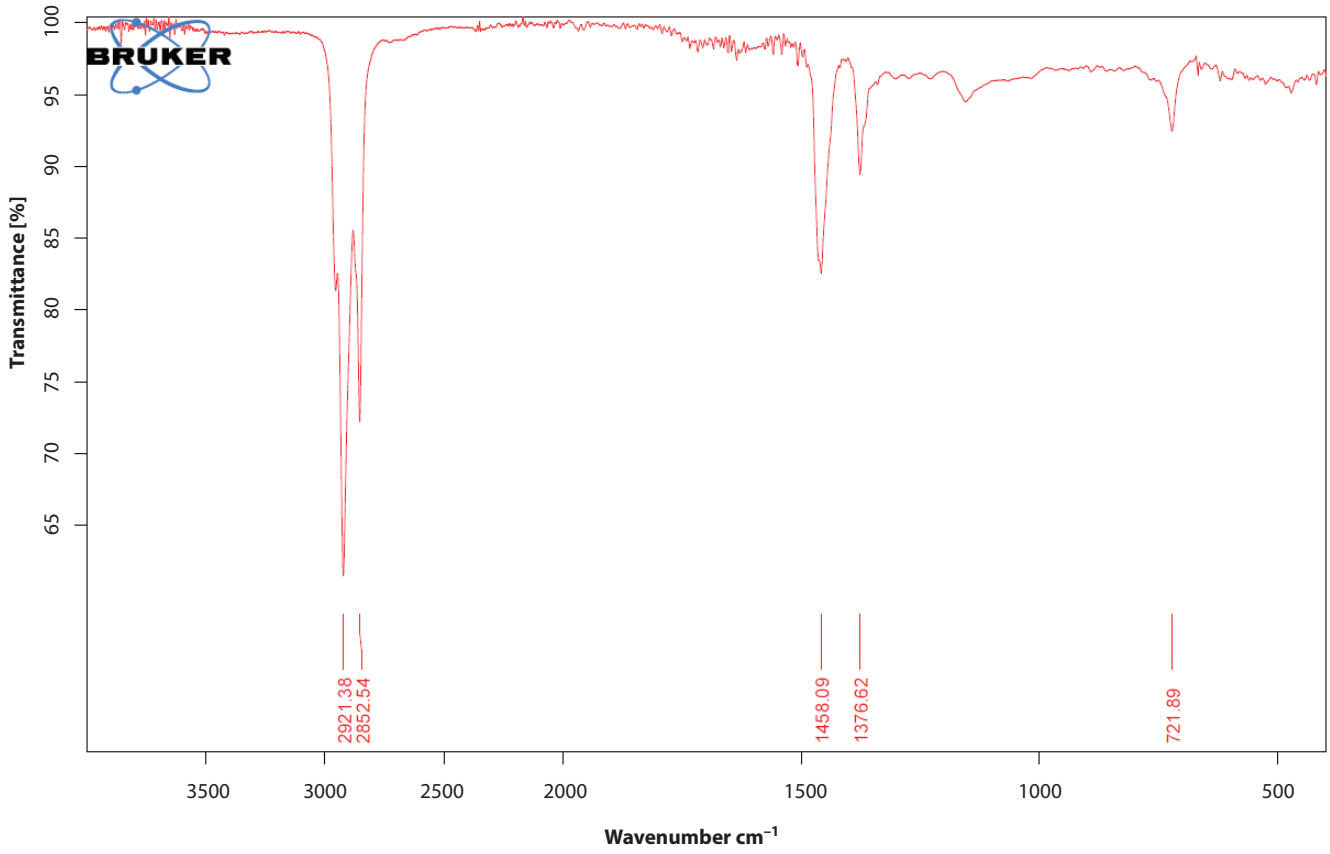

Figure 7 Spectrum of sample B

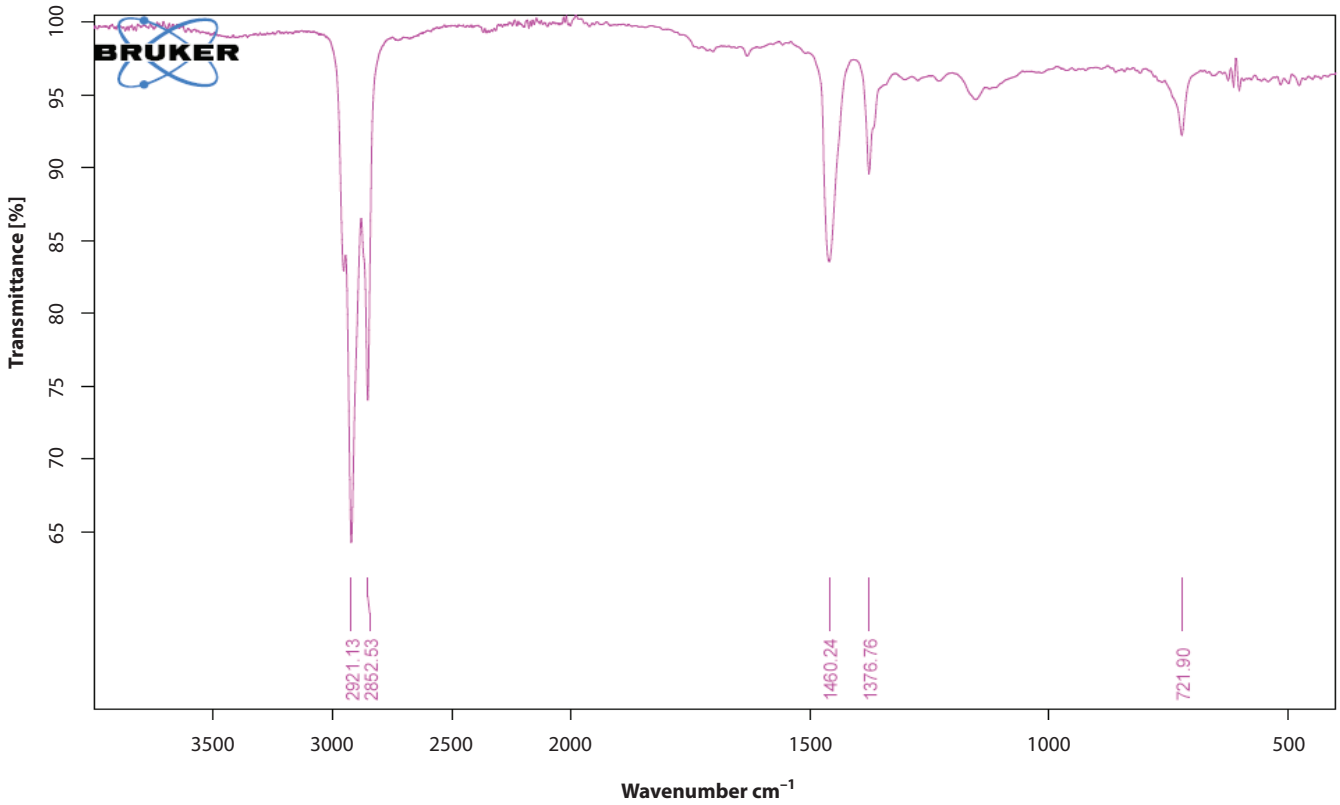

Figure 8 Spectrum of sample C

it can be said that there was a slight improvement in the density of the treated samples compared to untreated EO.

FT-IR analysis of EO

In this study, the VEO was used as a base oil to identify the adsorption process's effectiveness by comparing it with the treated EO samples. Figures 4 and 5 show the FT-IR spectrum of VEO and UEO (sample II). On the other hand, Figures 6 to 8 show the FT-IR spectrum of treated EO samples.

Table 1 compares component wavelength among the VEO, untreated UEO, and treated EO samples. From the table, it was understood that VEO contains alkane compound of wavelength 2921.21 cm^{-1}, 1460.67 cm^{-1}, 1376.85 cm^{-1}, 722.01 cm^{-1}, whereas other components such as alkene, aldehyde, CH_3, carbonyl compound, and carboxylic acid were undetected. This indicates that the VEO does not contain external contamination. Meanwhile, in untreated UEO, alkane was present at wavelength 2921.17 cm^{-1}, and 1460.71 cm^{-1}, alkene at 721.94 cm^{-1}, aldehyde 2852.48 cm^{-1}, and CH_3 at 1376.73 cm^{-1}. However, the treated EO samples were

Table 1 Comparison of components in EO samples

Samples	Wavelength (cm^{-1})					
	Alkane	Alkene	Aldehyde	CH_3	Carbonyl Compound	Carboxylic Acid
VEO	2921.21 1460.67 1376.85 722.01	Undetected	Undetected	Undetected	Undetected	Undetected
UEO	2921.17 1460.71	721.94	2852.48	1376.73	undetected	undetected
A	2921.47 1460.43	721.89	2852.54	1376.84	undetected	undetected
B	2921.36 1458.09	721.89	2852.54	1376.62	undetected	undetected
C	2921.13 1460.24	721.90	2852.53	1376.76	undetected	undetected

shown a range of wavelengths that are similar to untreated UEO. The absorption band at the 2900 cm^{-1} region and bands around 1460 cm^{-1} and 1377 cm^{-1}, which correspond to C-H stretching and bending vibrations, indicate hydrocarbon compounds. The bands around 1377 cm^{-1} are associated with SO2 stretching vibration, which confirmed the presence of sulfonate salts. The band intensity at 721 cm^{-1} indicates that some VEO components, particularly additives, have been destroyed during car usage [13].

Briefly, it was understood that the VEO does not have any components that affect the oil's purity because it is not contaminated with external impurities. In contrast, the untreated EO and the treated EO samples exhibited alkene, aldehyde, and methane. However, carbonyl compounds and carboxylic acid were not found throughout the analysis. From the comparison among untreated UEO and treated EO samples, it can be said that the acid-clay treatment using FE was not effective in treating the oil due to the similar component found with a similar range of wavelengths.

UV-Vis spectroscopy analysis of EO

Figure 9 shows the absorbance of the oil at a wavelength of 400 nm. The figure shows that treated UEO is not significant since only a FE clay treatment cycle was done. Sample A does not differ from untreated UEO, while samples B and C somehow have a more substantial absorbance value than the UEO. This may be due to external errors while conducting the equipment. However, absorbance reading's repeatability could also be due to the instrumental noise, possible fluctuations between solutions, and possible dust particles on the cell windows or in the solution. Experimental determination of repeatability uncertainty should be made using repeated measurements involving taking the cell out of the spectrometer and inserting it again; preferably, a spectrum of other sample types should be scanned in between [14].

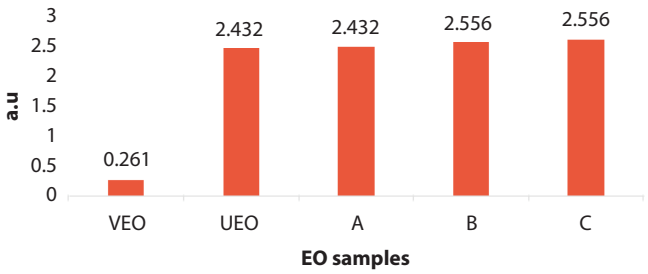

Figure 9 Comparison of absorbance unit in samples

AAS analysis of EO

EO's metal content is a very important parameter as the metal content in an oil sample can increase the metal parts' rate of corrosion [12]. The results of metals concentration of iron (Fe), copper (Cu), and lead (Pb) are shown in Table 2. The table shows that all three metals were not detected in VEO since it shows negative readings throughout the data. This indicates that the

Table 2 Metal concentration of EO samples

Samples	Metal contents (ppm)		
	Fe	Cu	Pb
VEO	-0.6774	-0.4389	-1.3228
UEO	4.4905	0.5212	-1.3069
A	7.4875	-0.3554	-1.2909
B	8.1136	-0.3196	-1.2750
C	7.8365	-0.0155	-1.2591

VEO does not contain any metal contaminants. Table 2 shows that untreated EO has a Cu content of 0.5212 ppm, whereas the rest of the treated EO samples show negative data. This proves that Cu content was removed in the treated samples of A, B, and C through acid-clay treatment. In addition to that, Fe is the most common engine wear product present in EO. Its concentration in UO depends mainly on the lubrication conditions inside the engine. Fe in base oils is not particularly desirable and is usually removed from such oil [15]. However, from the data obtained, the Fe content in each treated EO sample happened to be more than the Fe content of untreated UEO. This could be due to improper filtration or external contaminants that affect the readings. On the other hand, Pb metal was not detected in any of the samples.

CONCLUSION

In conclusion, it can be said that the UEO shows positive water content. It also shows that the treated samples did show improvement in density and sludge formation. The sludge formation increased owing to the increase of acid concentration. However, 15% of HCl concentration forms the heavier mass of sludge. From the comparison among untreated UEO and treated EO samples, it can be said that the acid-clay treatment using FE was not effective in treating the oil due to the similar component found with a similar range of wavelengths. The absorbance readings are higher than UEO, which are 2.432 and 2.556. This is probably due to short cycles of clay treatment to finally see the improvement. Lastly, Pb was not detected in any of the samples.

Conversely, the Cu content in treated EO was reduced and not detected compared to the UEO. This shows that the acid-clay treatment can remove the copper contaminant. Nevertheless, for further study, the investigation towards the temperature, settling time, mixing, pressure, centrifugation speed, and time could also significantly affect the yield and recycled oil qualities.

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