

Used Industrial Oil Recycling Using Acid with Low Cost Adsorbents

S M Anisuzzaman^{1#}, Duduku Krishnaiah², Sariah Abang², Marianah Taib²

¹ Energy Research Unit (ERU), Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, MALAYSIA.

² Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, MALAYSIA.

#Corresponding author. E-Mail: anis_zaman@ums.edu.my; Tel: +6088-320000; Fax: +6088-320348.

ABSTRACT The main objective of this research is to study the potential properties of used industrial oil (UIO) using acid-clay treatment method. Acid treatment was done using glacial acetic acid followed by clay treatment using activated carbon (AC) or treated river sand (TRS). This study showed that a correlation of acid volume to the sludge formation in UIO. For hydraulic oil (HO) and automatic transmission fluid (ATF), it can be seen that the used HO results in a higher mass of wet and dry sludge formed as compared to the EO and ATF. The Fourier transform infrared spectroscopy (FTIR) showed that soot, oxidation and sulfation in ATF became undetected after the treatment. Initially, oxidation and sulfation peaks were detected by the presence of a sharp peak around 2173 cm⁻¹ and 1717 cm⁻¹ for ATF samples, while for HO samples, the treatment method was only able to reduce the soot content to an undetectable level. In recycled EO samples, both soot and oxidation problems were resolved. This study also proved that the theory of using TRS as an alternative low cost adsorbent can be an alternative adsorbent although the UIO treated with AC showed better result.

KEYWORDS: Activated carbon; Treated river sand; engine oil; hydraulic oil; automatic transmission fluid

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INTRODUCTION

In general, impurities such as additives that remained in used oil (UO) can cause the problem to the re-refining activity and in overall affects the final quality of the base oil reclaimed (Wang *et al.*, 2014). Contaminants such as heavy and light hydrocarbon, polycyclic aromatic hydrocarbon and other polymers may present in the used industrial oil (UIO). This contaminant is not preferable because it may lead to dioxin formation (Thomas & McCreight, 2008). Silica content sourcing from antifreeze and brake fluid leads to catalyst poisoning, paraffin from fuel slops disposal cause lube opacity, styrene presence causes fouling and sulphur arise from engine leakage cause pollutions (Xing *et al.*, 2017).

There are four main contaminants that can be found in used hydraulic oil (HO) which is native, ingresses, internally generated contaminant and contaminated new oil. Numerous methods exist to recover the UIO to its base oil form and to remove the contaminants. (Hamad *et al.*, 2005; Rincón *et al.*, 2007; Scapin *et al.*, 2007; Kamal & Khan 2009; Emam & Shoaib, 2012; Al-Zahrani & Putra, 2013; Hamawand *et al.*, 2013; Omolara *et al.*, 2015; Rudyk & Spirov, 2017; Lou *et al.*, 2018). Usually, the method is a combination of acid treatment and solvent extraction to earn a final product with better quality and yield. The treatment using clay or adsorbent can be improved by the addition of catalyst (Bhaskar, *et al.*, 2004). However, this process has two main problems specifically the production of acidic sludge and clay treatment that requires the uses of adsorbent such as activated carbon (AC), kaolin, alumina, silica gels, etc.

Several studies were conducted on the recovery of UIO using adsorbent through the process called adsorption (Ofunne & Maduako, 1990; Wambu *et al.*, 2009; Yadav *et al.*, 2012; Sabour & Shahi, 2018; Anisuzzaman *et al.*, 2019). Typical river sand (RS) contained metal contents such as lead, zinc, copper and calcium (Danh *et al.*, 2011). The adsorbent properties of RS rely on its active site which is in the form of silicate and quartz (Yadav *et al.*, 2012).

This study is mainly focused on the ability and properties of RS on the adsorption of contaminants from UIO. The RS sample was rehydrated and activated in the oven several times to remove the water and volatile contaminants. Followed by acid treatment then clay treatment using AC or treated sharp sand (TRS). At the end, the treated UO was analyzed. The characteristics of the reclaimed UO were measured using Fourier transform infrared spectroscopy (FTIR).

METHODOLOGY

UIO Sampling

Used HO sample was supplied by local shipyard engineering in Malaysia, while used engine oil (EO) and used automatic transmission fluid (ATF) were obtained from a small local workshop. All these three UIO samples were treated using acid-clay treatment and the final recycled oils obtained were compared to the virgin oil (VO). RS was obtained from a local hardware store. The AC (NORIT) was purchased from Sigma-Aldrich, which is a coconut shell based in powder form with ~100 mesh particle size.

Experimental Procedure

RS was rinsed with warm water followed by distilled water until clear water was obtained to remove any earthen impurities. The RS was semidried and washed with cyclohexane and 0.3M nitric acid (HNO₃). The RS sample was washed with distilled water several times until the solution was no longer acidic and was dried in an oven at 300°C for 2 h to allow complete dry of sand (Ofunne & Maduako, 1990). By paying attention to the boiling point of the UIO samples, the samples were allowed to heat up to 250°C in the oven for approximately 1 h. This was to allow total evaporation of water and volatile components that were present in the samples. After that, the samples were cooled down to room temperature. 100 mL of dehydrated UIO was mixed with 20 mL acetic acid, followed by heating and stirring using a hot plate at room temperature for 1 h. After that, the mixture was centrifuged at 300 rpm for 1 h to separate the base oil and the contaminants. The sludge formed after centrifugation was weighed. Initially experiment was carried out with AC. The mixture of sludge and base oil was heated to 250°C for 30 min and then centrifuged to separate the base oil. The final oil obtained was analyzed. Adsorption experiment using TRS was conducted followed the same procedure as the AC.

Characterization of UIO

The density of the base oil was measured using hydrometer method (ASTM D1298). The viscometer (Brookfield Programmable Viscometer DV-III + Rheometer) was used to determine dynamic viscosity at 40°C. The molecular compounds of used and recycled oil were analysed using FTIR which focused on four important parameters which were soot, sulphation, nitration and oxidation.

RESULTS AND DISCUSSION

Sludge Formation

After the acid treatment and centrifugation, clear reddish base oil was formed at the top layer and sludge at the bottom layer of the centrifuge tubes. Table 1 shows that the weight of sludge increased as the volume of acetic acid added increased (Sample F, G and H) in the EO. The sludge from Sample H had an emulsion and yellow in colour. Thus, high mass of sludge was favourable as more metal contaminant was removed (Hamawand *et al.*, 2013). However, in this study, the analysis

of the sludge was not conducted. Sample C and D from HO produced a higher weight of wet sludge and dry sludge as compared to sample E from EO and samples A and B from ATF.

Table 1. Sludge formation

Sample	V _{acid} (ml)	M _{wet sludge} (g)	M _{dry sludge} (g)
A (ATF + AC)	20	1.3	1.1
B (ATF + TRS)	20	1.9	1.6
C (HO + AC)	20	19.8	19.2
D (HO +TRS)	20	23.3	22.6
E (EO + AC)	20	2.5	2.1
F (EO+TRS)	20	2.4	2.1
G (EO +AC)	30	3.1	2.7
H (EO + AC)	40	4.5	4.2

Density

As shown in Figure 1, all the UIO samples have higher densities compared to their respective VO. According to Hamawand *et al.*, 2013 density rises with the presence of rising amounts of contaminants. The purpose of this study was to improve the density of the recovered oil so that it will be lower or closer to the VO. Sample A which was clay treated with AC recorded a density of 0.772 g/mL, while sample B which was treated with RS recoded a density of 0.826 g/mL. By comparing to the density of used ATF oil which density was found to be 0.891 g/ml, both types of adsorbents were able to improve the density, but AC gave better density results than the RS. Sample C was clay treated with AC and D was treated with RS. Sample C has a density of 0.818 g/mL while sample D was 0.837 g/mL. While in the EO samples of E, F, G and H treated with AC and RS gave slightly closer density to the virgin EO which was 0.844 g/mL.

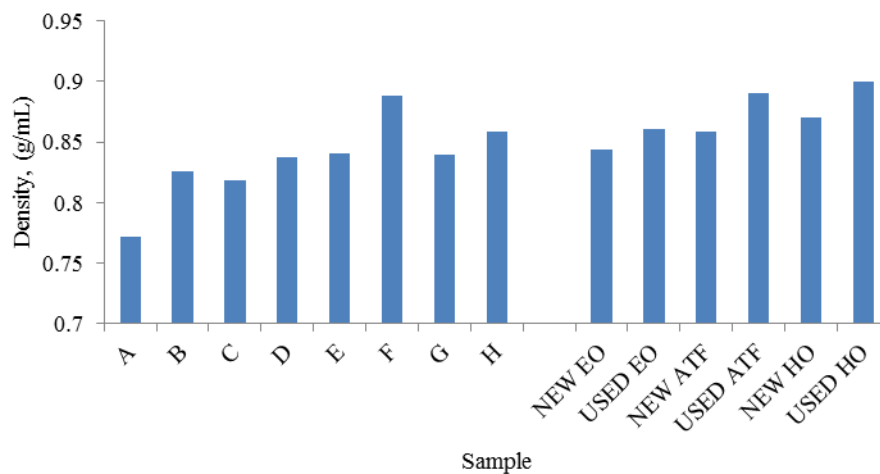


Figure 1. Effect of oil composition on density

Viscosity

Figure 2 shows that all the samples improved in their viscosities conducted at 40°C. For Samples A and B, viscosity was recorded 29.3 and 26.4 cSt, respectively. For the virgin ATF viscosity was found to be 36 cSt. While for HO, sample C viscosity (28.6 cSt) was closer to the virgin HO (32 cSt) compared to sample D which had a viscosity 25.1 cSt. Both samples A and C were treated with AC, thus it can be said that AC was better than RS in improving the oil viscosity. For the EO samples, sample H had the highest viscosity (71.4 cSt), indicating that the volume of acid used can also influence the viscosity of the oil to some extends. Results from the four samples of EO, higher acetic acid volume in combination with AC treatment showed in better viscosity.

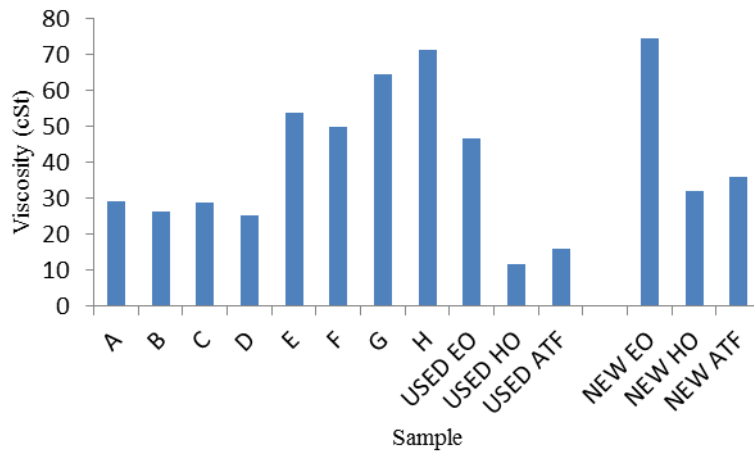


Figure 2. Effect of oil composition on viscosity

Analysis of Fourier-Transform Infrared Spectrometer (FTIR)

The adsorption properties of the sand are actually based on the kaolinite and silica those are present abundantly in RS. However, kaolinite clay is not the only component that is present in RS. Hence, the FTIR analysis was done on the untreated RS to analyze other compounds that are presented in Figure 3.

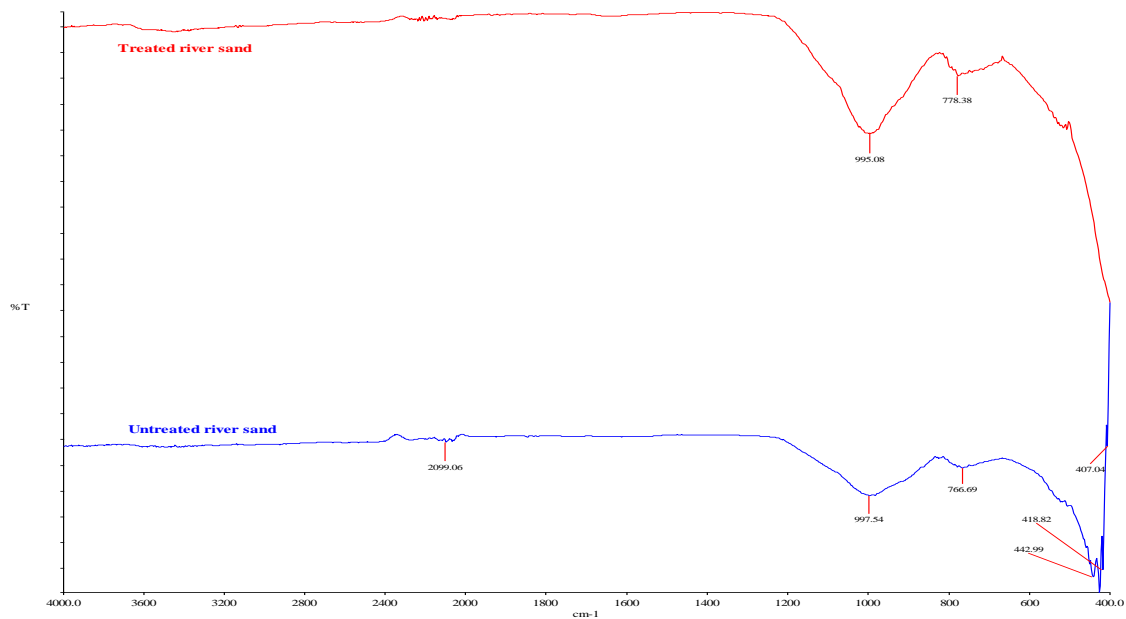


Figure 3. Comparison of before and after treatment of RS

The FTIR shows that untreated RS besides kaolinite also contained quartz and microcline. Quartz was detected as sharp peak at 767 cm⁻¹ and microcline in three sharp peaks at wavenumber of 443, 418 and 407 cm⁻¹ (Kamar *et al.*, 2008; Ochieng, 2016). After the treatment, RS was analysed and it was found that microcline wavenumber were reduced to undetectable (UD) level (Table 2).

Table 2. Wavenumber of RS before and after treatment

Sample	Wavenumber(cm ⁻¹)		
	Kaolinite	Quartz	Microcline
Untreated RS	998	767	443, 418 and 407
TRS	995	779	UD

It was observed that the FTIR absorption bands appeared at 775-780 cm^{-1} , suggesting the existence of quartz in oil samples. The shape of absorption in quartz can be explained by ascribing the bands in the region 775 cm^{-1} due to Si-O symmetrical stretching vibrations and 795 cm^{-1} due to Si-O symmetrical stretching vibrations. Quartz in river sand usually presents in the form of silica. Both silica and kaolinite are common adsorbents that are used in the treatment of UIO. Figure 4 shows FTIR analysis of ATF sample A treated with AC.

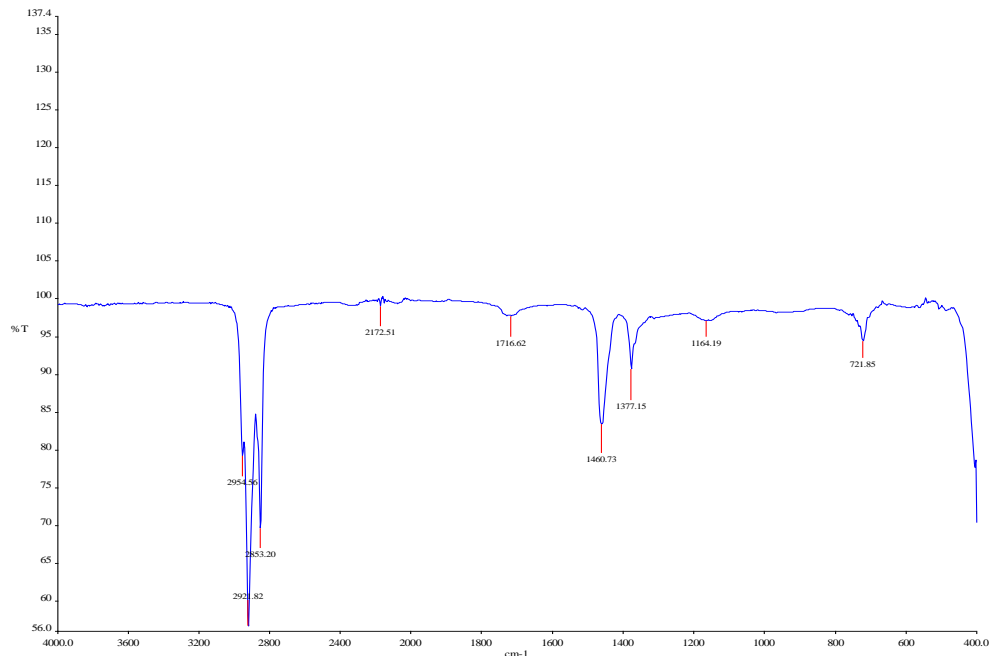


Figure 4. FTIR analysis of used ATF sample A

Table 3 shows the presence of soot at detectable wavenumber of 2173 cm^{-1} , but after treatment it reduced to UD peaks. The same trend can also be seen in the sulfation number. There were no significant changes in nitration and gasoline peaks. It can be said that the acid clay treatment was effective in reducing the soot and sulfation wavenumber. Although soot and sulfation presence in a low concentration in ATF samples the acid-clay treatment was able to remove these contaminants. A peak at about 722 cm^{-1} indicated gasoline. A nitration peak was visible at wavenumber of 1460 cm^{-1} .

Table 3. FTIR data of ATF sample

Sample	Wavenumber (cm^{-1})				
	Soot	Oxidation	Nitration	Sulfation	Gasoline
Virgin ATF	UD	UD	1460	UD	710
Used ATF	2173	1717	1461 and 1377	1164	722
A(AC)	UD	UD	1459 and 1377	UD	721
B(RS)	UD	1716.51	1461, 1377 and 1290	UD	722

Figure 5 shows the FTIR analysis of HO sample C treated with AC.

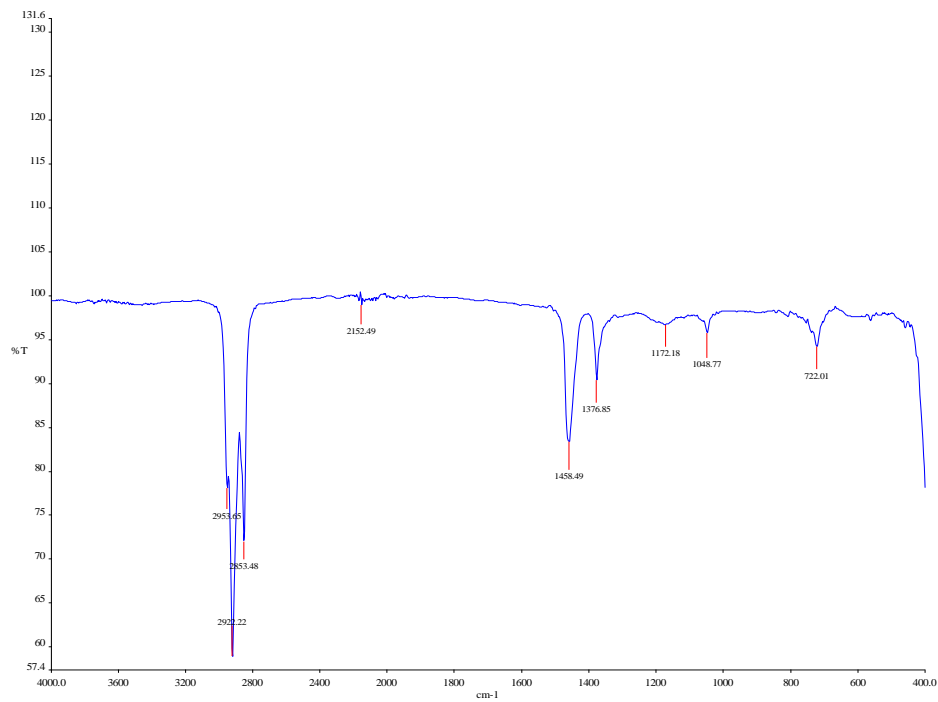


Figure 5. FTIR analysis of used HO sample C

Table 4 shows that soot was detected in used HO samples and nitration, sulfation and gasoline was detected in HO samples (Usman & Kayode-sote, 2011). It was also found that in the recovered HO samples, oxidation and sulfation cannot be reduced using acid-clay treatment. However, after acid treatment and clay treatment with AC and TRS, the soot was UD. The sulfation number was also reduced from 1172 cm^{-1} to 1131 after AC treatment. Both nitration and gasoline peak were remained unchanged. Acid clay treatment was effective in reducing the soot but was not able to reduce oxidation, nitration, sulfation and gasoline. Acid-clay treatment could not reduce oxidation and sulfation in the recycled HO samples. The acid-clay treatment with both AC and TRS successfully removed the soot from the used HO.

Table 4. FTIR data of HO sample

Sample	Wavenumber (cm^{-1})				
	Soot	Oxidation	Nitration	Sulfation	Gasoline
New EO	UD	UD	1460	1200	737
Used HO	2153	UD	1459 and 1377	1172	722
C (AC)	UD	1733	1458, 1377 and 1285	1131	722
D (TRS)	UD	1732	1458, 1377 and 1285	1124	722

Figure 6 shows the FTIR analysis of EO sample H treated with AC

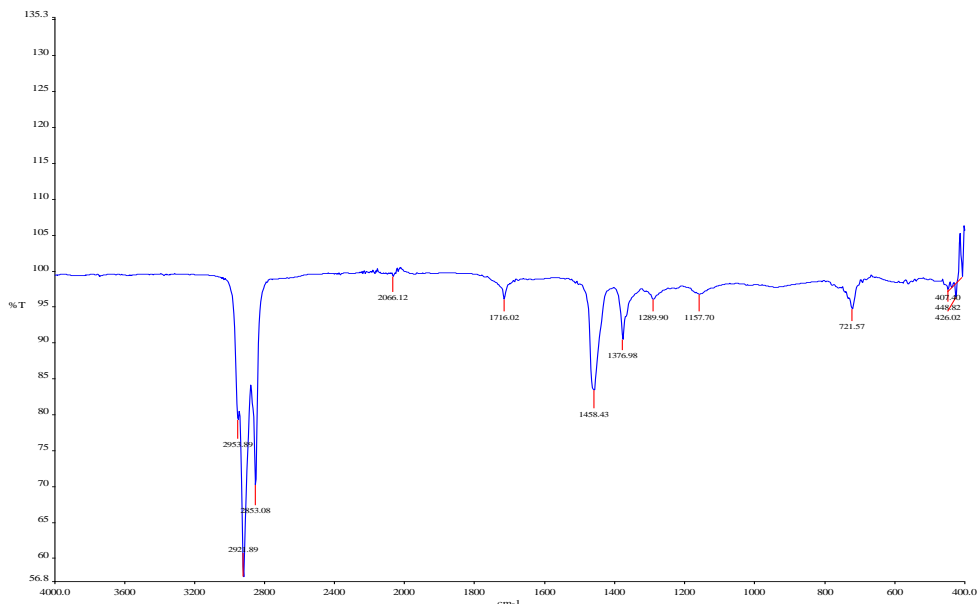


Figure 6. FTIR result of used EO sample H

Table 5 shows the presence of soot and oxidation in the used EO. Soot and oxidation can cause engine to operate inefficiently. Oxidation in EO is usually due to the inevitable effect of exposure of EO to high temperature and pressure. Oxidation problem can also be detected visually by analyzing the color of the EO, the darker the color the higher the oxidation problem. These two lethal EO problems were resolved by acid-clay treatment. After treatment, both soot and oxidation were not detected in the sample. However, nitration, sulfation and gasoline showed no change of peaks which indicated the three compounds were still present in the samples. Comparison of the results shows that the recovered EO was comparable to the virgin EO.

Table 5. FTIR data of EO sample

Sample	Wavenumber (cm-1)				
	Soot	Oxidation	Nitration	Sulfation	Gasoline
Virgin EO	UD	UD	1450 and 1381	UD	721.00
Used EO	2066	1716	1458 and 1377	1158	722
E	UD	UD	1460 and 1377	1157	721
F	UD	UD	1458 and 1377	1156	722
G	UD	UD	1461 and 1377	1157	721
H	UD	UD	1461 and 1377	1158	726

CONCLUSION

In this investigation acid-clay treatment was used to remove contaminants from UIO. The reclaimed oils have a better and improved quality than the untreated used ATF, EO and HO. It can be seen that higher acid volume resulted in higher sludge formation. Both adsorbents were able to improve the density of UIO, but AC showed better density results than TRS. The acid-clay treatment showed different effects on different types of industrial oil. All the samples showed an improvement in their viscosities at 40°C. Soot, oxidation and sulfation were UD after the treatment in ATF. In recovered EO, both soot and oxidation problems were resolved. The FTIR analysis showed that contaminants in RS such as microcline can be removed by HNO₃ treatment. The treatment could not

remove kaolinite which was the key to the absorbent properties of RS. However, GC/GCMS analysis may be carried out to support the FTIR data.

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