

Article

## Recycling of Waste Engine Oils Using a New Washing Agent

Ihsan Hamawand <sup>1</sup>, Talal Yusaf <sup>1,\*</sup> and Sardasht Rafat <sup>2</sup>

<sup>1</sup> Faculty of Engineering and Surveying, National Centre for Engineering in Agriculture, University of Southern Queensland, Toowoomba 4350, QLD, Australia; E-Mail: ihsan.hamawand@usq.edu.au

<sup>2</sup> Faculty of Engineering and Science, University of Koya, Koya KOY45 AB64, Iraq; E-Mail: sardashtrafat@yahoo.com

\* Author to whom correspondence should be addressed; E-Mail: talal.yusaf@usq.edu.au; Tel.: +61-7-4631-2691/1373.

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**Abstract:** This paper addresses recycling of waste engine oils treated using acetic acid. A recycling process was developed which eventually led to comparable results with some of the conventional methods. This gives the recycled oil the potential to be reused in cars' engines after adding the required additives. The advantage of using the acetic acid is that it does not react or only reacts slightly with base oils. The recycling process takes place at room temperature. It has been shown that base oils and oils' additives are slightly affected by the acetic acid. Upon adding 0.8 vol% of acetic acid to the used oil, two layers were separated, a transparent dark red colored oil and a black dark sludge at the bottom of the container. The base oils resulting from other recycling methods were compared to the results of this paper. The comparison showed that the recycled oil produced by acetic acid treatment is comparable to those recycled by the other conventional methods.

**Keywords:** waste recycling; waste engine oils; engine oils; waste oils; used engine oils

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### 1. Introduction

Waste engine oil is a high pollutant material that requires responsible management. Waste engine oil may cause damage to the environment when dumped into the ground or into water streams including sewers. This may result in groundwater and soil contamination [1]. Recycling of such contaminated materials will be beneficial in reducing engine oil costs. In addition, it will have a

significant positive impact on the environment [2–4]. The conventional methods of recycling of waste engine oil either requires a high cost technology such as vacuum distillation or the use of toxic materials such as sulfuric acid. These methods also produce contaminating by-products which have highly sulfur levels, especially in the Kurdistan region/Iraq. Lubricant oils have been used primarily for reducing friction between moving parts of various machinery or equipment, minimize material wear, improve the efficiency of equipment /machinery and for fuel and energy savings. Access to lubricants is essential to any modern society and not only does lubrication reduce friction and wear by interposition of a thin liquid film between moving surfaces, but it also removes heat, keeps equipment clean, and prevents corrosion. One of its important applications includes gasoline and diesel engine oils [5]. Waste lubricating oil refers to the engine oil, transmission oil, hydraulic and cutting oils after use. It is also refers to the degradation of the fresh lubricating components that become contaminated by metals, ash, carbon residue, water, varnish, gums, and other contaminating materials, in addition to asphaltic compounds which result from the bearing surface of the engines [6]. These oils must be changed and removed from the automobile after a few thousand kilometers of driving because of stress from serious deterioration in service. The amount of lubricating oils that is collected annually in Europe and USA is very large, approximately 1.7 to 3.5 million tons. This large amount of waste engine oils has a significant impact on both economical and environmental aspects. They cost millions of dollars to manufacture and represent a high pollutant material when disposed of. If discharged into the land, water or even burnt as a low grade fuel, this may cause serious pollution problems because they release harmful metals and other pollutants into the environment [7].

A recommended solution for this issue is the recovery of the lubricating oil from the waste oil. Recycling processes using nontoxic and cost effective materials can be an optimum solution. Acid-clay has been used as a recycling method for used engine oil for a long time. This method has many disadvantages; it also produces large quantity of pollutants, is unable to treat modern multigrade oils and it is difficult to remove asphaltic impurities [8]. Solvent extraction has replaced acid treatment as the method of choice for improving the oxidative stability and viscosity/temperature characteristics of base oils. The solvent selectively dissolves the undesired aromatic components (the extract), leaving the desirable saturated components, especially alkanes, as a separate phase (the raffinate) [9]. In one study [10] a mixture of methyl ethyl ketone (MEK) and 2-propanol was used as an extracting material for recycling used engine oils. Although the oil resulting from this process is comparable to that produced by the acid-clay method, its cost is high. Expensive solvents and vacuum distillation are required to carry out this method [11,12]. Recently [13] propane was used as a solvent. Propane is capable of dissolving paraffinic or waxy material and intermediately dissolved oxygenated material. Asphaltenes which contain heavy condensed aromatic compounds and particulate matter are insoluble in the liquid propane. These properties make propane ideal for recycling the used engine oil, but there are many other issues that have to be considered. Propane is hazardous and flammable therefore this process is regarded as a hazardous process. Also, the extraction involves solvent losses, and highly skilled operating maintenance. In addition, extraction occurs at pressures higher than 10 atm and requires high pressure sealing systems which makes solvent extraction plants expensive to construct, operate and the method also produces remarkable amounts of hazardous by-products [14].

Membrane technology is another method for regeneration of used lubricating oils. In this method three types of polymer hollow fiber membranes [polyethersulphone (PES), polyvinylidene fluoride

(PVDF), and polyacrylonitrile (PAN)] were used for recycling the used engine oils. The process is carried out at 40 °C and 0.1 MPa pressure. The process is a continuous operation as it removes metal particles and dusts from used engine oil and improves the recovered oils liquidity and flash point. Despite the above mentioned advantages, the expensive membranes may get damaged and fouled by large particles [15].

Vacuum distillation and hydrogenation are two other methods that can be used for recycling used engine oil [16]. The Kinetics Technology International (KTI) process is a combination of vacuum distillation and hydrofinishing. This method removes most of the contaminants from the waste oil. The process starts with atmospheric distillation to eliminate water and light hydrocarbons. This is then followed by vacuum distillation at a temperature of 250 °C. The final stage is hydrogenation of the products to eliminate the sulphur, nitrogen and oxygenated compounds. This stage is also used to improve the color and odor of the oil. The product can be of quality standard (Gp.I) with a yield of approximately 82% and minimized polluting by-products. The disadvantage of this method is the high investment cost [17,18].

In this research glacial acetic acid was used for recycling used engine oils. The method provides a lower cost process in comparison with the conventional methods due to the low cost of the acid and the moderate conditions of the process. The recycled oil obtained by this method has been shown to have potential for reuse as an engine lubricant.

## 2. Experimental Apparatus and Procedure

### 2.1. Experiment

For the purpose of this study a series of experiments have been carried out for two kinds of collected oils. The oils were collected from car oil change shops and from personal cars after 3000 to 3500 km in use. The type of base oil used in this study is Ravenol (VSi SAE 5W-40), manufactured in Werther, Germany. In order to confirm the ability of glacial acetic acid to separate the base oil from the contaminated substances many random experiments were carried out. The first experiment was carried out with the oils collected from the shops. The oil was heated to a temperature of over 250 °C for one hour, for the purpose of evaporating the water and the volatile substances in the used oil. This is to mimic the procedure used by the acid-clay method. The oil was then cooled to room temperature (16 °C, winter) and then equal amounts of this oil (10 mL) were added to a number of beakers. Different quantities of glacial acetic acid were then added to the used oils in the beakers. The amounts of the acid added were 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2 mL to each 10 mL sample. These samples then mixed at 600 rpm for half hour and heated on a hot plate stirrer (LabTech, ES35A-Pro) to a temperature of 25 °C. The beakers were open to the atmosphere. Then the oils resulting from the stirring and heating were centrifuged (Sigma, 2-6E, Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) immediately for a quarter hour at a speed of 3000 rpm. No separation was observed after this process, besides the absence of change in the treated used oil color. This may be due to the heating which may result in evaporation of acetic acid. This may also be due to the low period of interaction between the acid with the used oil. The second set of experiments were done by increasing the mixing time to half an hour and later to one hour, followed immediately by centrifugation. For the

second and third times no separation occurred and the absence of and color changes in the treated used oil was noted.

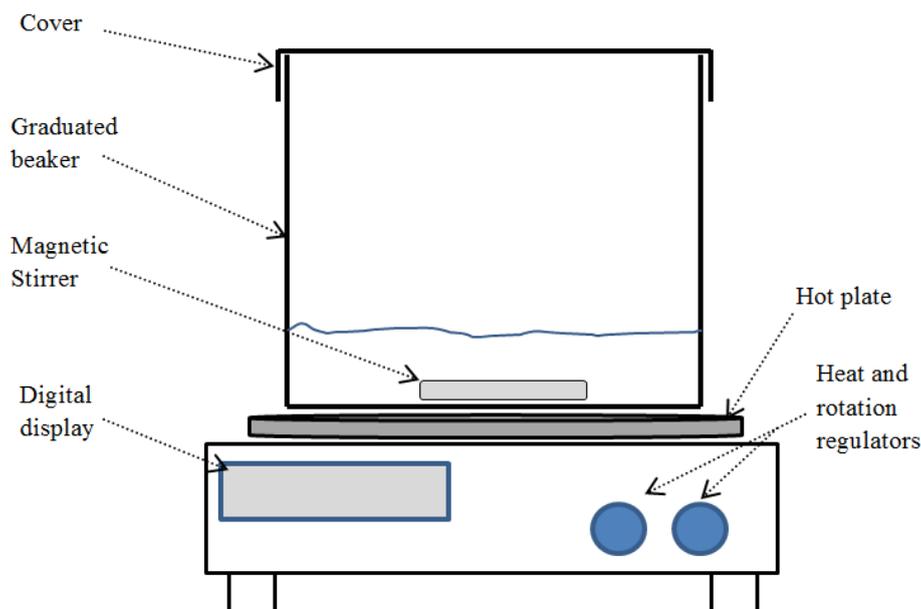
The third experiment was undertaken using covered beakers and the mixing process was performed for one hour at room temperature. The mixture was then left at room temperature for 24 hours before being placed in the centrifuge. Two layers were separated, a clear reddish lubricant oil layer and sludge at the bottom of the test tube. The lube oil separated from the sludge easily because the sludge was concentrated at the end of the test tubes. Both the lube oil and the sludge were weighed. In order to measure the weight of the sludge, the test tube was heated and then the sludge was removed from the tube using pieces of cotton. The cotton has been weighed in advance and the cotton with the sludge was dried in an oven (Memmert, UF110, Schwabach, Germany) at 50 °C for 24 hours. After drying, the weight of the sludge was confirmed to be 0.2 to 0.4 gm/10 gm sample of the used oil. The balance used in weighing is from Denver Instrument (Denver, S/SI-603, Denver, CO, USA).

The results indicated that the amount of sludge increased as the amount of acid added to the samples increased, up to a certain limit. Up to the 1.0 mL acid added/10 mL used oil the sludge collected was black in color, rigid and compacted in a small area in the bottom of the test tube after the centrifugation process. The sludge changed significantly after increasing the acid volume above 1.0 mL/10 mL used oil. The sludge became more like an emulsion and yellow in color, and it also occupied a quarter of the test tube. The experiments done with the first kind of the lubricant oil (the oil collected from the shops) were repeated for the second kind, personal cars lubricant oils of the Ravenol brand (VSi SAE 5W-40) collected after being in use for 3000 to 3500 km. The treatment procedure performed was similar to that applied for the oil collected from the shops. The experiments carried out using the used oil from personal cars gave better results regarding the clarity compared to the treated used oil collected from the oil-change shops. It worth noting that the oil-change shops in Koya city collect used oil from both compression ignition (CI) and spark ignition (SI) engines crankcases.

## 2.2. Experimental Procedures

Used cars lubricant oils have been collected from car oil-change shops in Koya city/Erbil-Iraq and personal cars after being in use for 3000 to 3500 km. These oils were collected in containers of 20 L each and then after mixing well by hand shaking for 15 min they were subdivided into smaller containers of 5 liters.

The recycling process started with removing the contamination from the used engine oil. Glacial acetic acid was mixed with the used engine oil using a ratio of 0.8 mL acetic acid to 10 mL used engine oil. This was followed by stirring in a closed container at room conditions (room temperature and pressure) for one hour. The mixture was left for 24 hours at room conditions and then underwent centrifugation for one hour to separate the base oil from the contaminants. The separated base oil was then mixed with kaolinite at a ratio of 1 mL oil to 4 g kaolinite. The kaolinite was added to remove the dark color and the smell which result from oxidation of some components in the oil. This was achieved by heating to a temperature slightly higher than 250 °C, followed by centrifugation for 30 min. This process produced a yellow clear base oil and an amount of sludge very close to the initial weight of the kaolinite used plus 5 wt%. The sludge measurement followed the same procedure in Section 2.1. Figure 1 below illustrates the schematic diagram of the test rig used in carrying out the experiments.

**Figure 1.** Schematic diagram of the test rig.

The second step in the recycling process was measuring the chemical and the physical properties of the resulting materials by performing oil analysis (OA). The materials that have undergone analysis are: the base engine oil produced by the acetic acid-clay method, base oil produced by local companies in Kurdistan region using the sulfuric acid-clay method, base oil resulting from vacuum distillation-clay treatment, base oils (Ravenol, VSi SAE 5W-40), used engine oil and the by-product (sludge).

Oil analyses (OA) is the laboratory analysis of the engine oils' physical and chemical properties, suspended contaminants and wear debris. Oil analysis is performed during routine preventive maintenance to provide meaningful and accurate information on lubricant and machine condition. By tracking oil analysis sample results over the life of a particular machine, trends can be established which can help eliminate costly repairs. Oil analysis can be divided into three categories:

- Analysis of oil physical and chemical properties including tests such as: Flash Points by Cleveland Open Cup Tester ASTM D 92 [19], Pour Point ASTM D 97 [20], Viscosity Index ASTM D 2270 [21], Water and Sediment ASTM D 4007 [22], Rams bottom Carbon Residue ASTM D 524 [23], Total acid number (TAN) ASTM D 664 [24], Total Base Number (TBN) ASTM D 4739 [25], Refractive Index ASTM D 1218 [26], and Density (Specific Gravity) ASTM D 1298 [27].
- Analysis of metallic contained by atomic absorption spectrometer (AAS).
- Analysis of oxidative components by a Fourier Transform Infrared Spectrometer (Thermo Scientific, Thermo Mattson Nicolet 300-FTIR). The carbonyl groups have absorption peaks in the range of  $1700$  to  $1750\text{ cm}^{-1}$ .

The metallic content analysis was performed by atomic absorption spectrometry using a fast sequential atomic absorption spectrometer (Varian, AA280 FS). Before the analysis the used engine oil sample was heated to  $60\text{ }^{\circ}\text{C}$  and stirred to ensure homogeneity of the sample, it was then mixed with 10 volumes of kerosene [28]. Sets of organometallic standards of metal (Zn, Cd, Cu, Fe, Ca, Pb, Sn, Mg and Mn) 4-cyclohexylbutyric acid salts were prepared and metal concentrations were determined

by introducing the test solutions of engine oil samples into the flame of the atomic absorption spectrophotometer and recording the responses. Metal concentrations were determined from the calibration curve that was obtained from standard solutions. Standard solutions for all metals in engine oil samples were prepared according to Varian Techtron Pty LTD and ASTM D 4628-2 [29,30].

The specification of the apparatus used to carry out the experiments and the oil analysis are presented in Table 1.

**Table 1.** Specifications of the apparatus used in the experiments.

Apparatus	Type	Model	Specifications
Scale	Denver	S/SI-603	Scale range: 0–600 g, readability: 0.001 g and accuracy: 0.002 g
Oven	Memmert	UF110	Forced air circulation, resolution of display for set point values 0.1 °C up to 99.9 °C, 0.5 °C from 100 °C to 300 °C, dimension (w × h × d): 560 × 480 × 400 mm
Hot plate	LabTech	ES35A-Pro	Speed range: 0–1500 rpm, heating rate 6 K/min, heating temp. Range: ambient to 340 °C, dimension: 280 × 160 × 85 mm, display: analog scale.
Centrifuge	Sigma	2-6	Speed pre-selection up to 4000 rpm, low speed operation from 100 rpm, stainless steel bowl
Atomic Absorber spectrometer (AAS)	Varian	AA280 FS	Flame AA instrument, PC-controlled, double-beam Atomic Absorption spectrometer with Fast Sequential operation.
Fourier transform Infrared spectrometer (FT-IR)	Thermo Scientific	Thermo Mattson Nicolet 300-FTIR	FTIR machine equally handles solids and liquids

### 3. Results and Discussion

#### 3.1. Physical and Chemical Properties

##### 3.1.1. Flash Point

The flash point of an engine oil is the lowest temperature to which the oil must be heated under specified conditions to give off sufficient vapor to form a mixture with air that can be ignited spontaneously by a specified flame. The flash point of engine oil is an indication of the oil's contamination. A substantially low flash point of an engine oil is a reliable indicator that the oil has become contaminated with volatile products such as gasoline. In the presence of 3.5% fuel or greater in used engine oils the flash point will potentially reduce to below 55 °C. The flash point is also an aid in establishing the identity of a particular petroleum product. The flash point increases with increasing molecular mass of the oil. Oxidation would result in formation of volatile components which leads to decrease the flash point. [31]. Table 2 shows flash point values of different samples. The flash point of the base oil (Ravenol, VSi SAE 5W-40) is 232 °C because it contains many different additives which contribute to improving its flash point. In contrast, the flash point of the measured used engine

oil is 158 °C. This decrease in flash point is a result of contamination with fuel and oxidation products [31]. On one hand, the table clearly shows that the flash point of the base oil is highly affected by adding sulfuric acid (185 °C, row 9). On the other hand it is slightly affected by adding acetic acid (210 °C, row 10) which indicates the destructive and complex effect of sulfuric acid even on the virgin oil. The flash point of the base oil produced using acetic acid treatment combined with vacuum distillation (220 °C, row 4) is giving comparable results to that produced by professional companies using sulfuric acid (222 °C, row 2) and the marketed base oil (232 °C, row 1). The comparable results between the flash points of the two recycling methods are clearly showing the ability of glacial acetic acid to restore the used engine oil.

**Table 2.** Analysis of results of physical and chemical properties of different oil samples.

No	Samples	Flash point °C	Pour point °C	Kinematic viscosity@ (40 °C)	Kinematic viscosity@ (100 °C)	Viscosity index	Refractive index	Specific gravity
1	Base engine oil (Ravenol, VSi SAE 5W-40)	232	−13	195.62	18	100.27	1.4886	0.8818
2	Marketed engine oil Recycled from used engine oil by professional recycling companies using acid (H <sub>2</sub> SO <sub>4</sub> ) clay method and evaporation after adding the required additives	222	−10	169.5	16	97.07	1.4869	0.8828
3	Used engine oil (being in use for 2000–3000 km)	158	−5	136.6	13.5	89.11	1.4763	0.9261
4	Oil resulting from recycling the used engine oil by acetic acid (adding CH <sub>3</sub> COOH + mixing + clay treatment + centrifugation) + vacuum distillation	220	−9.8	61.5	7.8	89.00	1.4833	0.8697
5	Oil resulting from recycling the used engine oil by acetic acid (adding CH <sub>3</sub> COOH + mixing + clay treatment + centrifugation)	190	−9	80.25	8.5	82.47	1.4812	0.8768
6	Oil resulting from recycling the used engine oil by sulfuric acid (adding H <sub>2</sub> SO <sub>4</sub> + mixing + clay treatment + centrifugation)	200	−9	72.5	9	84.45	1.4822	0.8707

Table 2. Cont.

No	Samples	Flash point °C	Pour point °C	Kinematic viscosity@ (40 °C)	Kinematic viscosity@ (100 °C)	Viscosity index	Refractive index	Specific gravity
7	Oil resulting from pretreatment of the used engine oil by acetic acid (adding CH <sub>3</sub> COOH + mixing + centrifugation)	165	−8	130.5	13	91.84	1.4812	0.8838
8	Oil resulting from pretreatment of the used engine oil by sulfuric acid (adding H <sub>2</sub> SO <sub>4</sub> + mixing + centrifugation)	180	−7	120	12	95.22	1.4785	0.8707
9	Oil resulting from mixing the base engine oil with acetic acid (adding CH <sub>3</sub> COOH + mixing)	210	−11.8	182.7	15.6	89.18	1.4865	0.8717
10	Oil resulting from mixing the base engine oil with sulfuric acid (adding H <sub>2</sub> SO <sub>4</sub> + mixing)	185	−9.5	175.6	7.8	89.30	1.4786	0.8707

### 3.1.2. Pour Point

The pour point of an engine oil is the lowest temperature at which the oil will remain in a flowing state. Most engine base oils contain waxes and paraffins that solidify at cold temperatures. Engine oils with high wax and paraffin content will have a higher pour point. Pour point is highly affected by an oil's viscosity, and engine oils with high viscosity are characterized by having high pour points. The pour point of an engine oil is an important variable, especially when starting the engine in cold weather. The oil must have the ability to flow into the oil pump and then be pumped to the various part of the engine, even at low temperatures [32]. Table 2 shows the pour point values of different samples. Acids are added to the base oil to examine their effect on the oil's composition. The pour point of the base oil was not notably affected by the addition of acetic acid. There was a small change in the pour point of around 1.2 °C, but this value rose to 3.5 °C when sulfuric acid was added. It is also obvious that recycling the used oil with acetic acid combined with a vacuum distillation gave remarkable results (−9.8 °C) and it is very comparable to the oil recycled using the acid-clay method (−10 °C). The result of the acetic acid method is before adding the required additives to the oil. It is important to mention that the oil treated by acid-clay method before introducing the required additives only measures a pour point of −9 °C (row 6).

### 3.1.3. Kinematic Viscosities

Viscosity is a state function of temperature, pressure and density. There is an inverse relationship between viscosity and temperature, when the temperature of the engine oil decreases the viscosity

increases and *vice versa*. Viscosity testing can indicate the presence of contamination in used engine oil. The oxidized and polymerized products dissolved and suspended in the oil may cause an increase of the oil viscosity, while decreases in the viscosity of engine oils indicate fuel contamination [33]. Oxidation of base oils during use in an engine environment produces corrosive oxidized products, deposits, and varnishes which lead to an increase in the viscosity [33]. Kinematic viscosity for different samples at two temperatures is shown in Table 2. The same viscosity test results have been predicted when acetic acid is added to the base oil at 40 and 100 °C. Kinematic viscosity at 40 °C was slightly affected by the addition of acetic acid to the base oil (182.7 cSt). The same result was predicted at 100 °C. The base oil lost only 13% of its original kinematic viscosity value. However, while the kinematic viscosity of the base oil was not greatly affected by the addition of sulfuric acid at 40 °C, it lost more than 50% of its value at 100 °C. These results show the destructive effect of sulfuric acid on the oil. It would appear that recycling the used oil with acetic acid (row 5) or sulfuric acid (row 6) is giving very comparable results at both temperatures (40 °C and 100 °C). The results of recycling with both methods reduced the kinematic viscosity of the used oil from 13.5 to 8.5 and 9 cSt, respectively. This means that the two methods are effective in removing the oxidized products, deposits, and varnishes from the used oil [33]. This may also mean removing the additives which have been added to enhance the viscosity.

#### 3.1.4. Viscosity Index

Viscosity Index is strictly an empirical number and indicates the effect of change in temperature on viscosity. A high viscosity index indicates a small change in viscosity with temperature, which also means better protection of an engine that operates under vast temperature variations. Viscosity index improvers is among the common additives that improve the efficiency of the oil, however, engine oil with a high addition level of viscosity index improvers tends to degrade more rapidly. A high viscosity index is due to the absence of aromatic and volatile compounds. It also means good thermal stability and low temperature flow behaviors [34]. Table 2 shows very similar effects of both acids on the viscosity index when added to the base oil. The table shows that the viscosity index of the recycled used oil with acetic acid 89.00 (row 4) deviated slightly from that of the used oil 89.11 (row 3). This clearly indicates the low destructive effect acetic acid has on the viscosity index improver additives. It also seems that clay treatment contributes to a reduction in the viscosity index by approximately 10%, reduced from 91.84 (row 7) to 82.47 (row 5).

#### 3.1.5. Refractive Index

Refractive index (RI) is the ratio of the light velocity in vacuum to the light velocity in substances at a specific temperature. The measurement of the refractive index is very simple, and requires small quantities of the samples. The refractive index can be used to provide valuable information about the composition of engine oils. Low values of refractive index indicate the presence of paraffin material while high values indicate the presence of aromatic compounds. It is also used to estimate other physical properties such as molecular mass [35]. Table 2 shows a base oil refractive index value of 1.4886. This is due to the presence of additives like polymers, polar organic compound, organic compounds, different metals, copolymers of olefins and hydrogenated diene styrene copolymers [35]. These components increase the molecular mass of the base oil and consequently its refractive

index [35]. The results also indicate the low destructive action of the acetic acid, mixing the base oil with this acid reduces the RI by a small fraction of around 0.2%. In contrast, the addition of sulfuric acid reduces the RI by 0.7%. The same results are predicted after the recycling of the used engine oil with acetic acid and sulfuric acid.

### 3.1.6. Density (Specific Gravity)

Specific gravity is the ratio of the mass of volume of substance to the mass of the same volume of water and depends on two temperatures, at which the mass of the sample and the water are measured. Specific gravity is influenced by the chemical composition of the oil. An increase in the amount of aromatic compounds in the oil results in an increase in the specific gravity, while an increase in the saturated compounds results in a decrease in the specific gravity. An approximate correlation exists between the specific gravity, sulfur content, carbon residues, viscosity and nitrogen content [36]. Used engine oils specific gravity increases with the presence of increasing amounts of solids in the used engine oil. One percent of weight of solids in the sample can raise the specific gravity by 0.007 [36]. Used engine oil is contaminated with oxidized and condensed products rich in carbon. As shown in Table 2, base oil has a specific gravity of 0.8818, which is low compared to the used engine oil specific gravity of 0.9261. The high value of specific gravity of used engine oil is due to the presence of oxidation products, metals and contamination. Both acids have almost the same effect on the specific gravity when added to the base oil. The oil's specific gravity resulted from treatment by acetic acid combined with a vacuum distillation (0.8697) which is quite good compared to the virgin oil (0.8818), however this is before the introduction of the required additives to the recycled oil.

### 3.2. Water and Sediments

Water is generally referred to as a chemical contamination when suspended in engine oils. Water contamination of engine oil affects the oil quality, condition and wear of engines in service. The water content in engine oil is governed by the oil composition, physicochemical properties, production technology and conditions of storage and use. Water created in engine oil is a result of: absorbing moisture directly from the air (oil is hygroscopic), condensation (humid air entering oil compartments), heat exchanger (corroded or leaky heat exchangers), combustion (fuel combustion forms water which may enter the lubricant oil through worn rings), oxidation (chemical reaction) and neutralization (when alkalinity improvers neutralize acids formed during combustion), and free water entry (during oil changes). Water can prompt a host of chemical reactions such as hydrolysis of compounds and atomic species including oil additives base stock and suspended contaminants. In combination with oxygen, heat and metal catalyst, water is known to promote the oxidation and the formation of free radicals and peroxide compounds. Water attacks additives such as oxidation inhibitors, rust inhibitor, viscosity improver and the oil's base stock forming sludge. The water and sediment content of engine oil is significant because it can cause corrosion of equipment and problems in processing [37]. As shown in Table 3, base oil has water and sediment content values of zero due to the dehydration steps involved in producing base oils. In addition, introducing additives to the oil is minimizing the ratio of water and sediment to zero or near zero. It is obvious from the table that adding sulfuric acid to the virgin oil leads to different results to those seen when adding acetic acid. Water and sediments content of the

base oil after adding the sulfuric acid is 0.6 mL/25 mL sample, compared to adding acetic acid <0.01 mL/25 mL sample. This clearly states the high reactivity of sulfuric acid with the materials that form the oil, one reaction being oxidation. The sulfuric acid-clay treatment shows a water content of <0.01 mL/25 mL sample because this method involves evaporation of the oil for more than one hour which helps in reducing the water content to this level. The same result as the sulfuric acid-clay method was achieved when adding acetic acid combined with vacuum distillation.

### 3.3. Carbon Residue

The amount of carbonaceous residue remaining after thermal decomposition of engine oil in a limited amount of air is also called coke or carbon forming tendency. The test for carbon residue can be used at the same time to evaluate the carbonaceous depositing characteristics of engine oils used in internal combustion engines. The carbon residue value of engine oil is regarded as indicative of the amount of carbonaceous deposits engine oil would form in the combustion chamber of an engine. It is now considered to be of doubtful significance due to the presence of additives in many oils. For example, an ash-forming detergent additive can increase the carbon residue value of engine oil yet will generally reduce its tendency to form deposits [38]. The carbon residue in base oil produced from raw petroleum materials is 0.55 wt%, which is 0.27 wt% lower than that produced by the recycling of used oil by the sulfuric acid-clay method, as shown in Table 3. This may be due to the complex reactions of the oil's components with sulfuric acid which may increase the sulfur content of the oil. A more precise relationship between carbon residue and hydrogen content, (H=C) atomic ratio, nitrogen and sulfur content have been shown to exist [38]. The recycling of the used oil by acetic acid combined with a vacuum distillation appears to provide better results. The carbon residue of this oil is slightly higher by 0.04 wt% than the base oil. As shown in the table, adding acetic acid to the base oil has increased the carbon residue by only 0.08 wt%. In contrast, adding sulfuric acid led to a greater increase in the carbon residue by 0.69 wt%. This clearly indicates the formation of components that have direct influence on the carbon residue of the oil.

### 3.4. Total Acid Number (TAN)

Total Acid number (TAN) is the weight (in milligrams) of potassium hydroxide required to neutralize one gram of the materials in the oil that will react with (KOH) under specific test conditions. The usual major components of such materials are organic acids, soaps of heavy metals. As engine oils are subjected to elevated temperatures, the process of oxidation occurs. Oxidation leads to the formation of organic acids in the engine oil. Total acid number (TAN) has been considered to be an important indicator for engine oil quality, specifically in terms of defining oxidation states. The presence of oxygen, in most engine oils environments, and hydrocarbons which make up the base oil lead to some reactions. This reaction may lead to the formation of carbonyl-containing products (primary oxidation products), subsequently these undergo further oxidation to produce carboxylic acids (secondary products) which results in an increase in the TAN value [39]. In addition, with time and elevated temperature, the oxidation products formed then polymerize leading to precipitation of sludge which decreases the efficiency of engine oil and causes excessive wear [39]. As shown in Table 3, the TAN of the used engine oil is measured to be 4.5 mg (KOH)/g (sample) which is much higher than

the TAN of the base oils [0.02 mg (KOH)/g (sample)]. This is due to the presence of organic, inorganic, heavy metal salts, ammonia slots, resin, water and corrosive materials which result from the oxidation process that occurred at elevated temperatures in the engine [39]. The addition of sulfuric acid to the base oil has increased the TAN by 1 mg (KOH)/g (sample) compared to addition of acetic acid. It has been interpreted that the low acidity of the used oil when recycled with sulfuric acid is mostly due to the evaporation stage and clay processing rather than the acid action. The recycled oil by sulfuric acid without these two processes (row 8) is high in TAN around 2 mg (KOH)/g (sample).

**Table 3.** Analysis results of sediments and acidity of different samples.

No.	Samples	Water and Sediment (mL)	Carbon residue (Wt %)	(TAN) mg KOH/g(sample)	(TBN) mg KOH/g(sample)
1	Base engine oil (Ravenol, VSi SAE 5W-40)	Zero	0.55	0.02	3.55
2	Marketed engine oil. Recycled from used engine oil by professional recycling companies using acid (H <sub>2</sub> SO <sub>4</sub> ) clay method and steaming after adding the required additives	<0.02	0.82	0.14	2.8
3	Used engine oil (being in use for 2000–3000 km)	0.9	1.82	4.5	0.11
4	Oil resulting from recycling the used engine oil by acetic acid (adding CH <sub>3</sub> COOH + mixing + clay treatment + centrifugation) + vacuum distillation	<0.01	0.59	0.15	-
5	Oil resulting from recycling the used engine oil by acetic acid (adding CH <sub>3</sub> COOH + mixing + clay treatment + centrifugation)	<0.01	0.88	0.56	-
6	Oil resulting from recycling the used engine oil by sulfuric acid (adding H <sub>2</sub> SO <sub>4</sub> + mixing + clay treatment + centrifugation)	<0.01	0.99	0.7	-
7	Oil resulting from pretreatment of the used engine oil by acetic acid (adding CH <sub>3</sub> COOH + mixing + centrifugation)	0.013	1.65	1.8	-
8	Oil resulting from pretreatment of the used engine oil by sulfuric acid (adding H <sub>2</sub> SO <sub>4</sub> + mixing + centrifugation)	0.8	1.07	2	-
9	Oil resulting from mixing the base engine oil with acetic acid (adding CH <sub>3</sub> COOH + mixing)	<0.01	0.62	1.5	2.5
10	Oil resulting from mixing the base engine oil with sulfuric acid (adding H <sub>2</sub> SO <sub>4</sub> + mixing)	0.6	1.23	2.6	0.5

### 3.5. Total Base Number (TBN)

Internal combustion engine oils are formulated with a highly alkaline base additives package to neutralize the acidic products composition. The TBN is a measure of this package and it may be used as an indication for the engine oil's replacement time. This is because TBN depletes with time in service. Higher oil TBN values are more effective at neutralizing acids for longer periods of time. The rate of consumption of the additives is an indication of the projected service life of the oil [40]. As shown in Table 3 adding acetic acid to the base oil causes a small decline in the alkalinity of the oil from 3.55 to 2.5 mg KOH/g (sample). In contrast, adding sulfuric acid has reduced the alkalinity of the base oil by 96%. It is also obvious that the alkalinity is a result of the additives because the used oil's

alkalinity is only 0.11 mg KOH/g (sample). TBN values for base oil (row 1) and that recycled using the sulfuric acid method (row 2) are 3.55 mg KOH/g (sample) and 2.8 mg KOH/g (sample), respectively. These values show higher TBN values than the TBN value of used engine oil [0.11 mg KOH/g (sample)]. This is due to the presence of a high alkaline additive package that was not depleted and has the ability to neutralize large quantity of acids, organic, inorganic bases including amino compounds and certain salts of heavy metals [40]. Used oil's TBN is low due to the depletion of the additive package as a result of the high temperature and the acid effect of water and oxidant product contamination. Base oil mixed with glacial acetic acid and concentrated 98% H<sub>2</sub>SO<sub>4</sub> have TBN values 2.5 mg KOH/g (sample) and 0.5 mg KOH/g (sample), respectively. This clearly illustrates the lower effect of acetic acid on the oil's components.

### 3.6. Engine Oil's Metallic Content

Metals are regarded as heteroatoms found in engine oil mixtures. The amounts of metals are in range of a few hundred to thousands of ppm and their amounts increase with an increase in the boiling points or decrease in the API gravity of the engine oil. Engine oils' metallic constituents are associated with heavy compounds and they mainly appear in the residues. Base and base engine oils have very little metal content, which indicates their purity. Some metals present in virgin oils in high concentrations are in the form of various additives which improve the performance of the engine oil. Many others are introduced in to the oils after using due to depletion of various additives, engine bearings or bushings, and dilution of the engine oil with fuel containing metal additives [41]. Metals are found in used engine oil in two forms:

- Metal particulate contamination

Metallic particulates enter the engine oil as a consequence of the breakdown of oil-wetted surfaces due to ineffective lubrication, mechanical working, abrasion erosion and/or corrosion. Metallic particles from deteriorating component surfaces are generally hard and increase the wear rate as their concentration in the oil increases.

- Elemental (Metals)

Many oil constituents contain metallic elements that have been added to enhance the oil's efficiency. In general, metals in engine oils regarded as contaminants that should be removed completely in order to produce suitable base oil for producing new virgin oil [42]. Copper (Cu) is introduced to engine oils after use from bearings, wearing and valve guides. Engine oil coolers can also be contributing to copper content along with some oil additives [43]. The recycled oil with acetic acid combined with a vacuum distillation has a copper concentration of 0.4 ppm compared to zero ppm in oil recycled by sulfuric acid as shown in Table 4. This is because sulfuric acid is more reactive with copper than acetic acid and forms a precipitate. Magnesium is normally introduced into engine oil in an additive package. Magnesium is regarded as the most common wear metals in used engine oil and is present in virgin oil in the form of magnesium phenates and magnesium salicylates that behave as antioxidants at high temperatures [44]. Table 4 shows that the concentration of magnesium (Mg) in the base oil was affected more when sulfuric acid was added compared to acetic acid. This is again is due to the reactivity of sulfuric acid with the Mg, which may lead to precipitated compounds. Chromium

presence in engine oil is normally associated with piston ring wear. High levels can be caused by dirt coming through the air intake or broken rings. Chromium may indicate excessive wear of chromed parts such as rings and liners [45]. As Table 4 is showing, the amount of chromium is very low, even in the used oil because this metal is persisting only in some parts of the engine. The recycling with acetic acid combined with a vacuum distillation seems to reduce the amount of this metal from 1.5 ppm to 0.2 ppm. The same result is shown in Table 4 in regards to tin. Tin is introduced into the oil after use from piston wear, certain shaft types, bearings or bushings and valve guides [46]. Tin must be removed completely from base oils because it is regarded as a contaminant. Lead (Pb) is associated with bearing wear, fuel source (leaded gasoline), and contamination due to the use of galvanized containers [47]. Lead concentration in virgin oils is zero because it is regarded as a base oil contaminant. Used engine oil has a lead concentration of 14.6 ppm as shown in Table 4. This is due to dilution of the engine oil by leaded gasoline that has been treated with tetraethyl lead as anti-knocking and engine part wear. The recycling with acetic acid combined with a vacuum distillation is very active in removing this metal. It helped to reduce the used oil content of this metal from 14.6 to 0.4 ppm. The most common wear metal in a car's engine that is introduced into the engine oil after a period of use is iron. Iron comes from many various places in the engine such as liners, camshafts and crank shaft, pistons, gears, rings, and oil pump. Iron concentration in engine oil depends on the bearing conditions inside the engine. If a bearing fails, iron concentrations in used engine oil increases. In the engine, the wear rises at a faster rate during the starting of the engine [48]. Base oils must be free from iron completely because it participates in producing oxidation products due to different chemical reactions. It is also clear that recycling with acetic acid combined with a vacuum distillation is very efficient in completely removing the metal. Zinc is introduced to base oil in the form of additives package as anti-oxidant, corrosion inhibitor, anti-wear, detergent and extreme pressure tolerance. Zinc is introduced in to base oil as additives, such as [49]:

- Zinc diethyldithiophosphate (ZDDP), which functions as an oxidation inhibitor that increases the oxidation resistance of the oil.
- Zinc dithiophosphates, this is not only acts as an anti-oxidant, but also acts as a wear inhibitor and protects the engine metals against corrosion.
- Zinc dialkyldithiocarbamates, this compound is mainly used as anti-oxidants but it is also has extreme pressure activity.

Zinc concentration in the base oil is 1,200 ppm, as shown in Table 4. This is added to the base oils as part of multi-functional additives for improving the oils' performance. The used engine oil content of zinc is 1280 ppm. The increase in the zinc concentration in used engine oil results from wearing of the galvanized piping. Adding sulfuric acid to the base oil leads to the reduction in zinc content by 28% compared to 11% with acetic acid. Sulfuric acid reacts with zinc to produce precipitated compounds. Manganese (Mn) is introduced from wear of cylinder liners, valves, and shafts [50]. As shown in Table 4 only a small amount of manganese is present in the used engine oil. Recycling with acetic acid combined with vacuum distillation is very effective in complete removal of this metal. Cadmium (Cd) is introduced in the engine oil as a contaminant during use. Base oils are free from cadmium [51]. It is clear from Table 4 that cadmium only has a count of 1 ppm in the used oil and it can be completely removed by acetic acid treatment.

**Table 4.** Analysis results of metal content of different samples.

No.	Samples	Cu (ppm)	Mg (ppm)	Cr (ppm)	Sn (ppm)	Pb (ppm)	Fe (ppm)	Zn (ppm)	Mn (ppm)	Cd (ppm)
1	Base engine oil (Ravenol, VSi SAE 5W-40)	0	72	0	0	0	0	1200	0	0
2	Marketed engine oil. Recycled from used engine oil by professional recycling companies using acid ( $H_2SO_4$ ) clay method after adding the required additives	0	68	0	0	0	0	1050	0	0
3	Used engine oil (being in use for 2000–3000 km)	4.6	81	1.5	1.6	14.6	72	1280	1.5	1
4	Oil resulting from recycling the used engine oil by acetic acid (adding $CH_3COOH$ + mixing + clay treatment + centrifugation) + vacuum distillation	0.4	0.8	0.2	0.2	0.4	0	41	0	0
5	Oil resulting from recycling the used engine oil by acetic acid (adding $CH_3COOH$ + mixing + clay treatment + centrifugation)	1.6	3.2	0.7	0.7	3.2	3.2	81.6	0.5	0.4
6	Oil resulting from recycling the used engine oil by sulfuric acid (adding $H_2SO_4$ + mixing + clay treatment + centrifugation)	0.9	2	0.4	0.6	4.5	1.2	54	0.2	0.1
7	Oil resulting from pretreatment of the used engine oil by acetic acid (adding $CH_3COOH$ + mixing + centrifugation)	3.56	65	0.8	0.9	11.2	34	780	0.8	0.45
8	Oil resulting from pretreatment of the used engine oil by sulfuric acid (adding $H_2SO_4$ + mixing + centrifugation)	2.1	45	0.5	0.6	5.4	24.4	613	0.4	0.2
9	Oil resulting from mixing the base engine oil with acetic acid (adding $CH_3COOH$ + mixing)	0	65	0	0	0	0	1076	0	0
10	Oil resulting from mixing the base engine oil with sulfuric acid (adding $H_2SO_4$ + mixing)	0	57	0	0	0	0	865	0	0

Atomic Absorption Spectrometry (AAS) was used to measure the metals traces in the oil. The detection limits of the metals presented in Table 4 are shown in Table 5. It is obvious that the metals traces measured are far above the detection limit of the Atomic Absorption Spectrometry (AAS) used in the analysis.

**Table 5.** Detection limits of the AAS.

Element	Symbol	Detection Limit (ppm)
Copper	Cu	0.003
Magnesium	Mg	0.0003
Chromium	Cr	0.006
Tin	Sn	0.1
Lead	Pb	0.01
Iron	Fe	0.006
Zinc	Zn	0.001
Manganese	Mn	0.002
Cadmium	Cd	0.002

### 3.7. Sludge Analysis

A secondary oxidation phase occurs at high temperatures where the viscosity of the bulk medium increases as a result of the polycondensation of the difunctional oxygenated products formed in the primary oxidation phase such as carboxylic acids. Further polycondensation and polymerization reactions of these high molecular weight intermediates form products which are no longer soluble in the hydrocarbon. The resulting precipitate is called sludge. Under thin-film oxidation conditions, as in the case of a lubricant film on a metal surface, varnish-like deposits are formed. The polycondensation reactions lead to high molecular weight intermediates (sludge precursors) [52].

The sludge produced has been analyzed for metals content. The analysis was done for the sludge collected from three resources; sludge resulting from centrifugation of the used oil directly before carrying out any further treatment (column three), after treatment with sulfuric acid-clay and after treatment with acetic acid-clay. The sludge collected from direct centrifugation was very low in quantity due to failure of centrifugation alone to precipitate contaminant in the used oil. As shown in Table 6, the sludge resulting from acetic acid-clay treatment is richer in metals than the one treated with the sulfuric acid-clay method. This high content of metals explains the lower losses in the sludge weight (~70%) when heated to 800 °C for three hours compared to sulfuric acid-clay method (~95%). This confirms the ability of acetic acid to precipitate the metal content in the used oil by 25% more than the sulfuric acid method.

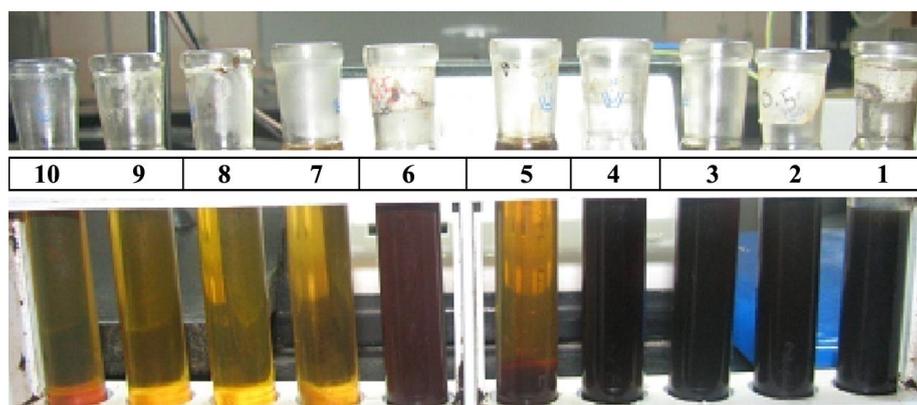
**Table 6.** Analysis results of the sludge.

Samples	Sludge Analysis		
	Sludge resulted from acid-clay method + centrifugation	Sludge resulted from acetic acid-clay method + centrifugation	Sludge resulted from used oil
Losing in ignition at 800 °C for 3 hours %	94.714	69.9417	95.448
Na	0.170	0.79	0.223
Cu	0.28	Nil	Nil
Pb	1.11	1.17	0.0736
Ag	Nil	Nil	Nil
Ni	0.058	0.64	Nil
Mg	0.28	3.74	Nil
V	Nil	Nil	Nil
Mo	1.33	1.91	Nil
Al	Nil	0.44	Nil
Sn	Nil	Nil	Nil
Ti	Nil	Nil	Nil
Ca	1.31	2.23	1.28
Ba	Nil	Nil	Nil
Cr	0.811	9.3	0.9655
SiO <sub>2</sub>	Nil	8.2	Nil
Total	99.5674	99.5217	98.0111

3.8. Color

Different categories of the engine oil were pictured to show the color changes that the oil went through during the process. As shown in Figure 2 and Table 7, the base oil (column 9) has changed color and become highly opaque (column 6) due to the vigorous reaction with sulfuric acid. In contrast, the base oil did not show any change in color when mixed with acetic acid (column 7) due to its low reactivity of acetic acid with the base oil. The acetic acid has shown a high reactivity with the contaminants in the used oil, and columns 5 and 8 show the base oil results from treatment with sulfuric acid and acetic acid, respectively. It is obvious that the base oil resulting from acetic acid treatment is brighter and has a clear yellowish color.

**Figure 2.** Pictures of the engine oil samples as described in Table 7.



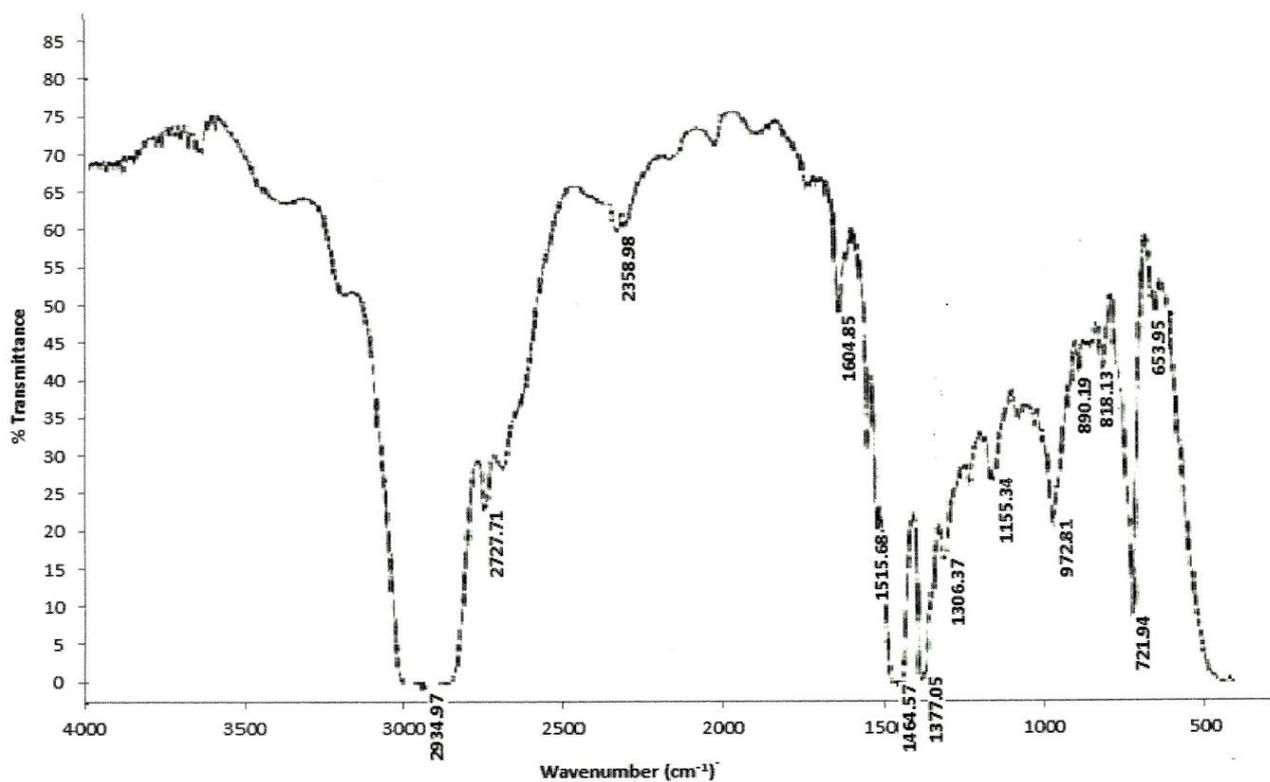
**Table 7.** Description of the engine oil samples in Figure 2.

No.	Description
1	Used engine oil
2	Used engine oil after centrifugation only
3	Used engine oil treated with sulfuric acid after mixing for 1 hour
4	Used engine oil treated with glacial acetic acid after mixing for 1 hour
5	Base oil produced by using sulfuric acid
6	Base oil (Ravinol type) + concentrated H <sub>2</sub> SO <sub>4</sub> + mixing for 1 hour
7	Base oil (Ravinol type) + glacial acetic acid + mixing for 1 hour
8	Base oil produced by using glacial acetic acid
9	Base oil (Ravinol type)
10	Base oil produced by vacuum distillation and clay treatment

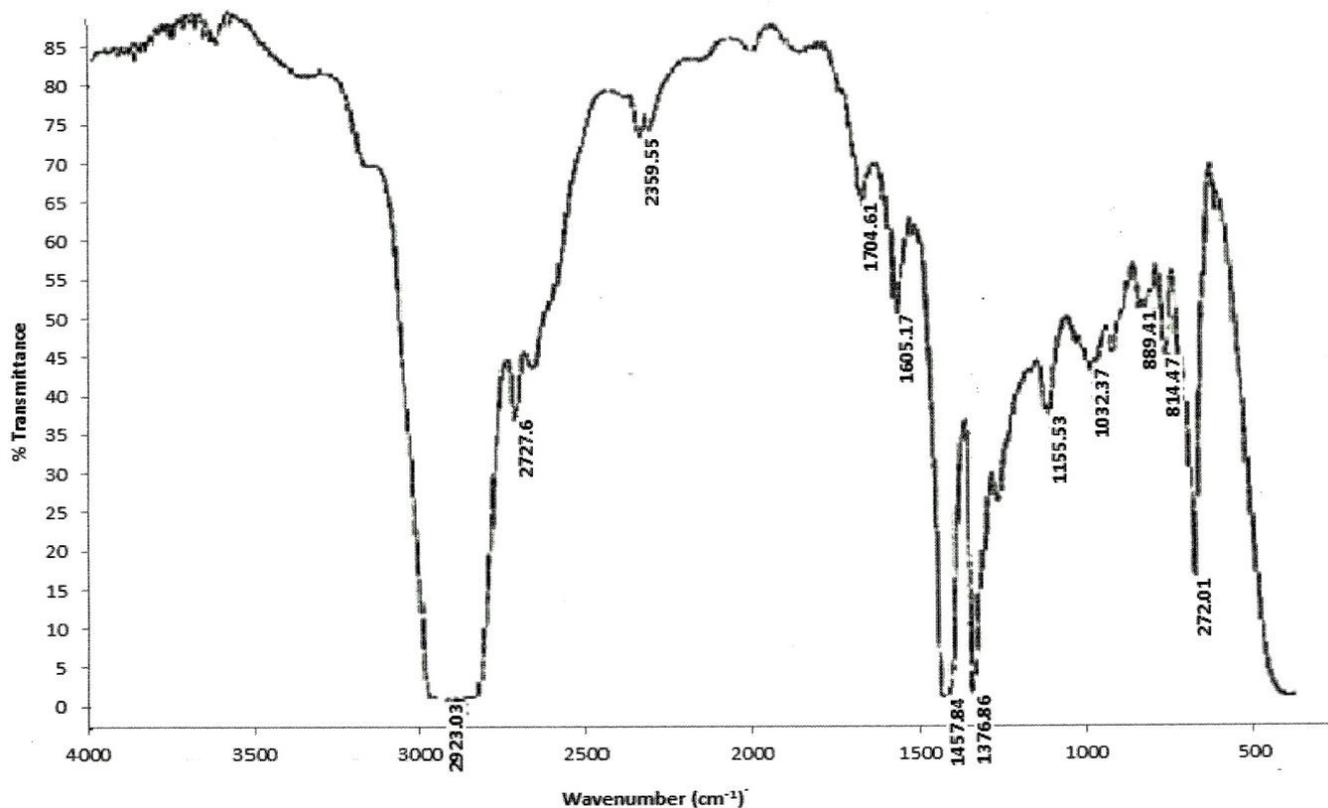
### 3.9. Engine Oil Oxidation Products Analysis

Oxidation of engine oil inside the engine is related to the availability of oxygen and in-cylinder pressure and temperature [52]. It can be divided into two types: oxidation at low and high temperatures. Oxidation of engine oil at low temperatures leads to alkylhydroperoxides ROOH, dialkylperoxides ROOR, alcohols ROH, aldehydes RCHO and ketones RR'C=O. In addition, cleavage of a dihydroperoxide leads to diketones RCO(CH<sub>2</sub>)<sub>x</sub>COR', ketoaldehydes RCO(CH<sub>2</sub>)<sub>x</sub>CHO, and hydroxyketones RCH(OH)–(CH<sub>2</sub>)<sub>x</sub>COR' [53]. At high temperatures (>120 °C) the engine oil oxidation process can be divided into a primary and a secondary oxidation phase. In the primary oxidation phase the initiation and propagation of the radical chain reaction are the same as discussed under low-temperature conditions, but selectivity is reduced and reaction rates increased. At high temperatures the cleavage of hydroperoxides plays the most important role. Carboxylic acids (RCOOH) form, which represents one of the principal products under these oxidation conditions. In a subsequent step they can react with alcohols R'OH to form esters (RCOOR'). The termination reaction proceeds through primary and secondary peroxy radicals, but at temperatures above 120 °C these peroxy radicals also interact in a non-terminating way to give primary and secondary alkoxy radicals [54]. The secondary oxidation phase happens at higher temperatures where the viscosity of the bulk medium increases as a result of the polycondensation of the difunctional oxygenated products formed in the primary oxidation phase. Further polycondensation and polymerization reactions of these high molecular weight intermediates lead to form sludge [53]. Reaction oxidation compounds in oil samples determined qualitatively by obtaining their IR spectra in a Fourier Transform Infrared Spectrometer (Thermo Scientific, Thermo Mattson Nicolet 300-FTIR). A spectral band at 1700–1750 cm<sup>-1</sup> indicated the presence of oxidation compounds, because of the fact that (C=O) bond strongly absorbs at this frequencies [55].

The IR results of the base oil as shown in Figure 3 and Table 8 showed no peaks of oxidized products which confirm its virginity. IR spectra for used engine oil show a medium peak at 1704.61 cm<sup>-1</sup> that indicates the presence of oxidation products in the used engine oil sample, as shown in Figure 4 and Table 9.

**Figure 3.** Results of analysis of base oil (Ravenol, VSi SAE 5W-40).**Table 8.** Results of analysis of base oil (Ravenol, VSi SAE 5W-40).

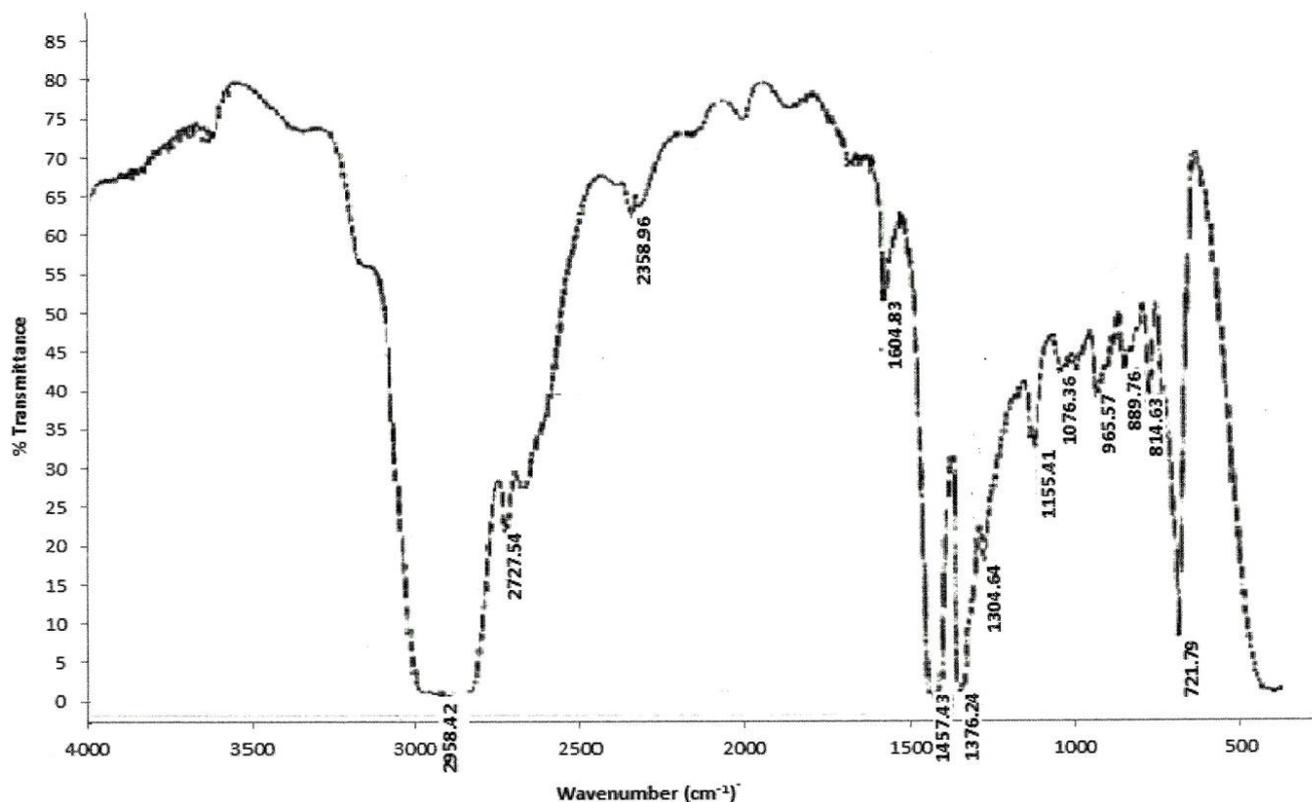
Frequency $\text{cm}^{-1}$	Type of vibration	Bond	Functional group
653.95	Stretch	C-X	Alkyl halide
721.94	Bending in plain (roking)	C-H	Alkenes
818.13	Out of plan bending	C-H	Alkenes
890.19	Out of plan bending	C-H	Alkenes
972.81	Out of plan bending	C-H	Aromatic
1155.34	Wagging	$\text{CH}_2\text{-X}$	Alkyl halide
1306.37	Wagging	$\text{CH}_2\text{-X}$	Alkyl halide
1377.05	Out of plan bending	C-H	Alkans
1464.57	Bending in plain (scissoring)	C-H	Alkans
1515.68	Stretch	C=C	Aromatic
1604.85	Stretch	C=C	Aromatic
2358.98	Stretch	$\text{C}\equiv\text{C}$	Alkynes
2727.71	Stretch	$\text{C}\equiv\text{C}$	Alkynes
2934.97	Stretch	C-H	Alkans

**Figure 4.** Results of analysis of the used engine oil.**Table 9.** Results of analysis of the used engine oil.

Frequency $\text{cm}^{-1}$	Type of vibration	Bond	Functional group
722.01	Bending in plain (Rocking)	C-H	Alkans
814.47	Out of plan bending	C-H	Aromatic
889.41	Out of plan bending	C-H	Aromatic
1032.37	Stretch	C-O	Carboxylic acid
1155.53	Stretch	C-O	Carboxylic acid
1376.86	Out of plain bending	C-H	$\text{CH}_3$
1457.84	Bending in plain (Scissoring)	C-H	Alkan
1605.17	Stretch	C=C	Aromatic
1704.61	Stretch	C=O	Carbonyl compounds
2359.55	Stretch	O-H	Carboxylic Acid
2727.6	Stretch	H-C=O:CH	Aldehyd
2923.03	Stretch	C-H	Alkan

IR spectra for used engine oil showed additional peaks at 1032.37, 1155.53 and 2359.55  $\text{cm}^{-1}$  which represent the primary oxydized products at high temperatures. The used oil treated by the acid-clay method still showed some oxydized components as illustrated in Figure 5 and Table 10.

**Figure 5.** Results of analysis of the recycled oil (after adding the additives) by acid-clay method in local companies in Kurdistan/Iraq.

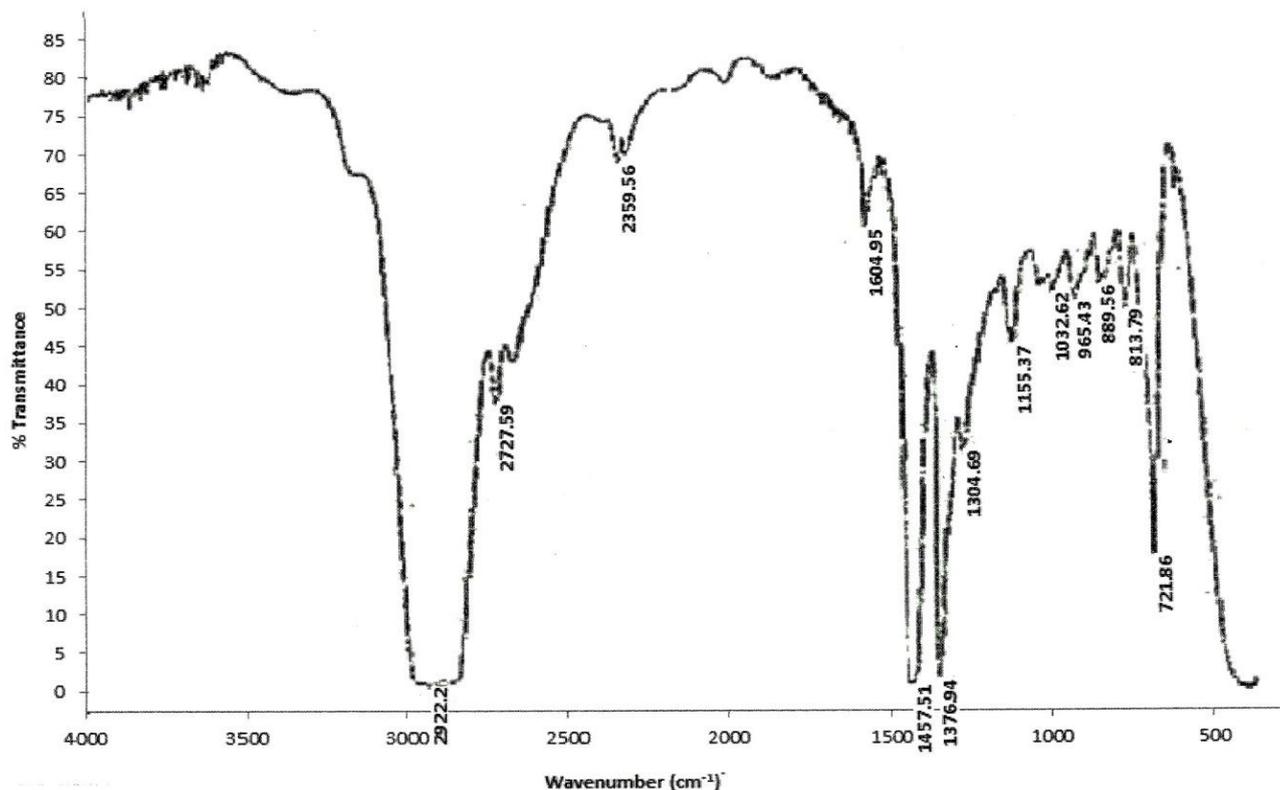


**Table 10.** Results of analysis of the recycled oil by acid-clay method in local companies in Kurdistan/Iraq.

Frequency $\text{cm}^{-1}$	Type of vibration	Bond	Functional group
721.79	In plan bending (Rocking)	C-H	Alkenes
814.63	Out of plan bending	C-H	Alkenes
889.76	Out of plan bending	C-H	Aromatic
965.57	Out of plan bending	C-H	Aromatic
1076.36	Stretch	C-O	Carboxylic acid
1155.41	Stretch	C-O	Carboxylic acid
1304.64	Rock	C-H	Aromatic
1376.24	Out of plain bending	C-H	$\text{CH}_3$
1457.43	In plain bending (Scissoring)	C-H	Alkans
1604.83	Stretch	C=C	Aromatic
2358.96	Stretch	O-H	Carboxylic acid
2727.54	Stretch	H-C=O:C-H	Aldehyde
2958.42	Stretch	C-H	Alkans

There are aldehyde components at  $1457.43 \text{ cm}^{-1}$  and carboxylic acids at  $1076.36$  and  $1155.41 \text{ cm}^{-1}$ . The only difference between the treatment by acid-clay method and vacuum distillation is the absence of aldehyde components as shown in Figure 6 and Table 11. The IR results of the base oil produced by the acetic acid-clay method are represented in Figure 7 and Table 12. This method gives the best results because it shows no aldehyde and no carboxylic acid at  $2359.56 \text{ cm}^{-1}$ .

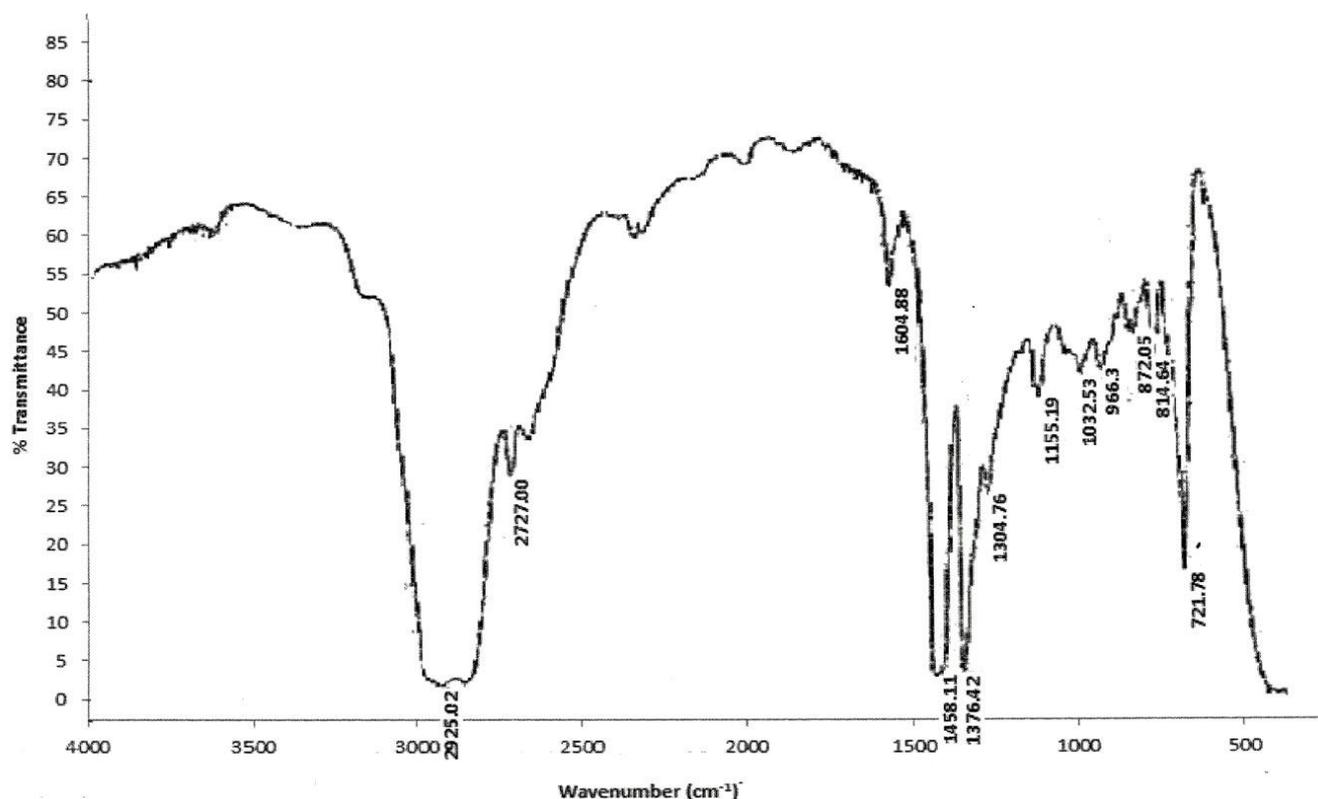
**Figure 6.** Results of analysis of the recycled oil (base oil only before adding the additives) by vacuum distillation-clay method in local companies in Kurdistan/Iraq.



**Table 11.** Results of analysis of the recycled oil (base oil only before adding the additives) by vacuum distillation-clay method in local companies in Kurdistan/Iraq.

Frequency $\text{cm}^{-1}$	Type of vibration	Bond	Functional group
721.86	In plan bending (Rocking)	C-H	Alkan
813.79	Out of plan bending	C-H	Aromatic
889.56	Out of plan bending	C-H	Aromatic
965.43	Out of plan bending	C-H	Alkan
1032.62	Stretch	C-O	Carboxylic acid
1155.37	Stretch	C-O	Carboxylic acid
1304.69	Rock	C-H	Alkans
1376.94	Out of plain bending	C-H	$\text{CH}_3$
1457.51	In plain bending (Scissoring)	C-H	Alkans
1604.95	Stretch	C=C	Aromatic
2359.56	Stretch	O-H	Carboxylic acid
2727.59	Stretch	C-H	Alkans
2922.2	Stretch	C-H	Alkans

**Figure 7.** Results of analysis of the recycled oil (base oil only before adding the additives) by acetic acid-vacuum distillation-clay method.



**Table 12.** Results of analysis of the recycled oil (base oil only before adding the additives) by acetic acid-vacuum distillation-clay method.

Frequency $\text{cm}^{-1}$	Type of vibration	Bond	Functional group
721.78	In plan bending (Rocking)	C-H	Alkenes
814.64	Out of plan bending	C-H	Alkenes
872.05	Out of plan bending	C-H	Aromatic
966.3	Out of plan bending	C-H	Aromatic
1032.53	Stretch	C-O	Carboxylic acid
1155.19	Stretch	C-O	Carboxylic acid
1304.76	Rock	C-H	Aromatic
1376.42	Out of plain bending	C-H	$\text{CH}_3$
1458.11	In plain bending (Scissoring)	C-H	Alkans
1604.88	Stretch	C=C	Aromatic
2727.00	Stretch	C-H	Alkans
2925.02	Stretch	C-H	Alkans

There are aldehyde components at  $1457.43 \text{ cm}^{-1}$  and carboxylic acids at  $1076.36$  and  $1155.41 \text{ cm}^{-1}$ . The only difference between the treatment by the acid-clay method and vacuum distillation is the absence of aldehyde components, as shown in Figure 6 and Table 11. The IR results of the base oil produced by the acetic acid-clay method are represented in Figure 7 and Table 12. This method gives the best results because it shows no aldehyde and no carboxylic acid at frequency  $2359.56 \text{ cm}^{-1}$ .

#### 4. Conclusions

This research has shown that used engine oil can be recycled by using glacial acetic acid. This method produces base oil comparable to that produced using conventional methods. Optimum conditions for recycling used engine oil using this method are room temperature and atmospheric pressure. The process for recycling is simple, as it only requires mixing at room temperature, settling, centrifugation and finally mixing with kaolinate. The base oil produced by the glacial acetic acid method is of comparable quality to that produced by the acid-clay method. Also, it has a potential to be reused in cars' engines after adding the required additives. The glacial acetic acid has shown almost no reaction with base oils, in contrast to sulfuric acid, however it reacted vigorously with the used oil. This clearly indicates that acetic acid is not affecting the original structure of the oil. Furthermore, this is most advantageous of using acetic acid in recycling of used oil. This new process of recycling of used engine oil did not emit poisonous gases like sulfur dioxide to the atmosphere. In addition, glacial acetic acid has less of a negative impact on the processing equipment compared with sulfuric acid. Lower amount of additives may be required for the base oil recycled by acetic acid-clay method due its low reactivity with the used oil. Further research is required in order to take this process to the commercial stage. However, while many variables have been studied in this research, there are many others that need investigation such as temperature, pressure, settling time, mixing, centrifugation speed and type of adsorbent.

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