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Virgin and recycled engine oil differentiation: A spectroscopic study

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Abstract

As a result of the changes that occur during their use, used engine oils tend to differ in chemical and physical composition from a virgin oil. In general recycled oils have: much higher water and sediment levels than virgin oil; relatively higher concentrations of organic compounds (oxidation products); and relatively higher levels of metals such as Fe, Cd, Cr, Pb, etc. Therefore, the aim of this work was to investigate, assess and to observe, by means of the physical and the chemical properties of the oils, atomic absorption (AA), inductive couple plasma (ICP) and Fourier transform infrared (FTIR) analyses the extent of the differences occurring between the virgin and recycled oil. In important part of this work was also the development of analytical techniques based on the use of FTIR spectroscopy; in relation to the rapid analysis of lubricants; in particular for the differentiation of virgin and recycled oil. The results obtained were expected to be useful for differentiation purposes, providing information on whether the metal concentrations and oxidation products could be an appropriate feature for differentiating a particular oil sample from the others. This work is categorized into a two-step procedure. Firstly, an evaluation of a typical FTIR spectrum of an engine oil sample (mono- and multigrade) is presented. The broad feature centered at 1716 cm^{-1} is due to the presence of carbonyl containing degradation products of oil. A band observed at 1732, 1169, 1154 and 1270 cm^{-1} assigned to the polymethacrylate stretching vibrations, allows the determination of viscosity modifier and pour point depressant additives. The observed differences in the specific spectral bands (1732, 1169, 1154 and 1270 and 1716 cm^{-1}) are investigated and discussed. Secondly, an analytical technique for the measurement of the levels of the wear metals is also applied.
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1. Introduction

Lubricating oils are used to reduce friction and wear by interposing a film of material between rubbing surfaces. Any classes of lubricating materials applied as a fluid are considered as lubricating oils (Foo et al., 2002). Lubricating oils mainly consists of two materials namely the base oil and the chemical additives. Various types of additives are blended with the base oil according to its grade and specific duty. These additives can be metallic detergents, ashless dispersants, zinc dithiophosphate, anti-oxidant/anti-wear, friction modifier, antifoam and pour point depressants.

Lubricating oils are the most valuable constituents in crude oil. Used lubricating oils are by-products of oil used in vehicles and machinery. They must be replaced on a regular basis in all operating equipment due to the contamination from dirt, water, salt, metals, incomplete products of combustion, or other materials. The principal source of contamination during oil use is the chemical breakdown of additives and the subsequent interaction among the resultant components to produce corrosive acids and other undesired substances (Mortier and Orszulik, 1997). In principle, the composition of a typical waste lubricating oil is a stable dispersion of undegraded base oil and additives with high concentration of metals, varnish, gums and other asphaltic compounds coming from the overlay of bearing surfaces and degradation of the fresh lubricant components (Jesusa et al., 2007). Chlorinated solvents may also be present in significant quantities as a result of the breakdown of additive packages and the addition of chlorine and bromine that act as lead scavengers in leaded gasoline. Polynuclear aromatic hydrocarbons (PAHs) are of particular concern due to

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their known carcinogenicity (El-Fadel and Khoury, 2001; Ahmad et al., 2005). Therefore, recycling and re-refining of waste into virgin lubricating oil may be a suitable option for protecting the environment from hazardous waste. Another benefit associated with waste lubricating oils recycling could be the economic gain due to the high price of mineral oils (Jelena et al., 2006).

At elevated temperatures, oil exposed to oxygen from the air, will oxidize (chemically combine with oxygen) to form a variety of compounds. The majority of these are carbonyl containing compounds (C=O) such as esters, ketones and carboxylic acids. As the oil degrades, a sequence of events occurs, each of which can be measured with an oil analysis. At first, the antioxidant additive package depletes. Then, the base oil oxidizes. Oil oxidation is a series of chemical reactions both initiated and propagated by reactive chemicals formed within the oil called free-radicals (Alistair, 1996).

Degradation of additives and differentiation of oil samples after various degrees of their use can be observed and studied by means of, for example, Fourier Transform Infrared (FTIR) spectroscopy (ASTM E-2412-0). This analytical instrument effectively provides a spectral snapshot of the presence of the base oil and other constituents. The method is based on the fact that specific molecular functional groups absorb in unique regions of the mid-infrared spectrum, allowing identification of additives, contaminants, oxidation products and breakdown products (Van de Voort et al., 2001). Among the metals, lead is usually present in elevated concentrations due to piston blow-by in engines using leaded gasoline. An elemental analysis of oils has special importance. Examination of the concentration of various metals in used lubricating oils is thought to be an effective and practical means of monitoring engine wear, often giving an early indication of a component failure (Janina, 1998; ASTM E-2412-0). The concentration of certain metals in lubricating oils can be determined in terms of trace element analysis (Janina, 1998; Gustavsen, 2001). Atomic absorption spectrometry (AA) and inductively coupled plasma (ICP) is the most often used analytical method for the determination of metals (Saba et al., 1985; ASTM D-4951). The determination of metal contents in a lubricating oil seems to be useful in the differentiation of virgin and recycled oil. However, very little information concerning this problem is available in the literature.

Engine lubricating oil does not ''wear out.'' A number of processes are available for purification and reprocessing of the lubricating oils. Recycling of the used lubricant is one option. At present, three methods are used for recycling: reprocessing, reclamation and re-refining. Reprocessing is used to make used oil suitable for combustion as burner fuel. Reclamation involves a higher degree of processing and is primarily used for industrial lubricants (George, 2003). Re-refining, one of them, requires the conversion of used oil to a product with similar characteristics or in general comparable in quality to those of virgin oil. Re-refining is the most complex of the three recycling processes and used petroleum refining techniques. Because of this, only a limited number of companies are involved in this process. Re-refining results in clean high quality

base stocks. Of course, quantities of contaminants in waste oil depend on several factors including type of original detergents and dilutants added to the virgin oil, storage location and management practices. The process typically involves, but is not limited to, pre-treatment by heat or filtration, followed by either vacuum distillation with hydrogen finishing or clay, or solvent extraction with clay and chemical treatment with hydro-heating (El-Fadel and Khoury, 2001; Mohammad et al., 1995). Some of these processes are not effective in removing the contaminants (wear metals and oxidation products) from the used lubricating oil and so must be combined with a more severe treatment in order to completely reprocess the used oil.

Current technologies allow used oil to be re-refined into a high quality base stock and several oil companies now market products that have been certified by the American Petroleum Institute (API). API Certification is the basis for warranty requirements of motor vehicle manufacturers and thus is used in specifications of motor oil buyers. Other technologies, such as simple filtration, have also been used to recycle used motor oil. Though not suitable for the production of high-grade lubricating oil, these technologies are often sufficient to make used oil useful as a substitute for virgin oil in fuel applications (Mortier and Orszulik, 1997). Improperly re-refined used oils are often also used as spurious oil or as duplicates of branded oils. They are often sold in the market at cheaper rates. The use of improperly re-refined or spurious oil in automobiles could not only damage them more rapidly, but would also lead to increased pollution load.

Many authoritative sources, as well as this study, have thoroughly substantiated that there is essentially no difference in virgin-base stock oils and re-refined-base stock oils. Thus, if the blending process is performed properly and no contamination is introduced in the packaging process, the re-refined end product will be equivalent to the virgin end product in every way. API-licensed re-refined oils must pass the same cold start and pumpability tests, rust and corrosion tests, engine wear tests, high temperature oil thickening tests, deposit tests and phosphorous tests that virgin oils are required to pass.

Because of the changes that occur during use, engine oils tend to differ in chemical and physical composition from virgin oil. In general recycled oils have: a much higher water and sediment levels than virgin oil; relatively higher concentrations of toxic organic compounds; and relatively higher levels of metals such as Fe, Cd, Cr, Pb, etc. Therefore, the aim of this work was to investigate, assess and to observe, by means of the physical and chemical properties, AA, ICP and FTIR analyses the extent of the differences between the virgin and recycled oil. The results obtained were expected to be useful for differentiation purposes, giving information on whether the metal concentrations, or concentration of oxidation products could be an appropriate feature for differentiating particular oil sample from the others.

2. Experimental

A wide variety of imported samples of virgin and recycled engine mineral-based oil (mono- and multigrade types) were

collected from Amman, Jordan. The samples were evaluated to determine any significant variations on the basis of the following: physical and chemical properties; wear metals; and Infrared spectra.

The chemical and physical parameters analyzed for are largely based on standardized analytical methods to provide an overall indication of the status of a lubricant. Key American Standards for Testing and Materials (ASTM) chemical methods such as the determination of kinematic viscosity and pour point are carried out. Table 1 summarizes the physical and the chemical parameters that will be analyzed in the virgin and the recycle engine oil samples. Also, there is more emphasis on structured condition monitoring to provide trending data for oxidation. This approach may be helpful in oil differentiation.

Elemental analysis was performed according to Shimadzu Plasma Emission Spectrometer ICPS-7510, radial view type CP/N 211-83400-06. The solvent technique was chosen to determine the metal concentration, constant experimental conditions were kept; hence, the comparative examinations were expected to provide satisfactory results. The following procedure was followed to prepare samples for examination. Three gram of the oil sample was weighed accurately and diluted in a 50 ml flask. The samples for ICP and AA measurements were prepared by dilution of these solutions 20, 50 or 100 times, according to the species of metal being determined, using xylene. All reagents used were of analytical-reagent grade.

Analytical spectra were taken using a Shimadzu IR Prestige-21/FTIR-8400 S with a resolution of $4 \, cm^{-1}$ at 64 scans. The data interval provided by the instrument for a resolution of $4 \, cm^{-1}$ is $1 \, cm^{-1}$. A small quantity ($\sim 2 \, \mu L$) of the sample was deposited with the use of a Pasteur pipette between two well-polished KBr disks, creating a thin film. Duplicate spectra were collected for the same sample. All spectra were recorded from 4000 to $400 \, cm^{-1}$ and the spectra were collected using Shimadzu IR Prestige-21 Windows Software. These tests were conducted at the laboratories of The Royal Scientific Society (RSS), Amman, Jordan.

This work is categorized into a two-step procedure. First, an evaluation of a typical FTIR spectrum of an engine oil sample (mono- and multigrade) is presented. The broad feature centered at $1716 \, cm^{-1}$ is due to the presence of carbonyl containing degradation products of oil (ASTM E-2412-0). These have been identified as lactones, esters, aldehydes, ketones, carboxylic acids and salts. A band observed at 1732, 1169, 1154 and $1270 \, cm^{-1}$ assigned to the polymethacrylate stretching vibrations, allows the determination of viscosity modifiers and pour point depressant additives. For the virgin and recycled engine oil differentiation process, FTIR spectra are collected for each oil sample in the regions $1000–1300 \, cm^{-1}$ and

$1600–1800 \, cm^{-1}$. The observed differences in the specific spectral bands (1732, 1169, 1154 and 1270 and $1716 \, cm^{-1}$) are investigated and discussed. These spectral bands refer to the remaining oxidation products, viscosity modifiers, and pour point depressants that were not removed by simple recycling and purification processes. Second, an analytical technique for the measurement of wear metals is also applied.

3. Results and discussion

Physical and chemical measurements provide important information. The viscosity of any fluid changes with temperature. For liquids, the viscosity increases as the temperature decreases and vice versa. Viscosity affects heat generation in bearings, gears, pistons, etc., due to internal fluid friction. Formation of lubricating films, rate of oil consumption, starting of machines at various temperatures, is all affected by viscosity. An effective proper viscosity is desired over a wide range of temperature (Saurabh, 2005). Variable thickness of oil by viscosity modifiers at low and high temperatures allows the formulation of multigrade oils. The multigrade oils are designed to provide adequate viscosity at high temperatures for engine protection and low viscosity at low temperatures for easy stability. The viscosity index is used as a measure of oil's response to temperature changes. In addition to affecting the viscosity–temperature relationship, viscosity modifiers affect a lubricant's other properties. These include pour point, dispersancy, and fuel economy (George, 2003). Pour point, which is an important property of base oils intended for blending into finished lubricants, is the lowest temperature at which movement of the base oil is observed. In order to meet the relevant pour point specification for a finished lubricant, it is often necessary to lower the pour point of the base oil by the addition of an additive. Conventional additives which have been used to lower the pour point of base oils are referred to as pour point depressants (PPDs) and typically are polymers with pendant hydrocarbon chains that interact with the paraffins in the base by inhibiting the formation of large wax crystal lattices. Commercial pour point depressants include polyalkylmethacrylates. High molecular weight polymethylacrylate derivatives can act both as viscosity modifiers and pour point depressants. When this chemistry is used for viscosity improvement, the need for a pour point depressant is minimized.

Inspection of the data in Table 2 summarizes the typical analytical results for eight monograde engine oil samples collected from the local market. A comparison of physical and chemical properties of these samples (Table 1) showed few significant variations especially in viscosity index and pour point. The typical viscosity index and pour point values for monograde engine oil (SAE 50) are around 100 and $-9 \, °C$, respectively. For sample numbers from 5 to 8, a very low pour point and a high viscosity index are observed for the typical monograde engine oil. This may probably mean a recycled base oil formulation. The remaining pour point depressant or viscosity index improver additive in the oil formulation after recycling can significantly affect the viscosity index and pour point and this should be considered in drawing inferences

Table 1
Physical and chemical parameters and their ASTM methods for an engine oil

Parameter	Viscosity	Flash point	Pour point	Copper corrosion	Wear metals	FTIR
ASTM method	D-445	D-92	D-97	D-130	AA or ICP (D-4951)	E-2412

Table 2
Physical and chemical properties of various mono- and multigrade engine oils

No. and SAE	Kinematic viscosity at 100 °C (cSt)	Viscosity index/ apparent viscosity (cP)	Flash point (°C)	Pour point (°C)	Base number (mg KOH/g)	Copper corrosion, 3 h at 100 °C
Monograde engine oil						
1-R 50	19.34	100	270	−9	9.89	1a
2, 50	17.25	110	262	−9	5.82	1a
3, 50	19.08	99	252	−18	8.86	1a
4, 50	18.44	127	233	−18	0.58	1b
5, 50	19.37	110	250	−24	3.02	1a
6, 50	12.50	109	229	−24	3.55	1a
7, 50	17.84	97	256	−33	5.56	1a
8, 50	18.53	93	265	−21	7.90	1a
Multigrade engine oil						
1-R′ 20W-50	18.92	8400 (−15 °C)	243	−24	6.51	1a
2-R′ 15W-40	15.07	5750 (−20 °C)	220	<−42	11.27	1a
3-R′ 20W-50	19.04	7664 (−15 °C)	232	−30	6.65	1a
4-R′ 20W-50	19.35	8900 (−15 °C)	234	−36	8.39	1a
5, 20W-50	14.65	14,500 (−15 °C)	241	−9	3.81	1a
6, 15W-40	12.50	10,500 (−20 °C)	229	−24	3.55	1a
7, 20W-50	17.84	9500 (−15 °C)	241	−9	5.46	1a

R: reference virgin monograde engine oil, SAE: Society of Automotive Engineer.
R′: reference virgin multigrade engine oil, SAE: Society of Automotive Engineer.

based upon the properties. O'Blasny (1978) stated in his patent that one problem inherent in reclaiming and recycling processes of used lubricating oils is the fact that those oils are conventionally provided with additives such as detergents, dispersants, pour point depressant and viscosity index improvers. These additives have in some instances made it difficult or impossible to adequately treat used oil by simple, well-known procedures, since these additives tend to inhibit separation of impurities such as naphthenic, aromatic and asphaltic from the reusable used oil. Therefore, a high value of viscosity index and lower value of pour point refer to that improper re-refining process. This will confirm that these samples are recycled oil and not virgin oils as an initial decision. This observation will also be confirmed by FTIR and elemental analyses.

Table 2 shows the physical and the chemical properties of various multigrade engine oils (20W-50 and 15W-40). For samples 5 and 7, a high pour point value is observed for typical multigrade engine oil. For samples 5 and 6, a high apparent viscosity at −15 and −20 °C is also observed (max. 9500 and 7500 cP, respectively). These results confirm that these samples are badly formulated.

Spectroscopic methods like FTIR analysis can provide significant information on the state of the oil itself and also to some extent information about the system where it is being used. As oil is exposed to oxygen of the air at elevated temperatures, oxidation of varieties of compounds may take place during the operation. As most of the additives have carbonyl groups, oxidation may lead to formation of carboxylic acids leading to decrease in the pH value of the oil, depleting the basicity of the oil and contributing to corrosion. Hence the degree of oxidation is a good indicator of oil degradation. In all lubricating systems, organic compounds exposed to high temperatures and pressures in the presence of oxygen will partially oxidize (react chemically with the oxygen). There are

a wide variety of by-products produced during the combustion process such as ketones, esters, aldehydes, carbonates and carboxylic acids, and the exact distribution and composition of these products is complex. Carboxylic acids contribute to the acidity of the oil and deplete its basic reserve as neutralization takes place (Neil, 2000). FTIR analysis can be used to identify formation of oxidation products.

FTIR is an analytical tool that has become increasingly prominent in lubricant analysis. This analytical instrument effectively provides a spectral snapshot of the base oil and the other constituents present. It is based on the fact that specific molecular functional groups absorb in unique regions of the mid-infrared spectrum, allowing identification of additives, contaminants and breakdown products. FTIR spectroscopy is a very powerful tool used to provide substantial information about the oil condition qualitatively rather than quantitatively (ASTM E-2412-0). This will detect the majority of the impurities left after the re-refining process. Used oil often has a high level of oxidation products and some wear metals like iron, copper and lead. In a good refining process this should be removed. Therefore, the FTIR method is being used to identify and quantify oil oxidation, even in the presence of additives (George, 2003).

Here, we attempt to standardize the measurement of lubricating oils in terms of absorbance units that can be correlated with virgin or recycled lubricating oils. This type of spectral information can be rapidly collected on an ongoing basis and via trending can be associated with specific lubricant conditions (e.g., oxidation). With the correct interpretation, a differentiation between virgin and recycled engine oil can be achieved along with an elemental analysis.

Fig. 1 shows a typical infrared spectrum of engine oil. Examination shows several absorption bands related to the additives in the regions $600–1300 \text{ cm}^{-1}$ and $1500–2000 \text{ cm}^{-1}$ (Janina and Pawel, 1999). Bands at 1731, 1169 and 1154 cm^{-1} (refer to polymethacrylate stretching bands),
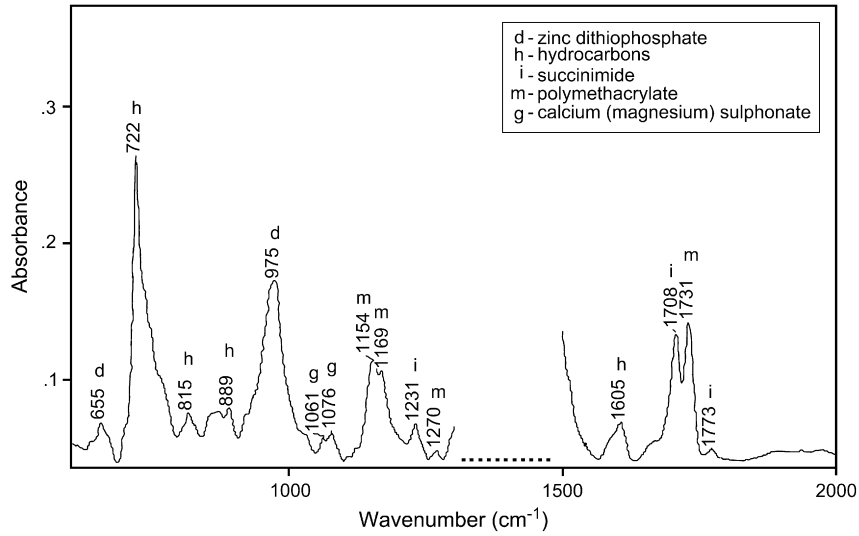
Fig. 1. Typical IR spectrum of engine oil (Janina and Pawel, 1999).

1773, 1708 and 1231 cm^{-1} (refer to succinimide stretching bands), 1076 and 1061 cm^{-1} (refer to calcium magnesium sulphonate stretching bands) and 975 and 655 cm^{-1} (refer to zinc dithiophosphate stretching bands) are shown in Fig. 1.

A major part of inadequate recycling process pollutants are expected to be oxidation products. It is due to the fact that, under normal service conditions, an important percentage of lubricant degradation results from the oxidation of the
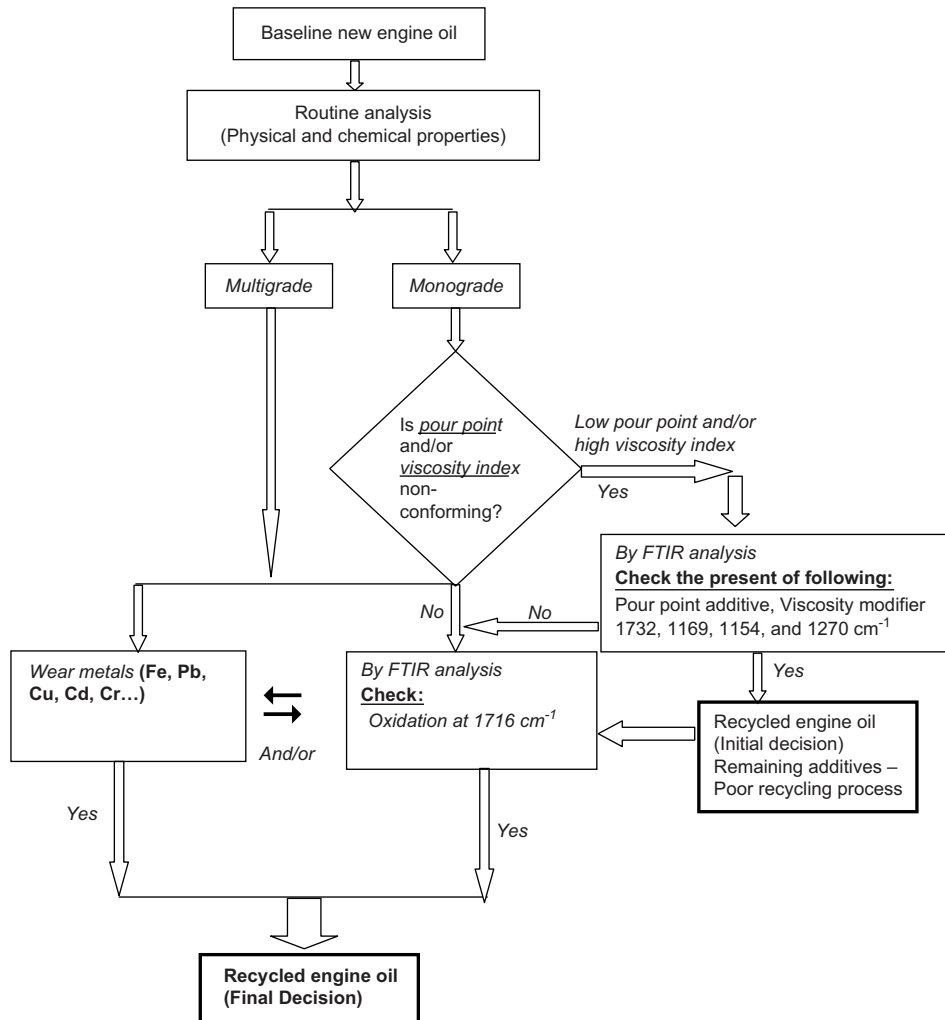
Scheme 1. Process flow diagram for virgin and recycled engine oil differentiation.

lubricating base oil. In this work, to analyze their existence in the engine oil samples we followed a two-step procedure. Firstly, an evaluation of a typical FTIR spectrum of the engine oil samples. If they showed a band at 1716 cm^{-1}, characteristic of oxidation compounds, such a presence was confirmed. Secondly, a band observed at 1732, 1169, 1154 and 1270 cm^{-1} assigned to the polymethacrylate stretching vibrations, allows the determination of viscosity modifier and pour point depressant additives that were not removed by simple recycling and purification processes (Scheme 1).

The spectra of mono- and multigrade engine oil samples are shown in Figs. 2 and 3, respectively. The spectra of all the samples show dissimilarity with that of the virgin oil. FTIR spectra of various engine oil samples show that notable differences exist in the band 1716 cm^{-1} assigned to the carbonyl stretching vibration of the oxidation products (ASTM E-2412-0). These have been identified as lactones, esters, aldehydes, ketones, carboxylic acids and salts. This feature is shown in Figs. 2a and 3a. The oil composition affects the exact position of the band and yields shifts when the proportion of the oxidation products changes. It shows that there are observable oxidation products in the base stock that were not removed by the used recycling process. However, a significant peak was noticed at around 1716 cm^{-1} due to the presence of carbonyl containing degradation products of oil. It is also shown that the concentration of oxidation compounds in the

samples no. 2–8 was higher than that required for the formulation of lubricating oil.

Qualitative evaluation of the FTIR spectra of the engine oil additives for the samples gave evidence that viscosity modifier and/or pour point additives (polymethacrylate polymer) are present in almost all oils except sample no. 1. This feature is shown in Fig. 2 and Table 3. There were significant absorption bands near 1732, 1169 and 1154 cm^{-1}, which are typical for methacrylates. These results are illustrated in Table 3. These tables are arranged so that the oxidation products and the remaining additives in oil samples can be readily compared to each other. The quantity of oxidation products and the remaining additives in the oil samples are described by two terms, namely high absorbance and low absorbance. For instance, sample no. 2 has a high quantity of oxidation products and remaining additives. These results are also confirmed by physical and chemical proprieties of the sample (Table 2). Table 2 shows that sample no. 2 has a high viscosity index. With sample no. 6, a very high absorbance at 1732 cm^{-1} is observed as a result of the residual presence of a viscosity modifier and/or pour point depressant additive in the oil sample. This result is also confirmed by the result shown in Table 2. A high viscosity index and low pour point values are obtained.

In relation to this, Jesusa et al. (2007) pointed out that the coextraction of oxidation compounds together with base oil may be affected by the presence of oil additives in the used
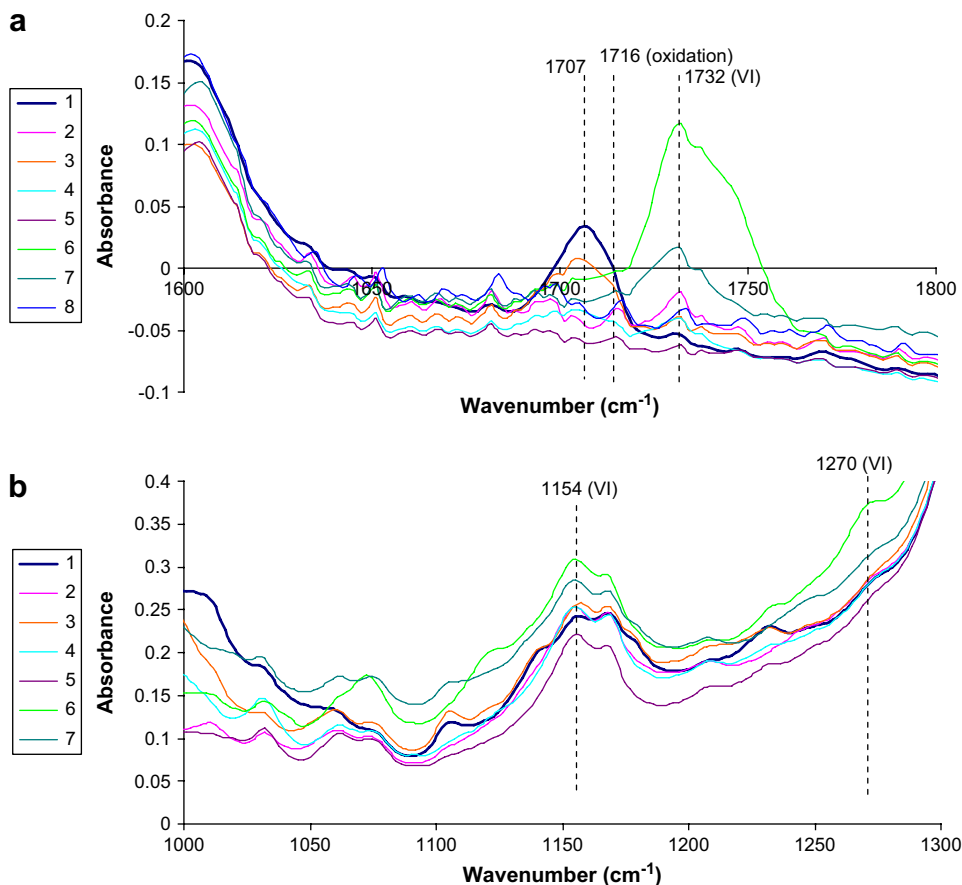
Fig. 2. FTIR spectra of various monograde engine oil samples (a) the regions 1600–1800 cm^{-1} and (b) 1000–1300 cm^{-1}.
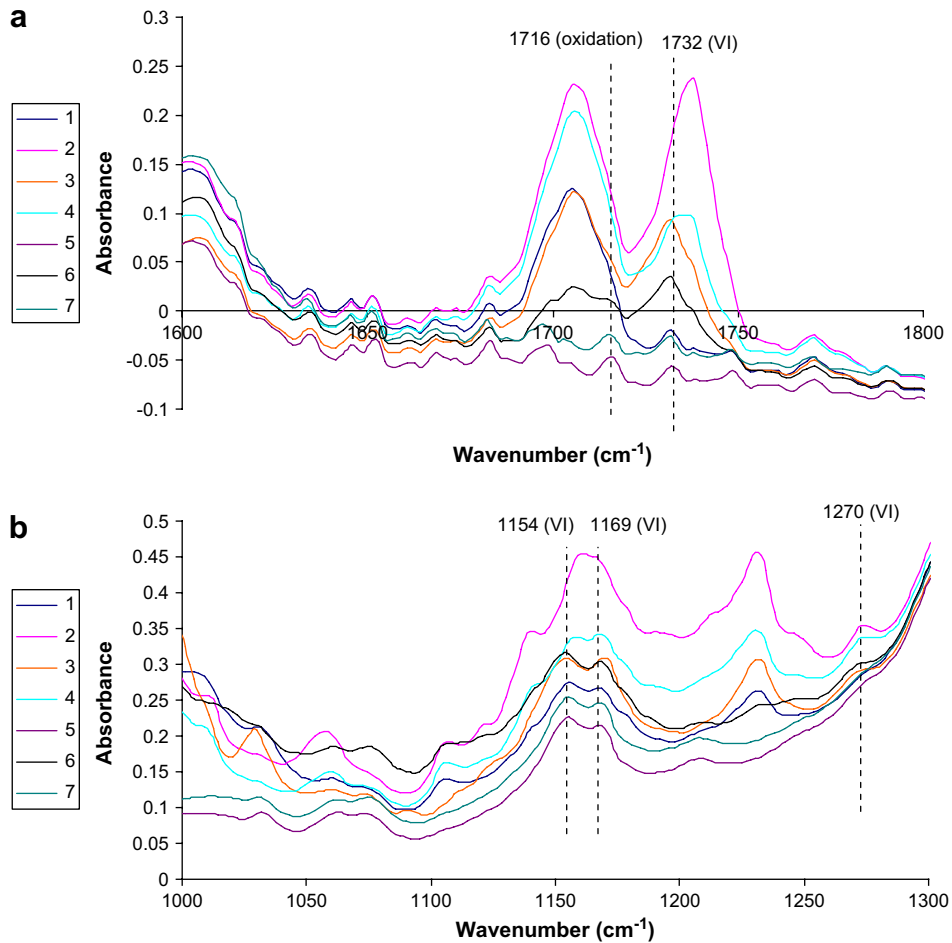
Fig. 3. FTIR spectra of various multigrade engine oil samples (a) the regions 1600–1800 cm^{-1} and (b) 1000–1300 cm^{-1}.

oil. In principle, the higher the number of interactions between oxidation compounds and additives, the more difficult will be the separation of oxidation products from used oil.

Wear metals are other important used oil components that should be removed to obtain a base oil suitable for the formulation of new lubricants. Inductively coupled plasma (ICP) analysis is used to monitor the efficiency of wear metal removal in recycled oil. Wear metal contamination of recycled oils occurs occasionally. ICP has an extremely good sensitivity in the parts-per-billion range for many metals (ASTM

Table 3
Oxidation products and viscosity modifier additives FTIR peaks of different mono- and multigrade engine oils

No.	1732 cm^{-1}	1716 cm^{-1}	1169 cm^{-1}	1154 cm^{-1}	1270 cm^{-1}	Result (VM remaining and/or oxidation)
Monograde engine oil						
1	×	×	✔	✔	×	Virgin
2	High	High	✔	✔	✔	High oxidation and high VM remaining
3	Low	×	✔	✔	✔	VM remaining
4	Low	Low	✔	✔	✔	Low oxidation and low VM remaining
5	V. low	Low	✔	✔	×	Low oxidation and v. low VM remaining
6	V. high	V. low	✔	✔	✔	V. low oxidation and v. high VM remaining
7	High	Low	✔	✔	✔	Low oxidation and high VM remaining
8	Low	High	✔	✔	✔	High oxidation and low VM remaining
Multigrade engine oil						
1	Low	×	✔	✔	✔	Virgin
2	V. high	×	✔	✔	✔	Virgin
3	High	×	✔	✔	✔	Virgin
4	High	×	✔	✔	✔	Virgin
5	Low	High	✔	✔	✔	High oxidation and low VM remaining
6	High	High	✔	✔	✔	High oxidation and high VM remaining
7	Low	High	✔	✔	✔	High oxidation and low VM remaining

×: Absent; ✔: present; VM: viscosity modifier.

D-4951). This is the level of contamination that may occur in recycled oils. Royal Scientific Society (RSS) has ICP capabilities and can monitor the efficiency of metals removal for recycled oils.

The analytical method was initially tested using 15 different kinds of fresh oils (virgin and recycled oil). Three samples of each oil were taken for the examination. Each sample was individually treated according to the procedure described above (experimental section), and then adequately diluted and measured. The mean values of the metal concentrations found for each kind of oil are given in Table 4. The elemental analysis was done to determine Si, Al, Cr, Fe, Cu, Cd and Pb, in the engine oil samples. These elements were selected as indicators for assessing the presence of mechanical wear and chemical corrosion that left after the re-refining process. Lead is mostly derived from lead in gasoline. The increase of Pb concentration may originate from fuel containing compounds of Pb mixed with oil during driving as well as from the wear of bearings or from lubricants in the motor (Ahmad et al., 2005).

Table 4 is arranged so that wear metals in oil samples can be readily compared to metals in the virgin lubricating oil. Samples of virgin lubricating oil were analyzed to determine if contaminants were present in the oil. No wear or contaminants were observed in the virgin engine oil samples. Iron and lead appear in higher concentrations in sample no. 6 (mono- and multigrade) as a result of weak recycling process. Therefore, the process used for recycling was not successful in removing heavy metals from oil. Table 4 also shows a high content of silicon. There were no notable differences in other metals between the various oil types. Ahmad et al. (2005) showed that hydrocarbon solvents can do a very efficient job in metal contaminant removal like iron, copper, nickel, calcium, magnesium and zinc compared to existing technologies. The lead removal in this process was better than the acid free process and worse than the acid clay process. They showed that the treated oil using this process possesses competitive properties compared to samples from existing processes.

It is observed that all impurities levels (wear metals and oxidation products) in mono- and multigrade engine oil sample no. 6 are higher than other samples. In particular, the concentration of oxidation compounds surpasses the established limit for an oil to be used in the production of new lubricants and it will need other recycling and purification process before it can become suitable for such use. Table 4 shows that wear metals removal was more noticeable than in the case of oxidation products separation and, therefore, the recycling and purification method used was more powerful in metal removal than the removal of oxidation products. However, a purity of the engine oil samples (mono- and multigrade) for wear metals was checked by elemental analysis and no remarkable metal concentrations were observed from the elemental analysis data except for sample no. 6 and 8. It is thus believed that almost all wear metals are extracted out after the recycling and purification processes.

To conclude, physical and chemical oil analysis has proven to be an effective tool for assuring the quality of the purification method. This study also implemented FTIR and elemental analysis simultaneously. They have proven to be an effective combination in the pursuit of management's differentiation goals. The final evaluation based on physical and chemical oil analysis, FTIR and elemental analysis of the above results is shown in Table 4. The above procedures are also illustrated in a process flow diagram as shown in Scheme 1.

4. Conclusion

From the above results it can be concluded that the recycling processes used for purification of the sample oils are not adequate, particularly in dealing with oxidation products and trace metals such as Pb, Fe and Si. The presence of oxidation products and trace metals in engine oils could primarily have a deleterious effect on equipment due to severe erosion. However, the use of more advanced methods

Table 4

Atomic absorption results of various mono- and multigrade engine oils and the final evaluation of the engine oil samples – recycled or non-recycled oil

No.	Wear metal (by atomic absorption) (ppm)							Final evaluation (recycled or non-recycled oil)
	Pb	Cd	Cu	Fe	Cr	Al	Si	
Monograde engine oil								
1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	9.4	Non-recycled
2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Recycled
3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Recycled
4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Recycled
5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Recycled
6	6.7	<0.5	<0.5	6.0	<0.5	<0.5	9.6	Recycled
7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.9	Recycled
8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	20	Recycled
Multigrade engine oil								
1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Non-recycled
2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Non-recycled
3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Non-recycled
4	<0.5	<0.5	<0.5	<0.5	<0.5	0.53	<0.5	Non-recycled
5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Recycled
6	8.3	<0.5	<0.5	9.1	<0.5	<0.5	10.5	Recycled
7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	Recycled

to remove such potential pollutants from waste oils involves higher preparation costs, making such oils uncompetitive with virgin oils.

However, the following general conclusions can be formulated on the basis of the investigations performed.

- Physical and chemical oil analysis has proven to be an effective tool for assuring the quality of the purification method.
- The power of infrared analysis lies in the fact that every compound has a unique infrared signature. In lubricant condition monitoring, this is employed to monitor key signature points in the spectrum to uniquely identify common contaminants and degradation faults particular to that type of system.
- Qualitatively FTIR and quantitative element analysis might be accepted as a good feature for differentiation between virgin and recycled engine oil samples. They have proven to be an effective combination in the pursuit of management's differentiation goals.
- The band at $1716 \, \text{cm}^{-1}$ is characteristic as oxidation products.
- The bands observed at 1732, 1169, 1154 and $1270 \, \text{cm}^{-1}$ assigned to the polymethacrylate stretching vibrations, allows the determination of viscosity modifier and pour point depressant additives that did not remove by simple recycling and purification processes.
- Different amounts of Pb and Fe in the sample no. 6 and the amount of oxidation products may indicate that they come from inadequate recycling process.
- If these re-refined oils are manufactured correctly, there is then no reason not to use them. The requirement is, above all, that the re-refining process is perfect and the oils are alloyed correctly just like virgin-base oils.

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