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Determination of carbon residue, ash content, and concentration of heavy metal in virgin and spent Iraqi lubricating oils

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Abstract

During the usage of lubricating oil, it will age, deteriorate, and lose efficiency due to its mixing with foreign matters that contain metal powder, filings, and other oils as well as additives, which result to changes in its chemical and physical properties compared to those of the virgin oil. The results showed that carbon residue and ash content for used oils increase when compared to those of the new one, but after vacuum distillation, it was decreased to 0.47 wt. %, and 0 wt. % respectively. The results of the determination of metals content (Iron, copper, magnesium, zinc, and manganese) demonstrated that there is an increase in the values for Fe, Cu, and Mg at the beginning of use and then settled off whereas no significant change was observed for additive elements (Zn and Mn) in virgin and used oil samples.

Key words: Carbon residue, Ash content, Heavy metal, Spent lubricating oils

Introduction

A lubricant oil can be defined as an oil product that divides the metal parts of an engine, reduces friction, and keeps it fresh (Jonathan, 1993). Lubricating base oils consist of aromatic, naphthenic, and paraffinic molecules with a small amount of sulfur, oxygen, and nitrogen-containing compounds inter-mixed within the three basic structures, most molecules are a combination of two or three of the basic hydrocarbon types but are classified by their dominant properties (ZHAO et al., 2008).

During service, the lubricating oil produces carbon residue precursors in the form of polynuclear aromatic systems that were not present in the original lubricating oil, but, these polynuclear aromatic systems cannot be detected and typically remain soluble in the used oil, depending on the character of the fuel oil to be blended with the used lubricating oil, the polynuclear aromatic systems may separate out as a solid phase with the potential of interfering with the performance of the injector nozzles, as a component of a high carbon residue, the polynuclear aromatic systems can be part of the cause of rapid carbon buildup and nozzle fouling (Speight and Exall, 2014).

The residual carbonaceous remaining after the thermal decomposition of engine oil in a limited amount of air is known as coke or carbon forming tendency; the carbon residue testing can also be utilized at the same time for evaluating the carbonaceous deposition characteristics of engine oils used in internal combustion engines. The residual amount of carbon in the engine oil as an indication of the number of carbonaceous deposits engine oil would form in the combustion chamber of an engine and now of considerable importance due to the presence of additives in many oils; for example, an ash-forming detergent additive can increase the residual value of engine oil carbon, yet generally reduces its tendency to form deposits (Nadkarni and Nadkarni, 2007).

Lubricating oil does not contain ash but it contains ash precursors, which are ash-forming materials found in heavy fuel oil are normally derived from the metallic salts and organometallic compounds found in crude oils. On the other hand, used lubricating oil typically contains metals and other ash-forming constituents produced in the oil during service, unless such materials are removed. Ash formation will ensue during combustion and depending on the use of fuel oil and used lubricating oil, it can have considerable harmful effects (Speight and Ozum, 2001; Hsu and Robinson, 2007; Gary et al., 2007; Speight, 2014).

Metallic elements are added to many oil compounds to enhance the oil's efficiency. Generally, metals in engine oils are as contaminants that should completely be removed in order to produce suitable base oil for producing new virgin oil (Aucélio et a., 2007). Metals are heteroatoms that are found in engine oil mixtures. Their value ranges from a few hundred to thousands of ppm, which increases with decreasing engine oil API gravity and increasing boiling point. Metal constituents are associated with heavy compounds and they appear mainly in residues. Base engine oils have very little metal, 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 into the oils after using due to the depletion of various additives and dilution of the engine oil with fuel containing metal additives (El Naga and Salem, 1984; Ali et al., 2019; Mirnategh et al., 2018; Zainy, 2019).

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The aim of the present investigation was the determination of carbon residue and ash content, as well as the distribution of some heavy metals present in virgin lubricating oil and those used for different driving distances.

Experimental Details

Materials and methods:

Virgin lube oil type Baghdad (15W-40), produced by the middle refineries company of Al-Daura Refinery, Baghdad, Iraq. This oil operated for 1000, 1500, and 2000 km driving distance were directly collected from a small saloon car, (Mercedes-Benz-Internal Combustion Engine) operated at different operating conditions were used. The study was conducted during November-December 2018. Flame atomic absorption (AA-7000 SHIMADZU) was used to determine the content of metals in lubricating oils. Vacuum distillation was carried out in a laboratory distillation unit to separate the spent 2000 km oil into two fractions, the lube oil fraction (235 ˚C- 475 ˚C) and a residue at +475 ˚C.

Determination of carbon residue and an ash content of oils, ASTM D- 482

2g of lubricant oil sample was weighed in a suitable crucible and carefully heated and ignited by flame until leaving a carbonaceous material only. Then, the carbon residue was calculated (ASTM D 482., 2003). After that, it was heated in a furnace at 775±25 ˚C until the carbonaceous material disappeared. The crucible was removed from the furnace and left to cool at room temperature, and the ash amount was calculated (Hameed et al., 2017).

Determination of metals content in the lubricating oil

The ash inside the crucible obtained in section 2.2, was dissolved in 50 ml aqua regia solution, consisting of 1 volume of HNO_3 and 3 volumes of HCl and poured in a hot plate and heated until the volume of solution reduced to half, then distilled water was added and the process was repeated 3 times. Finally, the solution reached the volume with distilled water and stored in a 250-ml volumetric flask. The determination of metals content (Iron, copper, magnesium, zinc, and manganese) in new, used, and recycled lubricating oils was done by using flame atomic absorption spectrophotometer and finally, the obtained percentage of metals in these solutions were converted to those in oils.

Results and Discussion

Carbon residue and ash contents data

The carbon residue of virgin oil was 0.825 wt. % and as expected, it increased with the time of use and became 1.590, 1.902, and 4.628 wt. % for those with a driving distance of 1000, 1500, and 2000 km, respectively. After vacuum distillation, the carbon residue of recycling oil decreased to 0.47 wt. %, which was close to the value of Iraqi specifications required for lube oils. The ash content was considered an important test in evaluating the purity of oils. It is known that the percentage of ash represents the residues of the mineral substances in oil and its low percentage represents evidence for the high-purity processed oil. The ash content for new oil was 0.567 wt. %. It was observed that when the oil was used for distances of 1000, 1500, and 2000 km, the ash contents increased to 1.230, 1.256, and 1.282 wt. %, respectively following the trends of carbon residue results and then it was reduced to 0 wt. % for the vacuum distilled oil (Table 3.1 and fig. 3.1). This was due to the internal pollutants resulting from the damage of the additives, as well as the external pollutants from the dust and the engine friction products (Hameed et al., 2017). Ash also results from extraneous solids such as dirt and rust (Hussein et al., 2014) in addition to oil organic mineral enhancers. It was found that the ash content reduced from 1.282 wt. % in the oil used at 2000 km to 0 wt. % in the recycled one. Thus, we used the residue after distillation to find the balanced values of the ash contents (Elaf and Shihab, 2019).

Table 1: Results of oils carbon residue and ash content values.

Type of oil	Carbon residue. Wt. %	Ash content, wt. %
Virgin	0.825	0.567
Used at 1000 km	1.590	1.230
Used at 1500 km	1.902	1.256
Used at 2000 km	4.628	1.282
Recycled oil	0.470	.0000
Distillation residue	4.055	2.230

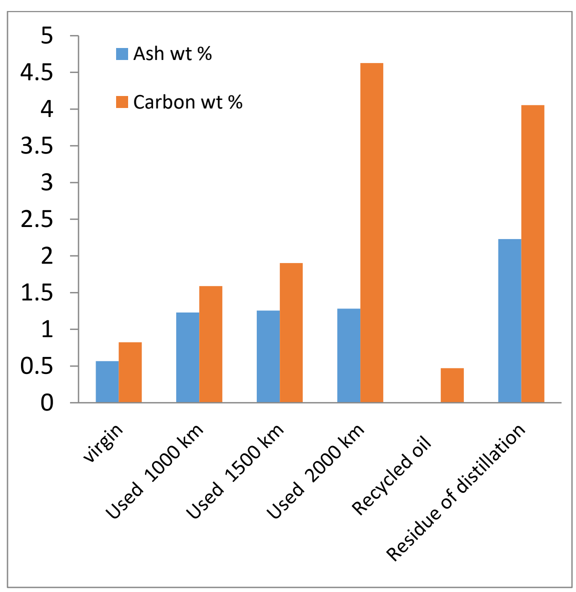

Figure 1: Distribution of carbon residue and ash content values in oils.

Elements analysis in oils

Table (3.2) shows the analysis of some originally present elements (Fe, Cu, and Mg) and those added as additives (Zn and Mn) in used lubricant oils. It is clear that iron, copper, and magnesium contents decreased in oil operated at 1000 km as a result of its deposition on the internal surfaces of engine forming a solid protective layer on it and hence, preventing further metal precipitation; so their concentrations increased in oils used at 1500 and 2000 km where their values were finally settled and became similar to those in new oil. On the other hand, the analyses showed that Zinc followed the same effect whereas manganese seemed not to exist in all oil samples. The most common metal wear in a car's engine that is introduced into the engine oil after a period of use is iron (Fe). Iron comes from various places in the engine such as liners, camshafts and crankshaft, pistons, gears, rings, and oil pump. The concentration of iron in the engine oil depends on the bearing conditions inside the engine. If the bearing fails, the concentration of iron increases in used engine oil. In the engine, the wear rises at a faster rate during the starting of the engine (Dabai and Bello, 2019). Copper (Cu), after use, is introduced into engine oils from bearings, wearing, and valve guides. Engine oil coolers can also be contributing to copper content along with some oil additives (Alder and West, 1972). Magnesium (Mg) is considered to be the most common wear metal in used engine oil and is presented in virgin oil in the form of magnesium phenates and magnesium salicylates that behave as antioxidants at high temperatures (Hopp, 1974).

Oils contain many additives, some of which including oxidation inhibitors, work to clean the engine or the dispersion of oil so as not to accumulate and block. Zinc is the most important additive, which is introduced to base oil in the form of additives package as anti-oxidant, corrosion inhibitor, anti-wear, detergent, and extreme pressure tolerance (Peterson and Kahn, 1970). In this study, as shown in Table 3.2, the analysis of elements presents in different oils showed that the amount of manganese (Mn) was zero, which indicates that the oil does not contain manganese as additives.

Table 2: Analysis of elements present in different oils.

Metal	Oil type	Concentration, (ppm)
Iron (Fe)	Virgin	12667.837
	Used at 1000 km	10732.500
	Used at 1500 km	11775.275
	Used at 2000 km	12693.962
	Residue of distillation	24411.466
Copper (Cu)	Virgin	9.837
	Used at 1000 km	9.487
	Used at 1500 km	10.562
	Used at 2000 km	12.362
	Residue of distillation	23.733
Magnesium (Mg)	Virgin	348.237
	Used at 1000 km	888.187
	Used at 1500 km	361.612
	Used at 2000 km	227.862
	Residue of distillation	438.192
Zinc (Zn)	Virgin	1618.15
	Used at 1000 km	672.562
	Used at 1500 km	750.287
	Used at 2000 km	1533.450
	Residue of distillation	2948.942
Manganese (Mn)	Virgin	0.000
	Used at 1000 km	0.000
	Used at 1500 km	0.000
	Used at 2000 km	0.000
	Residue of distillation	0.000

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