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Comparative Assessment of Thermo Chemical Properties of Different Consumable Automobile Oils in Respect of their Environmental Friendly Use

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Abstract: In this study thermo chemical characteristics of different virgin and waste engine oils (VWEO) have been demonstrated. The aim of this study was to assess thermo chemical properties of different consumable automobile oils of the local market of Multan Pakistan to have insight knowledge about their adverse environmental effects. Four vehicle engines and one air compressor engine were included in this research work. Fifteen VWEO samples including motorcycle engine oils ($M_1M_2M_U$), spark ignition (SI) engine oils ($S_1S_2S_U$), compression ratio ignition (CI) engine oils ($C_1C_2C_U$), air compressor engine oils ($A_1A_2A_U$) and hydraulic engine oils($H_1H_2H_U$) have been analyzed and compared for specific gravity, kinematic viscosity, viscosity index, pour point, flash point, total base number (TBN), total acid number (TAN), copper corrosion and sulfur contents by adopting international methods. Elemental analysis has been carried out by using atomic absorption spectrophotometer (AAS**).** The results of some of the samples were found within the allowable range. However, motorcycle engine oil M_2 and SI engine oil S_2 were found below the minimum test limits possibly due to the adulteration. Furthermore, the samples were subjected to elemental analysis for the purpose of their adverse environmental effects. In two samples lead (Pb) concentrations were found above the maximum allowable limits while in three samples Chromium (Cr) level was more than its upper allowable limit.

Keywords: Thermo-Chemical, Characteristics, Automobile Oils, Environmental, Hazardous

1. Introduction

The most important part of the machine system is engine oil or lubricant which can be defined as the petroleum product that lubricates the internal combustion engine by protecting its surfaces from rubbing. A good lubricant plays a vital role in modern industries in improving efficiency and operation of the engine and reducing its wear as well as friction (Udonne, 2011; Ogbeide, 2010).Thermal oxidations and other impurities like metal wear, dirt, chemicals and water are mingled into the oil making the oil unfit to be used more as a lubricant. In order to prolong the service life of the lubricant, it is compounded with certain additives like anti oxidants, pour point depressants and flash point improvers. However, the life of the additives diminishes after usage, as the oil becomes degraded particularly because of oxidation or thermal degradation (Bridjanian et al. 2006). Oxidation increases the viscosity of the oil due to sludge formation which in turn looses the oil's lubricant quality. The oil, at this stage needs to be replaced with fresh lubricant and the used oil is carefully stored for recycling because it is a valuable resource and great source of energy (Emam et al. 2013). Literature review shows that used engine oils contain poisonous materials like polychlorinated biphenyls (PCBs), heavy metals, degraded additives, halogen compounds, gums and carcinogenic polycyclic aromatic hydrocarbons (PAHs) which are very harmful to human health and aquatic life (Ogbuehi et al. 2011; Sterpu et al. 2012; Kamal et al. 2009; Assunceo et al. 2010; Boulding , 2005).

Used engine oil (UEO) can be burnt for energy purpose but this is subjected to the regulatory limits which is (in parts per million) 100 for lead (Pb), 10 for Chromium (Cr), 02 for Cadmium (Cd) and minimum flash point limit is 45 ^{o}C (Kreith, 1994). Flame Atomic Absorption Spectroscopy is reported to be used widely as an element detector with a broad

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detectable range of metals in respect of oil's quality monitoring (Ojeka, 2006).

The aim of this research is to determine the quality and capability of the fresh and used engine oils. There is a wide range of heavy metals in engine oils but in this paper only Cd, Cr and Pb have been determined in respect of health and safety measures.

2. Experimental

Different brands (as given in **Table-1**) of the virgin motorcycle engine oils coded as (M_1M_2), spark ignition engine oils (S_1S_2), Compression ratio ignition oil (C_1C_2), air compressor engine oils (A_1A_2) and hydraulic engine oil (H_1H_2) were purchased from local market of Multan, Southern Punjab, Pakistan.

Table 1: Samples Description

Sr. No.	Samples Code	Description
1	M_1	Bonus 150 motor cycle engine oil SAE 50
2	M_2	Extra Power motor cycle engine oil SAE 40
3	M_U	Used Motor cycle engine oil (M_1), being in use for 900Km.
4	S_1	Herculex-D petrol engine oil SAE 20W/50
5	S_2	Jasoma petrol engine oil SAE 20W/40
6	S_U	Used petrol engine oil (S_2), being in use for 2500Km
7	C_1	Zelix Gold diesel engine oil, SAE 20W/50
8	C_2	Torque diesel engine oil, SAE 20W/40
9	C_U	Used diesel engine oil (C_1), being in use for 2800Km
10	A_1	Air compressor engine oil ISO grade 32
11	A_2	Air compressor engine oil ISO grade 46
12	A_U	Used air compressor oil (A_1), being in use for 6 months.
13	H_1	Hydrolic oil ISO grade 15
14	H_2	Hydrolic oil ISO grade 22
15	H_U	Used hydrolic engine oil (H_1), being in use for 6 months.

These virgin samples were analyzed and after analysis the clear samples M_1, S_2, C_1, A_1 and H_1 were used in specific vehicles/engines (as given in **Table-6**) for a known time period and were analyzed again. All the virgin and waste oil samples were analyzed for following parameters.

i) Analysis of engine oil samples for specific gravity ASTM D-1298, Kinematic Viscosity at 100 and 40 ^oC ASTM D-445, Viscosity Index ASTM D-2270, Flash Point ASTM D-92, Pour Point ASTM D-97, Total Base Number (TBN) ASTM D-2896, Copper Strip Corrosion ASTM D-130, Total Acid Number (TAN) ASTM D-664 and Sulfur Contents ASTM D-1552 (ASTM International, 2015; ASTM International, 2004).

ii) Analysis for heavy metallic contents by Flame Atomic Absorption Spectrophotometer FAAS.(AAS-400 Analyst, Perkin Elmer, USA) following the procedures reported in ASTM D- 4628-2 (ASTM International, 2015).

Heavy metals concentration was determined by using calibration curve that was obtained from standard solutions. The standards prepared for metals were according to the Analytical measuring systems Pvt. Ltd. The description of the apparatus used in this study is presented in **Table-7.**

3. Results and discussion

Table 2, 3, 5 and figure 1-9 show physico-chemical properties of VWEO samples. The obtained results are the average of 2-3 repeat tests. The discussion of the results is given as follows.

3.1 Specific gravity

Specific gravity is the ratio of density of unknown sample to the equal volume of water. This parameter varies with temperature so the temperature must be known at which the density is measured. An increase in the amount of saturated compounds results in decrease of specific gravity while there is rise in gravity as aromatic compounds increase (Isah, 2013). In used oil specific gravity increases due to increasing amount of the solids. **Table-2 & Fig.1** show the density (specific gravity) of virgin and waste engine oils are (0.88-0.94). It was noted that the specific gravity of waste oils was greater as compared to fresh oils. This is due to the contamination of high molecular weight components to the used oil samples from inside the engine.

3.2 Kinematic Viscosity

Viscosity is a parameter which depends on temperature. Kinematic viscosity means resistance in the fluid's flow. High viscosity means high resistance in flow and vice versa. Viscosity decreases with increase in the temperature of the engine and vice versa. In used oil the presence of contamination can be indicated with help of viscosity testing. The polymerized and oxidized products, suspended and dissolved may cause an increase in the viscosity of the oil whereas fuel contamination indicates decrease in the viscosity of the engine oil. During use engine produces corrosive oxidized products, varnishes and deposits which cause increase in viscosity (Diaz, 1996). Kinematic Viscosity was measured at 100ºC (ranging from 3.90 cst-14.20 cst) and 40ºC (ranging from 13.99cst-162.19cst) and the results are tabulated in **Table-2**, Pakistan Standard Institution (PSI) specified limits are also given in **Table-8** and **Table-9** (PSI, 1990). Moreover, PSI did not specify viscosity at 40 ºC. Along with the usage of the samples the viscosity was observed to be increased due to oxidation and contaminants which damage the lubrication property of the oil.

Table 2: Samples analysis results for physico-chemical properties

Sr. No.	Samples	Specific Gravity	Kinematic Viscosity @100 °C	Kinematic Viscosity @40 °C	Viscosity Index	Pour Point°C	Flash Point°C
1	M_1	0.8869	14.20	141.09	98	-6	234
2	M_2	0.8842	12.80	138.02	82	-6	228
3	M_U	0.9012	11.92	105.62	102	-6	190
4	S_1	0.8910	18.38	158.59	130	-18	234
5	S_2	0.8918	16.22	139.74.	123	-18	168
6	S_U	0.8954	15.92	120.90	140	-18	180
7	C_1	0.8692	17.71	162.19	120	-18	236
8	C_2	0.8742	15.06	121.54	128	-18	232
9	C_U	0.8892	14.92	114.32	135	-18	187
10	A_1	0.9121	5.20	30.40	101	-29	246
11	A_2	0.9150	6.81	45.50	104	-29	242
12	A_U	0.9201	4.84	25.17	115	-29	190
13	H_1	0.9346	4.20	16.40	172	-29	238
14	H_2	0.9352	5.00	21.50	170	-29	234
15	H_U	0.9401	3.90	13.99	190	-29	192

3.3 Viscosity Index

Viscosity Index (VI) is being used in practice as a single number indicating temperature dependence of kinematic viscosity. A high VI indicates minor change in viscosity with temperature which gives a better protection to the engine operating under vast variations of temperature. For improving the oils efficiency VI improvers are added up. A high viscosity index indicates good thermal stability and low behavior of temperature flow (Singh H. et al., 1987). **Table-2 & figure-2** illustrate the viscosity index of different samples which ranges from 82 to190.The sample M_2 has VI 82 which is very less than Psi regulatory limit as given in **Table-9** (PSI, 1990). However, remaining other samples has viscosity index values within the standard limits.

3.4 Flash Point

Flash point (FP) of the lubricant can is the lowest temperature where the vapours of the oil start to catch fire. FP demonstrates the contamination of the engine oil. Low flash point of engine oil is a threat that the oil has become contaminated with the volatile products like gasoline or diesel. FP is directly related with the molecular mass of the oil. Thermal oxidation in the engine results in the production of volatile components hence longer chain (high molecular mass) compounds breakup into the smaller chain (low molecular mass) compounds which lead to decrease in the flash point (Lenoir, 1975). **Table-2 & figure-4** illustrate the Flash point of different samples. Here it is shown that sample S_2 has the flash point less than the minimum specified values PSI regulations. The results show that the flash point of the used oil samples is less than the fresh ones. This is due to increase of volatile compounds in oil produced because of thermal oxidation inside the engine.

Table 3: Analysis results for base number, Copper corrosion, Acid Number & Sulfur contents.

Sr. No.	Samples	TBN (mgKOH/g)	Copper Strip Corrosion @ 100 oC	TAN (mgKOH/g)	Sulfur (wt.%)
1	M_1	6.00	1a	0.04	0.06
2	M_2	5.50	1a	0.02	0.09
3	M_U	2.63	3c	4.40	0.28
4	S_1	11.60	1a	0.03	0.10
5	S_2	10.82	1a	0.02	0.12
6	S_U	7.59	2b	5.60	0.35
7	C_1	9.50	1a	0.04	0.11
8	C_2	9.82	1a	0.05	0.13
9	C_U	6.91	2c	4.80	0.38
10	A_1	12.50	2a	0.02	0.16
11	A_2	12.42	2a	0.02	0.14
12	A_U	9.07	3a	2.92	0.42
13	H_1	14.22	2a	0.06	0.21
14	H_2	13.97	2a	0.05	0.25
15	H_U	10.66	3a	3.32	0.53

3.5 Pour Point

Pour point is the temperature where the flow of the liquid ceases to exist. Generally, waxes and paraffin are contained in the engine base oils which easily solidify on cooler temperature. More the waxes and paraffin in the base oil more will be its pour point. The engine oil's pour point is an important variable especially in the cold areas. The oil must keep on flowing in the oil pump and then be pumped to the engine's various parts (Riazi M.R. et al., 1987). **Table-2 & figure-3** show the pour point value of various samples. Little decrease of pour point was observed in monograde (SAE-40 and 50) oil samples as compared to multigrade oil. In multigrade engine oil samples, no significant change was observed in pour point as the multigrade oil is a high viscosity and high grade engine oil with greater percentage of various additives.

3.6 Copper Strip Corrosion

When oil is contaminated by sulphur and its derivatives then it corrode the copper strip, this is called copper corrosion. All samples mentioned in **Table-1** were subjected to this test and the results have been presented in **Table-3 and figure-6.** The fresh samples were found within the safe limits of the Ministry of Petroleum Govt. of Pakistan (PSI, 1990). However, the used sample of monograde oil M_U shows greater tarnish rather than used multigrade oil. The used oil samples S_U, C_U, A_U and H_U were also found to be corroded.

3.7 Total Base Number

It is the measure of the alkalinity of oil or neutralization number. In order to neutralize acidic components, the engine oils are formulated with highly alkaline base additives. The TBN is utilized as a measure of this package and it is also helpful indication for the replacement time of the engine oil because TBN depletes as the service time passes. For the purpose of neutralizing acids high TBN values are more effective for longer periods of time (Kauffman, 1998).

The samples were analyzed for total base number and the results are summarized in **Table-3 and figure-5.** The results show that decline of alkalinity of the used oil sample M_2 is greater S_U, C_U, in A_U and H_U which show slight decline in alkalinity relative to the virgin engine oils.

3.8 Total Acid Number

Total acid number is the measure of the acidity of oil. In the engine oil total acid number comes positive due to the presence of heavy metal salts, organic, inorganic salts, water, resin and corrosive materials which results from the oxidation process that occurs at high temperatures in the engine. (Fox M.F et al., 1991). **Table-3 and figure-7** show the TAN values of different analyzed samples which indicates that used oil samples have greater TAN values than the virgin engine oils due to thermal oxidation inside the engine atmosphere.

3.9 Sulfur contents

Mineral acids like sulfuric acid cause corrosion inside the engine. These acids are oxidation products of sulphur compounds. During use, the hydrocarbons which are inherently unstable become oxidized soon (Rincon, 2005). The sulfur contents of used engine oils M_U, S_U, C_U, A_U and H_U are greater than the fresh samples as shown in **Table-3** and **figure-8**.

3.10 Metallic Contents

Metallic contents enter into the engine oil as result of breakdown of wetted surfaces due to improper lubrication, abrasion or erosion and mechanical working. Generally, in used engine oils metals are regarded as contaminants that should be removed completely for the sake of production of suitable base oil (Aucelio, R.Q. et al., 2007).

Table-4 Acceptable values and detection limits of the instrument.

Element	Symbol	Acceptable Limit(mgl^{-1})	FAAS Detection Limit (mgl^{-1})
Cadmium	Cd	2.00	0.80
Chromium	Cr	10.00	3.00
Lead	Pb	100.00	15.00

Chromium (Cr) and Cadmium (Cd) are coming in the engine oil as contaminants during use. However, base oils are free from chromium and cadmium (Kahn, H.L. et al., 1970; Robbins, W.K., 1975). Lead (Pb) is associated with contamination due to use of galvanized containers, fuel source (leaded gasoline) and bearing wear (Bertrand, 1980). **Table-5 and figure-9** demonstrate the above mentioned heavy metallic contents. Here it is observed that two samples M_U and S_U have shown lead (Pb) concentrations greater than the allowable limits and three samples S_U, C_U and H_U have indicated chromium concentrations greater than the upper specified limits. However, for cadmium concentrations all the results were found within the safe limit i-e less than 2 ppm.

Table 5: Heavy metallic contents in the samples

Sr. No.	Samples	Cd (ppm)	Pb (ppm)	Cr (ppm)
1	M_1	< 0.08	< 15.00	< 3.00
2	M_U	< 0.08	105.00	< 3.00
3	S_1	< 0.08	< 15.00	< 3.00
4	S_U	1.00	150.00	11.00
5	C_2	< 0.08	< 15.00	< 3.00
6	C_U	1.20	< 15.00	12.50
7	A_1	< 0.08	< 15.00	< 3.00
8	A_U	< 0.08	< 15.00	5.40
9	H_1	< 0.08	< 15.00	< 3.00
10	H_U	1.28	< 15.00	11.82

Table 6: Vehicles/engines used in this study.

Vehicle Name	Engine number	Model /Mark	Origin
Motor Cycle	6821353	CD 70/2014	Japan
Corolla car	Z 222420	Toyyotta/2014	Japan
Hiace Vagon	428411	Toyyotta/2014	Jappan
Compressor Engine	S 43104	Zhejiang	China
Rough Terrain Crane	712619	Kato Works	Japan

Table 7: Apparatus used in the experiment.

Apparatus	Model	Manufacturer
Viscometer Baths	VHC-220	Gallenkamp/England
Flash Point Apparatus (Open Cup)	DIN-51376,	Lauda- Germany
Centrifuge Machine	TS67310	Precision/USA
Magnetic Stirrer Hot Plate	SWT510/010E	Gallenkamp/England
Hydrometer	883823/A B.S 718	Poulten Selfe & Lee/England
Scientific Oven	Hot Box No.3	Gallenkamp/England
Digital Weight Balance	AS-220.R2	Redwag/USA
TBN Apparatus	940/960	Orion/USA
Muffle Furnace	FSE-621	Gallenkamp/England
Spectrophotometer	AA400-Analyst	Perkin Elmer/USA

Table 8: Pakistani Standard specified limits for multigrade oils [16].

Test description	SAE-20W/50	Test method
Specific gravity 60/60°F	-	ASTM D-1298
Kinematic viscosity at 100 °C	16.3-21.9	ASTM D-445
Viscosity index (min.)	120	ASTM D-2270
Flash point COC °C (min.)	201	ASTM D-92
Pour point °C (max.)	-18	ASTM D-97
Copper strip corr. at 100 °C	1 No.	ASTM D-130
Total Base No. mgKOH/g	-	ASTM D-2896

Table 9: Pakistani Standard specified limits for monograde oils [16].

Test description	SAE-50	Test method
Specific gravity 60/60°F	-	ASTM D-1298
Kinematic viscosity at 100 °C	16.3-21.9	ASTM D-445
Viscosity index (min.)	90	ASTM D-2270
Flash point COC °C (min.)	201	ASTM D-92
Pour point °C (max.)	-6	ASTM D-97
Copper strip corr. at 100 °C	1 No.	ASTM D-130
Total Base No. (mgKOH/g)	-	ASTM D-2896

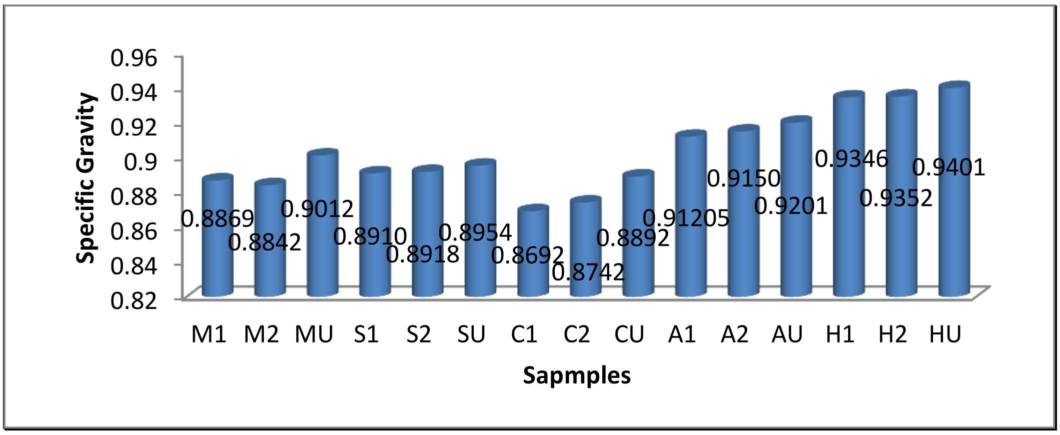

Figure-1: Graphical presentation of specific gravities of the samples.

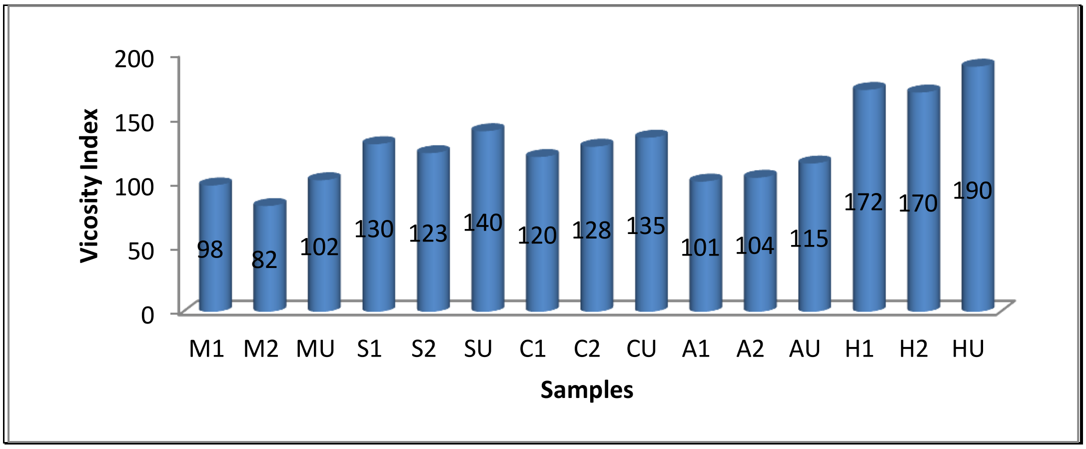

Figure-2: Graphical presentation of viscosity index for kinematic viscosity at 100 and 40 °C.

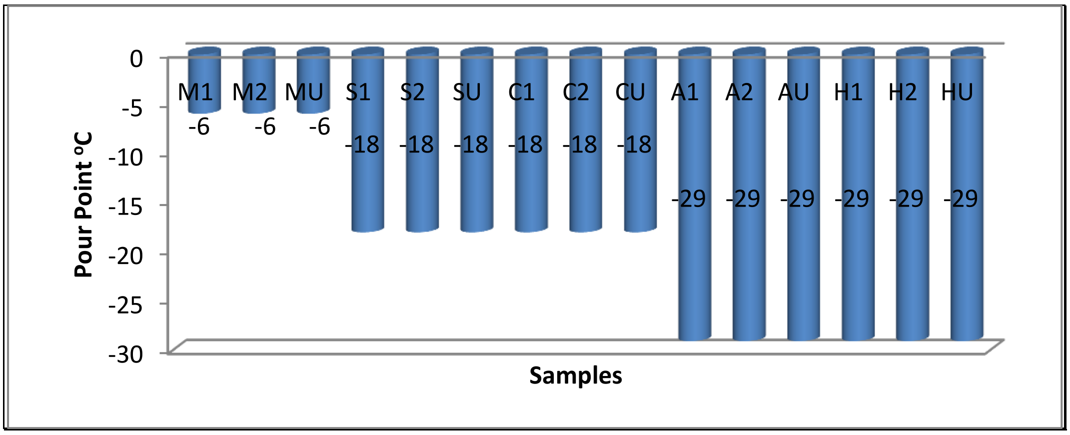

Figure-3: Graphical presentation of Pour Point (ºC) of the samples.

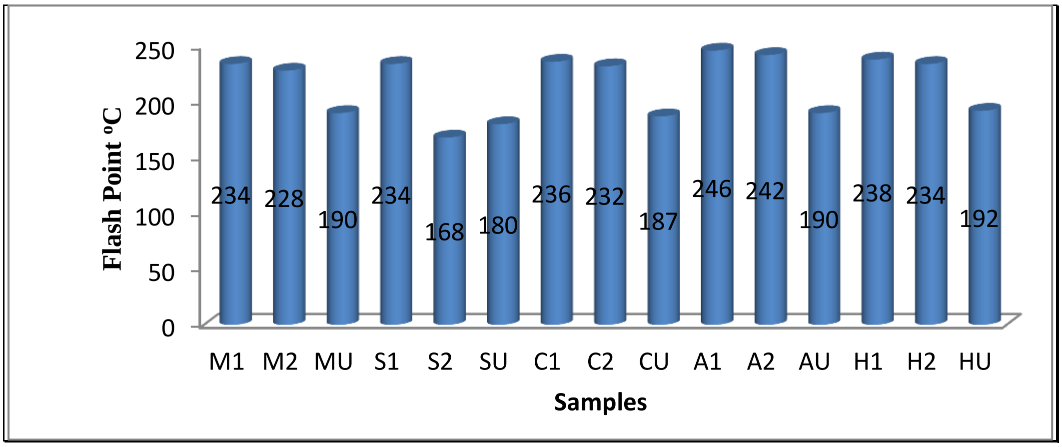

Figure-4: Graphical presentation of Flash Point (ºC) of the samples

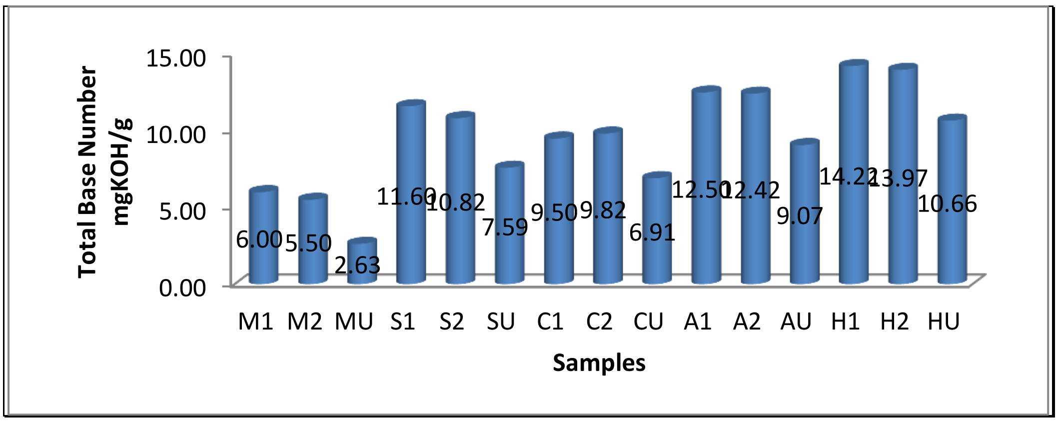

Figure-5: Graphical presentation of TBN of the samples

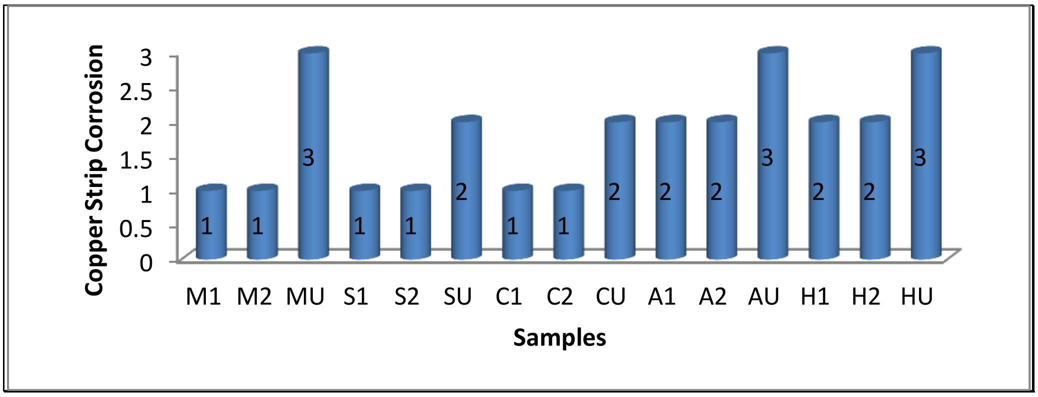

Figure-6: Graphical presentation of Copper Strip Corrosion of the samples.

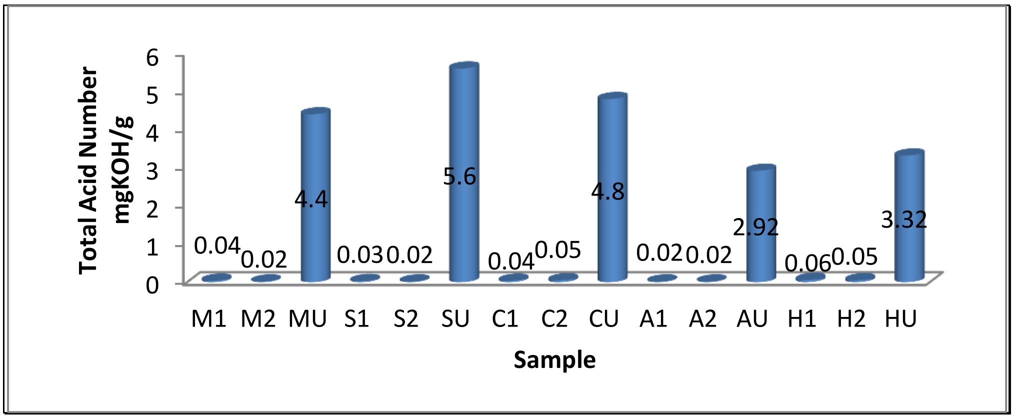

Figure-7: Graphical presentation of TAN of the samples.

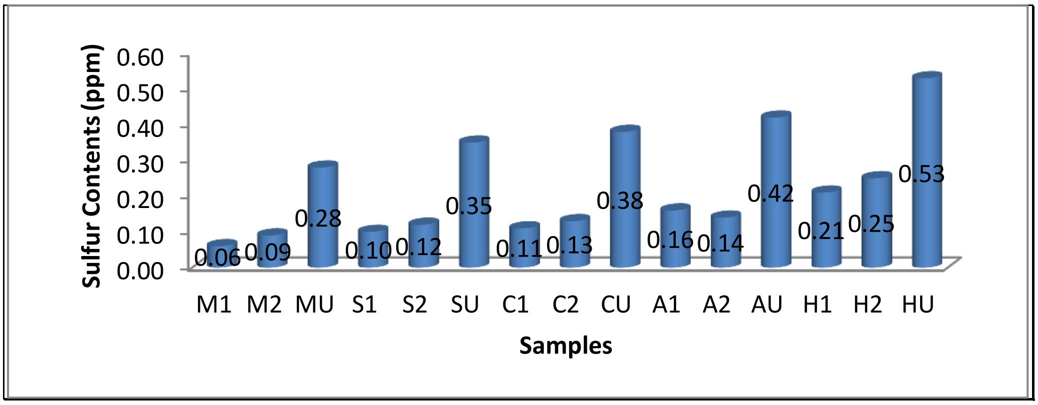

Figure-8: Graphical presentation of sulfur contents of the samples.

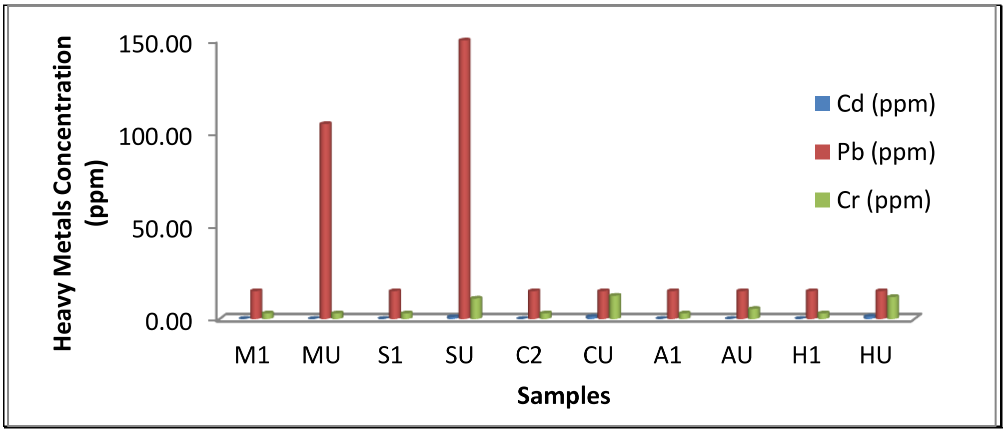

Figure-9: Graphical presentation of heavy metallic contents of the samples.

4. Conclusion

In this research work thermo chemical and elemental assessment of different virgin and waste engine oils (VWEO) has been carried out. Different samples were analyzed and compared for physical and thermo chemical properties like specific gravity, kinematic viscosity, viscosity index, pour point, flash point, total base number (TBN), total acid number (TAN), copper strip corrosion and sulfur contents by adopting ASTM (American Society of Testing and Material) standard methods. Analysis results of some of the samples were found within the range. However, motorcycle engine oil M_2 and spark ignition engine oil S_2 were found below the minimum test limits possibly due to the adulteration. Furthermore, VWEO samples were subjected to elemental analysis for the purpose of their adverse environmental effects. In two samples lead (Pb) concentrations were found above the maximum allowable limits while in three samples Chromium (Cr) level was more than its upper allowable limit. It is concluded that the elevated level of Pb in motor cycle engine oil suggests availability of leaded fuel at the local Patrol filling stations at Multan. Some of the engine oils sold was sub-standard products. For the better life of the vehicles or engines the oils may be purchased only form the registered companies. Sub standard oils may strictly be controlled by the local government authorities. In used engine oils elevated level of heavy metals like lead and chromium is a big threat to the environment. These contaminated waste oils may be stored, transported and recycled very much carefully. Further studies are required to reduce these contaminants in the used engine oil samples.

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