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# Evaluation of Physicochemical Characterization and Elemental Composition of used, Recycled, and Fresh Lubricating Engine Oils of Total Quartz and Hardex Brands

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**ABSTRACT:** Disposal of used engine oils directly into the environment poses severe pollution risk. This can however be checked if green approaches are employed in recycling the waste oil to base oil for further applications. Consequently, the objective of this paper is to evaluate the physicochemical characterization and elemental composition of used, recycled, and fresh lubricating engine oils of Total quartz and Hardex brands using appropriate standard procedures; to ascertain the suitability of the recycled oil for further automobile applications. The recycling process resulted in a 38% recovery of base oil from used Total quartz oil and 42% recovery from used Hardex oil. The examined quality parameters include color, flash point, pour point, carbon residue, specific gravity, ash content, viscosity index, kinematic viscosity, acidic value, total acidic number, and elemental composition (Fe, Cu, Al, Cd, Mn, Zn, Si). A summarized statistical analysis of all the data obtained using ANOVA showed a significant difference at a 95% confidence limit between reference data from fresh oil brands and used oils, indicating significant deterioration of lubricating properties in the used oils. Statistical analysis of quality index data from both recycled oil brands relative to the fresh oil brands showed no significant difference at $p<0.05$; which demonstrates the success of the green recycling technique. The findings show that the recycled base oil could be rebranded for further applications, therefore a green recycling approach on used engine oils should be encouraged due to its ecological and economic benefits.

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Lubricating oils are needed for the effective and efficient running of our automobile engines. Lubricants, either mineral-based or synthetic made, are the products derived from petroleum which is an essential natural resource used as the source of energy and raw material for almost all industries (Hussein *et al.*, 2014). Just as has been previously reported that petroleum and its derivatives cause severe environmental problems (Akpoveta *et al.*, 2011a, 2011b; Akpoveta *et al*., 2012; Akpoveta *et al.*, 2018; Akpoveta, 2020; Medjor *et al.*, 2012; Medjor *et al.*, 2017; Medjor *et al.*, 2018), used petroleum-based

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lubricants collected from oil change in automobile engines are slow in degradation and promote a serious pollution problem when discarded directly into the environment. Lubricants can be largely divided into two groups, namely mineral oil base lubricants and synthetic lubricants. Mineral oils demand more frequent changes compared to synthetic oils. Lubricants are classified as synthetic when they are chemically blended with additives and have reduced impurities with less thickness than mineral oils. Lubricating synthetic oils are often applied in modern automobile engines. Synthetic oils are commonly used in Nigeria for automobile engines due to their advantages over mineral oils. Among these advantages include; less changes and wear on parts, stable viscosity even at high temperatures, exceptional engine protection and longer use cycle, excellent flow at low temperatures, less formation of deposits, and optimized fuel consumption. The most commonly used synthetic oils in Nigeria include; Total quartz, Mobil, Hardex, Hi-speed, Forte oil, Conoil, Zic oil, Castro oil, etc. Continuous usage of lubricating oil on running automobile engines requires routine changes due to aging of the oil occasioned by wear, as the oil loses its functionality over time. It is also understood that used engine oil contains some components that mix with the oil when the engine is worn. These include iron, steel, copper, lead, zinc, barium, cadmium, sulfur, water and ash. Used waste engine oil contains hazardous pollutant chemicals, so it is more harmful to the environment than crude oil, which can cause both short-term and long-term adverse environmental effects (Zitte *et al*., 2016). The used lubricating oil becomes potentially collectible waste oil from the automobile engine where it is applied, with no post-usage second value. The release of such waste oils into the environment poses a serious threat to human health and a hazard to the environment. Waste or used lubricating oil is a high-pollutant material that requires responsible management. Waste synthetic lube oil from automobile engines has the potential to cause environmental problems when directly discarded into the soil, surface water, water bodies, and even sewers, resulting in groundwater and soil contamination. The waste or used oil arises from the aging and degradation of the fresh oil after being contaminated with components from the engine surface such as carbon residue, gums, varnish, metals, ash, water, and other materials. The direct disposal of waste engine oil into the environment in Nigeria is very rampant and has become a common routine for both specialized mechanical automobile repair workshops and roadside mechanic artisans. This they do out of ignorance, oblivious of the attendant environmental and health implications. There are little or no organized disposal practices for waste engine oil in cities in Nigeria. Bamiro and Osibanjo (2004) estimated the total national used oil-generating capacity in Nigeria to be over 200 million liters per annum in 2004. Over 75% of this figure represented contribution from used crankcase engine oil, while the remaining 25% came from industry-based used oil. This shows the alarming nature of waste engine oil generation in Nigeria. The common disposal methods varied from indiscriminate spraying on land, to pouring on bushes, gutters, and surface water. There is no known waste oil recycling or treatment facility in the country, making it difficult to curb the indiscriminate disposal of waste engine oil.

Recycling of the used oil if properly harnessed will not only be beneficial in reducing the cost of engine oil, as it becomes renewable, but will significantly mitigate the pollution problems associated with indiscriminate disposal of used lubricating oils from automobile engines into the environment, due to their low biodegradability. The indiscriminate direct disposal of the used oil and its attendant environmental consequences can be abated if green approaches are employed in recycling the waste oil to its original base oil with a post-treatment value. Developing environmentally safe and long-term sustainable solutions for recycling used synthetic lubricating oil in Nigeria will help in addressing the sustainable development goals (SDGs) associated with good health, clean environment, environmental sustainability, and conservation. Therefore, the study examines the green recycling approach and waste-to-wealth conversion of two commonly used synthetic lubricating oils (Total Quartz and Hardex Oil) for automobile engines in Nigeria. An evaluation of the physicochemical characteristics and quality index of the recovered base oil from the green recycling process to ascertain its functionality for automobile engine applications is also of research interest in this study. Consequently, the objective of this paper is to evaluate the physicochemical characterization and elemental composition of used, recycled, and fresh lubricating engine oils of Total and Hardex brands.

## MATERIALS AND METHODS

*Sample Collection:* Used Total quartz and Hardex synthetic lubricating oil were collected on the spot from servicing workshop centers in Asaba, Delta State, Southern Nigeria, during routine oil changes from automobile engines of vehicles. Vehicles for Total oil change were Toyota Camry, 2014 model with an estimated oil usage millage of 3000km, Toyota Rav4 2010 model with an estimated oil usage millage of 2500km, and Toyota Corolla 2012 model with an estimated oil usage millage of 3500km. While those for Hardex oil change were a Hyundai Salon car, a 2012 model with an estimated oil usage millage of 3300km, Kia Optima 2010 model with an estimated oil usage millage of 3000km, and a mercedez Benz C 200 2010 model with an estimated oil usage millage of 3500km. Fresh Total and Hardex oil were purchased from the manufacturing company distribution outlets in Asaba, Delta State. The brand of engine oil used in this study is the Total quartz 5000 SL 2-W-50W and Hardex quartz 5000 SL 20W-50W.

*Materials and Apparatus:* Nitric acid, Hydrochloric acid, Diethyl ether, Potassium hydroxide, Tetrahydrofuran, Propan-2-ol. Ethanol, Hydrometer, Viscometer, Furnace, Gen Lab Oven, MS-H280-pro Magnetic stirrer, Thermometer, Rotary evaporator, Weighing balance, HH-SWater bath, Atomic Absorption Spectrophotometer (Agilent technologies 55A model).

*Treatment, Recycling, and Recovery of Spent Engine Oil:* All samples for Total oil collected from different vehicles were bulked together to give a uniform representative sample for the used Total oil, with the same applying to Hardex oil. Oil recovery was achieved following procedures adopted by Misozu *et al.,* (2018); with some modifications for optimization of the base oil recovery. 150 g of potassium hydroxide pellet was weighed and dissolved in about 900 ml of distilled water and made up to 1000 ml. 300 ml of prepared KOH solution was boiled to $85^0$C. 100 g of the spent engine oil sample was dissolved in the boiled KOH solution in a separating funnel and agitated for a homogenous mixture. It was left to settle and the aqueous portion poured out into a conical flask leaving the sludge behind. The sludge portion left in the separating funnel was subjected to the same treatment again with another 300 ml boiled KOH at about $85^0$C to extract more aqueous components containing the purified oil. The aqueous portion obtained from the spent lubricant engine oil was then combined and subjected to solvent extraction using a blend of 50 ml tetrahydrofuran and 50 ml propane-2-ol for optimized solvent extraction efficiency. This results in the formation of two distinct layers, which are the aqueous component and the solvent containing the treated oil. The non-aqueous phase was then separated from the aqueous phase. This process was repeated three times with the aqueous phase to ensure that all treated oil trapped in the aqueous phase was recovered. The solvent extracted from the aqueous solution was then removed from the treated oil through the process of atmospheric distillation at $115^0$C with the aid of a rotary evaporator.

*Determination of Oil physicochemical characteristics:* The color of the lubricant oil was determined in the laboratory in open bright light condition by visual inspection. The specific gravity was measured directly using a hydrometer. Flash point was determined using the method outlined by Abhilash *et al.,* (2018). The standard test method for the pour point of crude oil was adopted for the determination of the pour point (ASTM D97-17b; https://ayalytical.com/methods/astm-d97). Kinematic viscosity and viscosity index were determined by adapted methods of Mohammed *et al.,* (2017). Carbon residue was determined using the standard testing method as reported (ASTM D 482, 2003). The Acid value was determined by the method of Dijkstra, (2016); while the total acid number was determined by standard outlined procedures and method (ASTM D664-24, 2024**)**. Ash content was determined following procedures adopted by Elaf *et al.,* (2019).

Metals (Iron, Copper, Aluminum, Cadmium, Zinc, Silicon and Manganese) content were determined using Atomic Absorption spectrophotometer, following procedures adopted by Elaf *et al.,* (2019) and Akpoveta (2020).

*Quality Control:* All reagents used were of pure analytical grade as purchased. The instruments employed were properly calibrated before analysis to avoid instrumental measurement errors. Fresh new oil brands were used as quality index references for evaluating the characteristics of the used oil and recycled oil. The solvent for the recycling process was carefully distilled out completely at the vapor pressure point of the solvent to avoid interference and mixing of the solvent component with the recovered base oil. Statistical analysis using ANOVA was employed for data treatment.

## RESULTS AND DISCUSSION

Results of physicochemical characterization of used oil, recycled oil, and fresh engine oil for both brands (Total quartz and Hardex oil) are presented in Tables 1 and 2. Characterization of both used and recycled oil was done comparatively to the fresh oil brand, to ascertain the effectiveness of the recycling process, as well as to measure the success of the green process. All chemicals used were isolated from the final base oil product recovered, making it a green recovery process. On visual inspection, black color was observed for the used oil of both brands (Fig. 1 and 4), when compared to the fresh Total oil (brownish pink, Fig. 2) and fresh Hardex oil (light yellow, Fig 5.) The black coloration of the used engine lubricant oils indicates the presence of impurities from the engine, and deterioration of the oil additives, due to the running engine at high temperature over time. The recycled Total oil showed a dull yellow coloration as can be seen in Fig. 3, while a light wine color is observed for the recycled Hardex oil as seen in Fig. 6. The disappearance of blackish coloration and closeness of color observed in the recovered base oil after treatment to the Fresh oil indicates significant removal of impurities from the spent oils by the green recycling process used. Blending the base oils with the right additives could restore its original color as seen in the fresh oil brands.

**Table 1:** Physicochemical characteristics of used Total oil, recycled Total oil and fresh Total oil samples

| **S/N** | **Total oil samples** | **Color** | **Flash point** | **Pour point** | **Carbon residue ($g/dm^3$)** | **Ash Content** wt. %. | **Specific gravity ($g/dm^3$)** | **Viscosity index Pa.s** | **Kinematic viscosity Pa.s** | **Acidic value g/KOH/g** | **Total acid Number g/KOH/g** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Used oil | Black | $314^0$C | $-27^0$C | 4.20±0.02 | 1.32 | 0.82±0.06 | 82.40±0.02 | 7.34±0.01 | 0.72±0.02 | 3.70±0.02 |
| 2 | Recycled oil | Dull yellow | $201^0$C | $-18^0$C | 0.16±0.01 | 0.04 | 0.86±0.03 | 61.00±0.01 | 4.25±0.02 | 0.23±0.03 | 1.50±0.01 |
| 3 | Fresh oil | Brownish pink | $280^0$C | $-12^0$C | 0.24±0.04 | 0.02 | 0.71±0.02 | 94.80±0.02 | 11.01±0.01 | 0.10±0.02 | 0.70±0.04 |

**Table 2:** Physicochemical characteristics of used Hardex oil, recycled Hardex oil, and fresh Hardex oil samples

| **S/N** | **Hardex oil samples** | **Color** | **Flash point** | **Pour point** | **Carbon residue g/dm3** | **Ash Content** wt. %. | **Specific gravity g/dm3** | **Viscosity index Pa.s** | **Acidic value g/KOH/g** | **Total acid Number g/KOH/g** | **Kinematic viscosity Pa.s** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Used Oil | Black | $341^0$C | $-32^0$C | 3.74±0.01 | 1.35 | 0.75±0.02 | 75.60±0.01 | 0.75±0.01 | 3.80±0.01 | 6.51±0.02 |
| 2 | Recycled Oil | Wine | $200^0$C | $-23^0$C | 0.19±0.03 | 0.03 | 0.81±0.04 | 80.90±0.02 | 0.18±0.03 | 1.61±0.02 | 5.24±0.03 |
| 3 | Fresh Oil | Light yellow | $285^0$C | $-14^0$C | 0.22±0.01 | 0.01 | 0.70±0.01 | 90.32±0.04 | 0.10±0.02 | 0.70±0.03 | 10.31±0.01 |

**Fig. 1**: Used Total oil

**Fig. 3**: Recycled Total oil

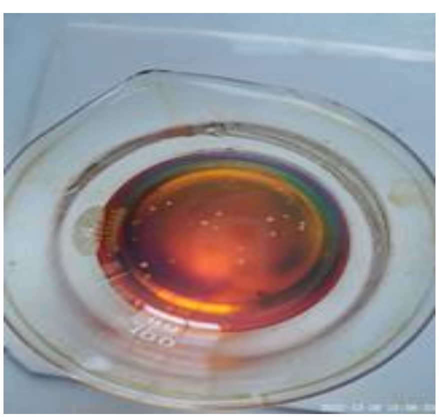

**Fig. 2:** Fresh Total oil

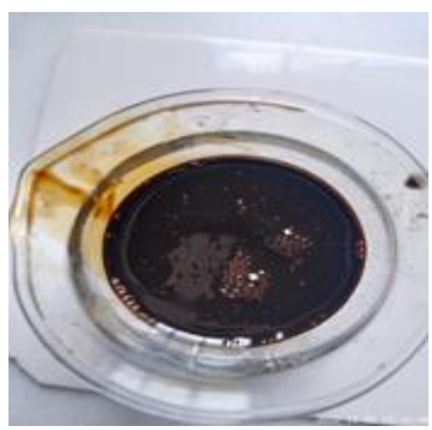

**Fig. 4**: Used Hardex oil

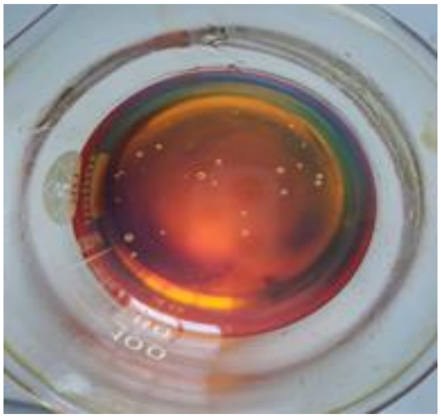

**Fig. 5**: Hardex fresh oil

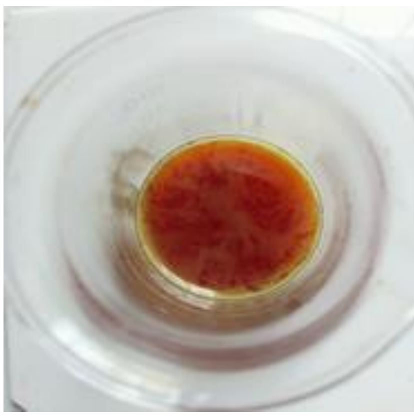

**Fig. 6**: Recycled Hardex oil

The flash point value is observed to be 314$^0$C, 280$^0$C, and 201$^0$C in the used Total oil, fresh Total oil, and recycled Total oil respectively; as seen in Table 1. Flash point is the minimum temperature at which the vapor above an oil will ignite when in contact with an ignition source. Having a high flash point indicates low flammability. The spent oil has a flash point of 314$^0$C which was significantly higher than the fresh oil with a value of 280$^0$C. A high flash point indicates less flammability and volatility of engine oil, which was greater in the spent oil due to the presence of non-volatile solute impurities and breakdown of additives occasioned by long usage of the oil in the engine. The much lower value of 201$^0$C observed in the treated oil is due to the removal of all non-volatile components as sludge during the green recycling process. The same trend is seen in Table 2 for the characterized flash point values obtained on the Hardex oil samples (Used Hardex oil- 341$^o$C, Fresh Hardex oil- 285$^0$C, and Recycled Hardex oil- 200$^0$C). Further post-recycling processes are required to improve the flash point property of the recycled base oils to a comparable state as observed in their fresh oil brands. The reduction in the flash point temperature after treatment is similar to the results obtained by Abhilash *et al*., (2018), using acid treatment on different spent lubricating oils. The trend here also correlates to that observed by Abdulaziz and Mahmood (2016) in their study of the recovery of base oil from spent automobile oil using elementary and binary solvent extraction.

The characterized pour point values for Total oil samples (Used Total oil: -27$^0$C; Fresh Total oil: -12$^0$C, Recycled Total oil: -18$^0$C) and Hardex oil samples (Used Hardex oil: -32$^0$C; Fresh Hardex oil: -14$^0$C, Recycled Total oil: -23$^0$C) are as seen in Tables 1 and 2 respectively. The pour point of a lubricant is the lowest temperature at which the oil will remain flowing. The much lower pour point values observed for the used oils (Total and Hardex used oils, Table 1 and 2) when compared to their original fresh brands are due to the colligative effect of the solute impurities in the used oil which resulted in their freezing point depression. The increase in pour point values from the used oil after recycling (-27$^0$C to -18$^0$C for Total recycled oil, and -32$^0$C to -23$^0$C for Hardex recycled oil) is due to the removal of colligative solute impurities as sludge which caused a depression in the freezing point of the spent engine oil. The pour point temperature which is a very important property of lubricating engine oil is the temperature at which the oil can no longer flow due to high viscosity. At this temperature, the engine can no longer start or run. The pour point temperature helps in ascertaining the temperature range at which the engine oil functions optimally; as this is an important property for determining the functionality of engine oils in cold humid regions. Lower pour point temperature in lubricating engine oil is desirable, so the addition of high-quality pour point depressants as additives to the treated oil can further lower the pour point of the treated oil, making it more efficient. The result is similar to that observed by Abdulaziz and Mahmood (2016) in their study of the recovery of base oil from spent automobile oil using elementary and binary solvent extraction.

The carbon residue present in the used Total oil sample, fresh Total oil and recycled Total oil was found as 4.20 g/dm$^3$, 0.24 g/dm$^3$, and 0.16 g/dm$^3$ respectively, as seen in Table 1. On the other hand, carbon residue was found to be 3.74 g/dm$^3$, 0.22 g/dm$^3$, and 0.19 g/dm$^3$ in used Hardex oil sample, fresh Hardex oil, and recycled Hardex oil respectively, as seen in Table 2. The higher values observed for the used oils when compared to their fresh brands (Tables 1 and 2) are due to the presence of carbonaceous impurities arising from both internal and external pollutants around the running engine; as well as aged additives in the oil. Hameed *et al.,* (2017) reported that high carbon residue in spent lubricating engine oil is due to internal pollutants that resulted from deterioration of additives in the oil, as well as external pollutants from dust and engine friction products. A reduction in the concentration of carbon residue was observed, as seen in Tables 1 and 2 (4.20 to 0.16 g/dm$^3$ for Total recycled oil, and 3.74 to 0.19 g/dm$^3$ for Hardex recycled oil), on recovery of the base oils from their used forms. This reduction is due to the removal of impurities existing as carbonaceous sludge materials.

The carbon residue of lubricating oil gives an indication of the propensity for that oil to further form carbonaceous residue under thermal conditions. The carbonaceous residue is known as carbon residue and it is also often referred to as coke or thermal coke.

The result and trend observed from the determination of carbonaceous residue in this study are similar to the report of the study by Elaf *et al*., (2019) in his determination of carbon residue, ash content, and concentration of heavy metal in virgin and spent Iraqi lubricating oils. The ash content is observed to be 1.32 wt.% for used Total oil, 0.02 wt.% for fresh Total oil, 0.04 wt.% for recycled Total oil; and 1.35 wt.% for used Hardex oil, 0.01 wt.% for fresh Hardex oil, 0.03 wt.% for recycled Hardex oil, as seen in Tables 1 and 2. The ash content is an important index in evaluating the purity of engine oils. The higher the ash content, the lower the purity of the oil and vice-versa. A low percentage of ash content in oil indicates its high purity processing. It is observed that ash content increased significantly when both oils were used at prolonged mileages (0.02/0.01-1.32/1.35 wt.%), and then reduced drastically after green recycling (1.32 to 0.04 wt.% for Total recycled oil, and 1.35 to 0.03 wt.% for Hardex recycled oil), as seen in Tables 1 and 2. The increased ash content is due to contributions from the internal pollutants and damaged additives in the oil due to prolonged aging, as well as external pollutants arising from dust and engine friction products. This position is supported by the report of 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. The reduction in ash content after recycling is due to the removal of extraneous contents as sludge, and eradicated immiscible components from the solvent extraction phase.

The determination of specific gravity for both oil brand samples showed increase in values when both oils (Total/Hardex) were used at prolonged mileages (0.71/0.70-0.82/0.75 wt.%), with further slight increase after green recycling (0.82 to 0.86 wt.% for Total recycled oil, and 0.75 to 0.81 wt.% for Hardex recycled oil), as seen in Table 1 and 2. The chemical composition and overall components that make up the oil influence the specific gravity of engine lubricating oils. Compositional changes brought about by oil deterioration after prolonged usage could account for the observed increase in gravity, even after recycling. The specific gravity of the recycled oil is in the same range as values reported for treated lubricating automobile oils of the same grade (Bridjanian and Sattarin, 2006; Sterpu *et. al.,* 2012).

The viscosity index was found as 82.40 Pa.s, 94.80 Pa.s and 61.0 Pa.s for used Total oil, Fresh Total oil, and recycled Total oil respectively, while 75.60 Pa.s, 90.32 Pa.s and 80.90 Pa.s were the observed viscosity index values for used Hardex oil, Fresh Hardex oil, and recycled Hardex oil respectively; as presented in Tables 1 and 2. It is seen that the viscosity index is quite higher in both brands of fresh oil (Fresh Total oil- 94.80 Pa.s, Fresh Hardex oil- 90.32 Pa.s) when compared to used oils (Used Total oil- 82.40 Pa.s, Used Hardex oil- 75.60 Pa.s) and even the recycled oil (Recycled Total oil- 61.0 Pa.s, Recycled Hardex oil- 80.90 Pa.s). A reduction in the viscosity index is due to the aging and deterioration of the oil over time as it is been used, which is an indication of reduced resistance to flow on the engine surfaces; a property of the oil which is inappropriate for the effective running of the engine. The recycled base oils require further additive blending and treatment to enhance their viscosity index, which is an important property for lubricating engine oils. The observed reduced viscosity index in both used oil brands agrees with the result of Ancelena *et al*., (2012) in their study of the regeneration of used engine lubricating oil by solvent extraction. The same trend is observed for the kinematic viscosity index results of both oil brands. Used Total oil, fresh Total oil, and recycled Total oil had kinematic viscosity values of 7.34 Pa.s, 11.01 Pa.s, and 4.25 Pa.s respectively, while kinematic viscosity values of 6.51 Pa.s, 10.31 Pa.s, and 5.24 Pa.s were recorded for used Hardex oil, Fresh Hardex oil, and recycled Hardex oil respectively; as presented in Tables 1 and 2. The observed trend is as explained for the viscosity index. Lubricity tends to decrease with reduced viscosity which affects engine performance.

Acid values determined for both oil brand samples (Total/Hardex) showed a significant increase in values after engine usage at prolonged mileages (0.10/0.10-0.72/0.75 g/KOH/g), with significant decrease in value after green recycling (0.72 to 0.23 g/KOH/g for Total recycled oil, and 0.75 to 0.18 g/KOH/g for Hardex recycled oil), as seen in Table 1 and 2. In a similar trend, total acid number for both oil brand samples (Total/Hardex) showed significant increase in values after engine usage at prolonged mileages (0.70/0.70-3.70/3.80 g/KOH/g), with significant decrease in value after green recycling (3.70 to 1.50 g/KOH/g for Total recycled oil, and 3.80 to 1.61 g/KOH/g for Hardex recycled oil), as seen in Tables 1 and 2. Acid value and Total acid number (TAN) are important quality indices of engine lubricating oil and are used as a guide in the quality control of lubricating oil formulations. It is also sometimes used to measure the extent of lubricant degradation. These two parameters measure the amount of acidity in lubricating oil samples. Total Acid Number (TAN) analyzes the amount of acidic components present in engine oil. The degree of depletion of oil additives, acidic contamination, and lubricant oxidation can also be evaluated from a determination of the acid number. At increasing temperatures, oxidation occurs, causing the formation of organic acids in the engine lubricating oils which affects the performance of the engine. Most times, oxidation over time and cumulative temperature effect can lead to a steady increase in acid number. High operating temperatures of the engine can also lead to the generation of increasing levels of weak organic acids. Gums and lacquers can be formed on engine metal surfaces which are undesirable for engine oils with high acid numbers. The high acid number also causes increased system corrosion. A combination of compounds with different corrosion properties also contributes to the acid number (Nadkarni, 2000). The high acidity observed in the used oil of both brands is due to redox reactions caused by the presence of impurities at high temperatures. The significant decrease in acid values after treatment to values close to those observed in their fresh oil brands shows a recovery of the oil characteristics in terms of its acid properties after recycling. It also indicates the effectiveness of the green recycling process.

**Table 3:** Elemental composition of spent oil, fresh oil and recycled oil samples

| S/N | Total oil samples | Fe (ppm) | Cu (ppm) | Al (ppm) | Cd (ppm) | Mn (ppm) | Zn (ppm) | Si (ppm) |
|---|---|---|---|---|---|---|---|---|
| 1 | Used Total oil | 14.84±0.04 | 17.83±0.01 | 22.44±0.07 | 3.11±0.01 | 78.42±0.02 | 174.63±0.01 | 3.14±0.02 |
| 2 | Recycled oil | 10.83±0.02 | 13.87±0.05 | 17.81±0.03 | 2.08±0.02 | 65.47±0.02 | 121.84±0.03 | 1.74±0.01 |
| 3 | Fresh Total oil | 1.78±0.01 | 4.78±0.08 | 15.21±0.01 | 1.27±0.03 | 59.41±0.01 | 110.21±0.05 | 1.89±0.04 |

**Table 4**: Elemental composition of spent oil, fresh oil and recycled oil samples

| S/N | Hardex oil samples | Fe (ppm) | Cu (ppm) | Al (ppm) | Cd (ppm) | Mn (ppm) | Zn (ppm) | Si (ppm) |
|---|---|---|---|---|---|---|---|---|
| 1 | Used Hardex Oil | 3.84±0.02 | 10.41±0.02 | 19.41±0.02 | 3.84±0.01 | 59.40±0.02 | 131.73±0.02 | 1.81±0.03 |
| 2 | Recycled Oil | 1.53±0.01 | 3.94±0.03 | 16.03±0.06 | 1.84±0.01 | 61.74±0.05 | 121.47±0.01 | 1.09±0.01 |
| 3 | Fresh Hardex Oil | 1.78±0.03 | 4.78±0.02 | 15.21±0.05 | 1.27±0.03 | 59.41±0.01 | 110.21±0.04 | 1.89±0.07 |

The results for the determination of the elemental composition of both oil brand samples are presented in Tables 3 and 4. Metal concentrations in used oil of Total brand (Fe:14.84ppm, Cu:17.83ppm, Al:22.44ppm, Cd:3.11ppm, Mn:78.42ppm, Zn:174.63ppm and Si:3.14ppm) were significantly higher than those in the fresh Total oil sample (Fe:1.78ppm, Cu:4.78ppm, Al:15.21ppm, Cd:1.27ppm, Mn:59.41ppm, Zn:110.21ppm and Si:1.89ppm) as seen in Table 3. The high value of the elements in the used Total engine lubricating oil is likely due to deposition and leaching of metals from the engine metallic surfaces due to friction and wear that resulted from the mechanical running of the engine. Reduced metal values in the recycled oil were found as Fe (10.83ppm), Cu (13.87ppm), Al (17.81ppm), Cd (2.08ppm), Mn (65.47ppm), Zn (121.84ppm) and Si (1.74ppm); when compared to the used oil (Table 3). The values were however still higher than those in the fresh Total oil (Table 3). Removal of metallic impurities that were chemically bound to sludge particles during the solvent extraction treatment process could have been responsible for the reduced metal levels in the treated oil. In the same manner, elemental determination in Hardex oil samples shows that all metals determined in the used Hardex oil were significantly higher than the metal content in the fresh Hardex oil. The values of metals in the used Hardex oil as presented in Table 4 are found as Fe (3.84ppm), Cu (10.41ppm), Al (19.41ppm), Cd (3.84ppm), Mn (59.40ppm), Zn (131.73ppm) and Si (1.81ppm); while metal values in the fresh oil are Fe (1.78ppm), Cu (4.78ppm), Al (15.21ppm), Cd (1.27ppm), Mn (59.41ppm), Zn (110.21ppm) and Si (1.89ppm). Metal values in the treated Hardex oil were determined as Fe (1.53ppm), Cu (3.94ppm), Al (16.03ppm), Cd (1.84ppm), Mn (61.74ppm), Zn (121.47ppm) and Si (1.09ppm); which are comparatively lower than metal values in the used oil (Table 4); except for manganese that was slightly higher. Leaching and erosion of metal components from the running engine are responsible for the observed increase in metal levels in the used oil, while removal of the metal impurities as sludge during the green recycling process accounts for the reduced metal levels after treatment. The high metal levels in the used oils underscores the need for treatment of used oil before disposal into the environment if necessary, to avoid the environmental consequence associated with heavy metal pollution. The metal contents in the treated oils reduced appreciably, but still require further treatment to enable more reduction of metal levels to reference values as seen in the fresh oil brands. This is necessary to ensure its applicability as rebranded lubricating oils from the recycled base oils; and also for safe disposal into the environment. The high values of metal concentrations present in both used oils and subsequent reduction after being subjected to treatment as seen in Tables 3 and 4 agree with the findings of Elaf *et al*., (2019) in their determination of carbon residue, ash content, and concentration of heavy metal in virgin and spent Iraqi lubricating oils. A summarized statistical analysis of all the data obtained showed a significant difference at a 95% confidence limit between reference values of data from fresh oil brands and the used oils, indicating significant deterioration of lubricating properties in the used oils. Statistical analysis of quality index data from both recycled oil brands relative to the fresh oil brands showed no significant difference at $p<0.05$; which suggests the effectiveness and success of the green recycling technique. Except for metals such as Fe and Cu in recycled Total oil only, all other metals in both recycled oils showed significant metal reduction on recycling, relative to their fresh oil brands. The percentage recovery of the oil was found to be 38% and 42% from 100ml of the spent Total and Hardex oil respectively after treatment. This shows a below-average recovery rate with about between 58-62% lost as sludge impurities. The percent recovery rate of oil from this study was smaller when compared to other similar studies (Ancaelena *et al*., 2012, Abdulaziz and Mahmood 2016). The treatment process therefore requires further improvement to enhance the oil recovery rate.

*Conclusion:* The treatment and recycling of the used oil from both brands is seen to improve the overall lubricating properties of the oils, enabling a post engine usage value. Recycling used engine oil will reduce the production cost of fresh lubricating oil brands if properly harnessed, bringing out the economic benefit of its regeneration and reusability, as well as preventing environmental pollution associated with its direct disposal. The findings show that the recycling process could enable rebranding for further reusability in automobile engine applications, therefore recycling of used engine oil should be encouraged due to its ecological and economic benefits. It is of both significant environmental and economic benefit for the establishment of recycling facilities using green processes for the regeneration of used engine oil in the country for further automobile applications.

*Declaration of Conflict of Interest:* The authors declare no conflict of interest in this study.

*Data Availability Statement:* Data are available upon request from the first author or corresponding author.

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