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Tribological Analysis of Molybdenum Disulfide (MOS_2) Additivated in the Castor and Mineral Oil Used in Diesel Engine

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Abstract: The lubrication phenomenon is used to reduce friction and wear between two rubbed surfaces, such as in engine and cutting processes. Different oils such as mineral oil and synthetic lubricant are being used for this purpose. With the passage of time, the demand of energy will get higher and natural resources and mineral lubricants will be diminished. Furthermore, biodegradation of mineral oil is too slow, and it remains on the surface of earth for a long period of time, creating atmospheric pollution. To overcome this problem, bio lubricants are being used to reduce wear and friction due to their high biodegradability. In order to increase the lubrication capacity of castor oil, a 1 wt. % concentration of MoS_2 nanoparticles was added to the base oil. Moreover, to stabilize the additives, 2 wt. % gum arabic and 1 wt. % Oleic acid (OA) were also added. Then, multiple tests, such as of physicochemical properties, Fourier transform infrared (FTIR), and atomic absorption spectroscopy (AAS) of synthetic lubricant and conventional lubricant, were carried out before and after the operational running of 100 h on the diesel engine for each lubricant at 75% throttle, 2200 rpm, and 50% of total load. The results show that the behavior of newly prepared MoS_2-based synthetic lubricant possessed higher characteristics in some physicochemical properties and was marginally lacking in other properties compared to shell lubricant. The flash point and specific gravity of synthetic lubricant were decreased compared to shell oil, with relative decreases of 0.27% and 1.15%, respectively. Ash and kinematic viscosity of 40 °C had a relative increase of 4.17% and 1.61%, respectively, and at a kinematic viscosity of 100 °C, the pour points and total base number (TBN) were relatively increased at 1.09%, 6.02%, and 1.38%, respectively, with respect to the properties of the shell lubricant. Moreover, this analysis evaluated that the reduction of wear and tear in synthetic lubricant regarding chromium (Cr), copper (Cu), and iron (Fe) was decreased by 21.12%, 3.39%, and 0.96%, respectively, but in the case of aluminum (Al) the wear and tear was marginally increased, at 1.17%, compared to shell lubricant. In the case of calcium (Ca) and zinc (Zn), the concentration was decreased by 3.59% and 17.41%, respectively. The FTIR analysis shows that all the peaks of the synthetic lubricant and shell lubricant were overlapping each other in the first three regions of the mid-IR spectra from 4000 to 1500 cm^{-1} and had the same functional groups—hydroxyl stretch (O-H), alkanes (C-H), carbonyls (C=O), aromatic amines (C-N), and alkyl halides (C-Br)—which were attached but fluctuating in the fingerprint region. The results show that shell lubricant can be replaced with MoS_2-based synthetic lubricant because the latter has superior friction reduction and load-bearing capability and can compete favorably with commercial shell oil in wear protection when additivated with MoS_2-based nanoparticles, and hence can be a good alternative for diesel engine oil.

Keywords: tribology; synthetic lubricant; MoS_2-based microparticles; Fourier transform infrared (FTIR); atomic absorption spectroscopy (AAS)

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1. Introduction

Tribology is the technological study of the various surfaces that interact in relative motion. The term 'tribology' was first used in 1967 by the Organization for Economic Cooperation and Development (OECD). The word 'tribology' is derived from the Greek word 'tribos', which means 'rubbing' [1]. In the domain of tribology, the coefficient of friction (COF) was defined. Many manufacturing industries have faced huge economic losses due to the rupture of manufacturing parts because of the failure of lubrication and wear. Friction is a major factor that causes wear and leads to energy loss. It is clear that tremendous techniques and methods have been brought into use to deal with friction. However, the lubrication technique was found to be the best to minimize the friction and wear parameters [2]. In the 21st century, the usage of engines in automobiles and in the industrial sector has been increased for power production and for different continual processes. In internal combustion (IC) engines, lubrication is a main tool being used to run and operate smoothly. Friction and wear are two key factors that are responsible for dissipating energy and failure of the system. Over the decades, mineral lubricating oils have been used to overcome friction and wear. Prices of crude oil are increasing day by day. The human population is increasing exponentially. Therefore, energy demand is also increasing [3]. In addition, mineral lubricants are being discarded into the environment after use. Due to their non-biodegradable nature, they remain on the surface of the earth and cause pollution. All of these factors have urged scientists to research bio lubricants due to their availability, economical rates, and specific biodegradable nature [4]. A lubricant is preferably used to lower the effect of friction and wear during the meeting of two surfaces. Different sorts of lubricants are being using in the market, such as liquids (oils) and semi-solids (grease), but the most commonly available lubricants are oil lubricants in the automotive industry [5]. A lubricant is considered good if it resolves tribological problems at elevated temperatures [6]. During the selection of lubricant, its environmental impacts and financial attainability are also determined [7]. Shear stability, cloud point, dynamic and kinematic viscosity, volatility, pour point, foaming characteristics, element content, flash point, density, ash, water tolerance, corrosiveness color, homogeneity, and elastomer compatibility are the 15 characteristics of lubricants in automotive engines that were recommended by research studies [8]. In the feature of biodegradability, it is imperative to note that vegetable oils, due the action of microorganisms, have 70 to 100% biodegradability. However, mineral oils have 15 to 35% biodegradability [9]. To alternate mineral oils with different bio-lubricants, the former properties need to be upgraded and enhanced. There are various modification techniques, like esterification/transesterification, selective hydrogenation, estoile formation, epoxidation, and the addition of different additives in the base oil to enhance their lubricating properties, such as oxidation and thermal stability. When contemplating the performance ability and durability of a lubricant, a very small amount of additives is added to the base oil. The basic role of these additivated lubricants is to enhance the tribological behavior of the rubbing surfaces. For the refinement and reformation of the friction and wear of contact surfaces, the surface additives have significant importance in tribology [10]. Contacts under high loads are cam followers and piston ring liners, which operate under boundary lubrication and mixed lubrication regimes, and are places where friction modifiers are used to reduce friction. Anti-wear additives effect tribological behavior of metal surfaces under lubrication [11]. For good lubrication, karana oil and rapeseed oil could be considered for improving engine performance characteristics. On the other hand, castor oil and palm oil have been used to reduce engine emissions [12]. Exhaust emissions emitted by the two-stroke gasoline engines pollute our environment. A lubricant oil formed from castor oil would reduce smoky emissions from 50 to 70% at a 1% oil–fuel ratio. The oil produced from castor oil acts as a smoke pollution reducer [13]. A comparison of the tribological properties of pure castor oil and 20W-50 high-quality crankcase oil was studied. The experiments were performed on four ball testers. This study concluded that castor oil lowers friction compared to conventional oil [14]. Different studies have explained that by using MoS_2 in 0.25%, 0.5% 0.75%, 1%, 1.25%, and 1.5% quantities in palm oil, it was shown that anti-wear and extreme pressure properties were improved [15]. By using different concentrations of CuO and MoS_2 in castor and molding oil, the tribological properties of the CK50 steel alloy and 2024-T4 aluminum alloy were analyzed. A pin-on-the-disk test was carried out to find the coefficient of friction and wear rate. Gum arabic was utilized as a surfactant to avoid the suspension problems of nanoparticles in base oil. The results demonstrated that using 1% by weight of MoS_2 in castor oil minimized the coefficient of friction [16]. The aim of this research is to replace conventional lubricants with synthetic lubricants because the latter have a biodegradable nature, are more economical, and pollute less compared to the former.

2. Materials and Methods

For the tribological analysis of synthetic lubricant with respect to conventional lubricant, the following materials and methods were adopted.

2.1. Materials

2.1.1. Base Oil

To form the synthetic lubricant, a base oil was used. There are multiple edible and non-edible bio-oils available commercially [17,18]. Due to the significant properties of castor oil compared to other oils, it was selected as the base oil to form the synthetic lubricant. The properties of castor oil are given below in Table 1, which shows that castor oil possesses higher viscosity, a lower pour point, and a maximum pH of 7.203, compared to other oils [19–21].

Table 1. Physiochemical properties of castor oil.

Properties	Castor Oil
Density (kg/m^3)	962.8
Fire point (°C)	335
Flash point (°C)	298
Cloud point (°C)	15.8
Specific gravity	0.9628
Viscosity (mPa·s)	686.26
Pour point (°C)	−33

2.1.2. Comparison of Castor Oil with Other Oils

Physicochemical characterization of castor oil revealed that the low acid value (0.91 mgKOH/g) and iodine value (83.5 gI_2/100 g), and the relatively high specific gravity (0.959) density (962.8 kg/m^3), pH value (7.203), and saponification (179.4 mgKOH/g) value, make it superior to other oils, as shown in Table 2 [20].

Table 2. Comparison of castor oil with other oils, "adapted with permission from Ref. [20]. 2011, N.A. Fakhri".

Properties	Units	Castor Oil	Rubber Seed Oil	Waste Cooking Oil	Canola Oil	Olive Oil	Sunflower Oil
Specific gravity at 30 °C		0.956	0.945	0.801	69.998	0.8883	0.8833
Acid value	(mgKOH/g)	0.91	37.80	3	0.650	3.220	0.524
Flash point	(°C)	197	152.0	305	217	210	93.3
Saponification value	(mgKOH/g)	179.52	255.25	186.3	178	193	195
Iodine value	(gI_2/100 g)	83.5	23.81	57.08	162.86	80.57	125.21
Kinematic viscosity at 40 °C	cSt	321.0	380.65	49.84	38.6	49.998	43.063
Pour point	(°C)	−33	106.0	−7.8	−18	3	−36
pH value		7.203	7.1	5.5	6.201	6.693	6.301

2.1.3. Shell as a Standard Lubricant

The conventional lubricant named shell helix HX3, a multi-grade motor oil, with a viscosity grade of 20W-50, was taken as a standard for the experiments. The physiochemical properties of shell lubricant are given in Table 3.

Table 3. Physiochemical properties of shell lubricant.

Properties	Shell Oil
Density (kg/m^3)	888
Flash point (°C)	215
Specific gravity	0.9628
Viscosity (mPa·s)	161
Pour point (°C)	−27

2.1.4. Additive

There are multiple additives available and recommended by researchers. The additive molybdenum disulfide (MoS_2) was used for this research. The purpose of the additives is to increase the lubrication between two rubbed surfaces and reduce the friction and wear between them [22]. To enhance the performance of the lubrication, MoS_2 was selected to reduce the wear and tear of the lubricant in the engine [17]. This additive was used in the form of nanoparticles [23]. The specifications of these nanoparticles are mentioned in Table 4, which indicates that the MoS_2 particles were imported from Sigma Aldrich. These particles were available in the form of nanoparticles and their average size was 60 nm. The color of these particles was black.

Table 4. Specifications of additive MoS_2.

Suppliers Information	MoS_2
Company	Sigma Aldrich
Grade standard	Electron grade
Purity	99%
Average particle size (nm)	60
Appearance	Black powder

2.1.5. Surfactants

When MoS_2 nanoparticles were added to castor oil using a magnetic stirrer and ultrasonic sonication bath under an examination of 72 h, it was found that the nanoparticles accumulated at the bottom of the bottle. The reason for this behavior was found to be that these particles have van der Waals forces, which keep them attracted to each other, and ultimately these particles formed an amalgamation shape and resided at the bottom of the bottle [24]. To overcome this problem of dispersion stability of MoS_2-based particles in castor oil, the surfactant, gum arabic, and oleic acid were used [25]. When oleic acid and gum Arabic were added to castor oil along with the nanoparticles, they played an important role to keep these particles dispersed in the base oil [17].

2.1.6. Specifications of Diesel Engine

Table 5 represents the specifications of the diesel engine used for experimentation. Diesel engine model number Lombardini-15 LD 315 was selected for the operational running of 100 h under 75% throttle, 2200 rpm, and 50% total load. This engine has 1 cylinder and has 1.2 L of oil sump capacity, with an oil consumption of 0.0030 L. The prepared synthetic lubricant based on MoS_2 was added to the engine oil sump tank and was run for 100 h. After testing the synthetic lubricant, similarly, shell lubricant was also run in the diesel engine for 100 h.

Table 5. Specifications of the diesel engine.

Description	Specifications
Engine model	Lombardini–15 LD 315
Cylinders	1
Displacement	315 cm^3
Bore	78 mm
Stoke	60 mm
Compression ratio	20.3:1
Max. torque @ rpm	15 Nm @ 2400
Oil consumption	0.0030 L
Oil sump capacity	1.2 L
Dynamometer attached	Hydraulic dynamometer
Cooling system	Air cooled
Mode of injection	Direct injection
Dry weight	33 kg
Recommended battery	12/44 (V/Ah)

2.2. Methods

For making the blends and testing the synthetic lubricant, the following tests and procedures were followed step by step.

2.2.1. Formulation

For the formation of the blends, a beaker of 1200 mL, an analytical balancer, a heating and magnetic stirrer, an ultrasonic bath sonicator, and glass storage jars were used in the Chemical Engineering lab of UET Lahore. According to the base oil capacity of the diesel engine, 1.2 L castor oil was taken. Then, MoS_2-based nanoparticles (1% by weight) were weighed on the analytical balancer and added to the castor oil. The beaker containing castor oil was put on the heating and magnetic stirrer [26]. The hot-plate temperature was maintained at 60 °C and the beaker was kept on it for 15 min as shown in Figure 1. Furthermore, beakers were kept in the sonicator bath at 50 °C for 20 min and then the blend was poured into the glass storage jar to check the stability of the nanoparticles, as shown in Figure 2 [27]. After the formation of the blends, the dispersion stability of the MoS_2-based synthetic lubricant was examined and an agglomeration of nanoparticles at the bottom of the beaker was observed. In order to resolve this problem, two surfactants, oleic acid (1% by weight) and gum arabic (2% by weight), were added to the blend to make the nanoparticles stable in the formation of the synthetic lubricant. Hence, with the addition of gum arabic and oleic acid, the issue of dispersion stability was resolved [25].

2.2.2. Equipment Used

The physicochemical properties were determined by using different kinds of apparatuses. The kinematic viscosity of the oil samples were measured using an Ostwald viscometer (ASTM D-445) at 40 °C & 100 °C. Ash content was determined by AOCS (method Ba 5a-49). The pour point and flash point were determined by using the temperature assembly with the ASTM D-97 and ASTM D-93 methods, respectively. Specific gravity and TBN were determined by using the ASTM D792 and ASTM D2896-11 methods, respectively. Similarly, different machines were used for the formulation of blends and to analyze the tribological behavior of the lubricants. In order to make the blends, an IKA heating and magnetic stirrer RH Basic 2 and an IABECH ultrasonic bath sonicator (LTUSB) were used. Moreover, for FTIR analysis to determine the qualitative study of the structural peaks of the synthetic and conventional lubricants, a Perkins Spectrum Two NIRM (near infrared reflective module) was used. Furthermore, for AAS analysis of different elements, Agilent 200 Series AA (240FS AA) was used.

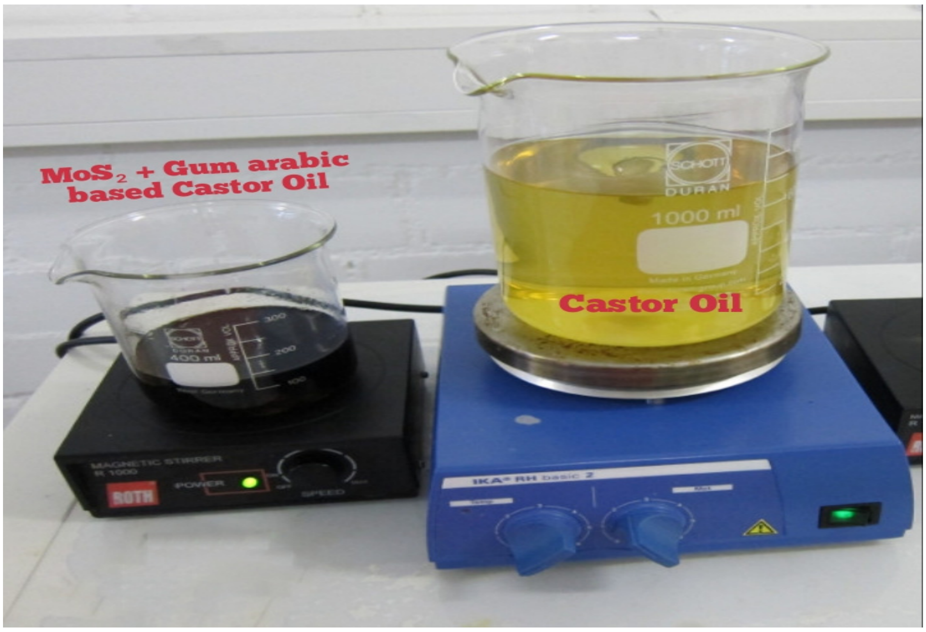

Figure 1. Formation of blends of synthetic lubricant on the magnetic stirrer.

Figure 2. During the blends formation of synthetic lubricant, two beakers were kept into Sonicator Bath for 20 min at 50 °C.

2.2.3. Testing of Fresh MoS_2-Based Synthetic and Shell Lubricants

For the determination of physicochemical properties such as kinematic viscosity at 40 & 100 °C, pour point, flash point, ash, total base number (TBN) and specific gravity of the synthetic lubricant and as well the conventional lubricant, samples of 500 mL of each lubricant were prepared [28]. For calculating the above-mentioned properties, the labs of the Chemical Engineering, Petroleum Engineering, Environmental Sciences, and Polymer Engineering departments at UET Lahore were used. Furthermore, for the investigation of elements such as iron (Fe), copper (Cu), chromium (Cr), zinc (Zn), calcium (Ca), and aluminum (Al) in the fresh MoS_2-based synthetic lubricant and fresh shell-based conventional lubricants, the experiments were conducted on an atomic absorption spectroscopy (AAS) machine [29,30]. Moreover, for the identification of tribological behavior of both fresh synthetic as well as conventional lubricants, the experiments were performed on a

Fourier transform infrared (FTIR) machine [31]. Both of these tests were carried out at the Humanitarian Sciences department of City Campus, UET Lahore.

2.2.4. Experimentation of Fresh Synthetic and Conventional Lubricants

After the testing of fresh MoS_2-based synthetic lubricant and fresh shell-based conventional lubricant, the prepared blend of fresh MoS_2-based synthetic lubricant was poured into the oil sump tank of the diesel engine and the diesel engine was operated for 100 h at 2200 rpm and 50% total load. Similarly, shell-based conventional lubricant was also added to the oil sump tank of the diesel engine for 100 h. After running on the engine, the physicochemical properties, FTIR, and AAS of the used biolubricants were calculated again and their results were compared for the analysis of tribological behavior [32,33].

2.2.5. Testing of Used MoS_2-Based Synthetic and Shell Lubricants

After the experimentation of 100 h of operational running of each lubricant in the diesel engine, assessments of the used samples of both lubricants were again carried out for the determination of their physiochemical properties, such as kinematic viscosity at 40 & 100 °C, pour point, flash point, ash, total base number (TBN), and specific gravity. Furthermore, these samples were taken for the same elemental based analysis, called atomic absorption spectroscopy (AAS). In the last, these used lubricants underwent the identification of structural behavior to understand the tribological-based changes in these lubricants by using Fourier transform infrared (FTIR) spectroscopy.

2.2.6. Flow Chart Diagram of Methodology

Figure 3 highlights the flow chart of the methodology to understand the complete research. First of all, the synthetic lubricant was prepared on the magnetic stirrer and in a sonication bath by adding the nanoparticles of MoS_2 and surfactant in castor oil. Then, the physiochemical properties of the prepared synthetic lubricant and the conventional lubricant were calculated. Furthermore, after discovering the properties of the synthetic lubricant and the conventional lubricant, on the basis of these properties the operational running hours of the engine were decided. After the completion of the running hours, the synthetic lubricant was again taken to the labs for the testing of physiochemical properties, Fourier transform infrared spectroscopy, and atomic absorption spectroscopy. In the last, a comparison of synthetic lubricant with shell lubricant before and after engine running was conducted.

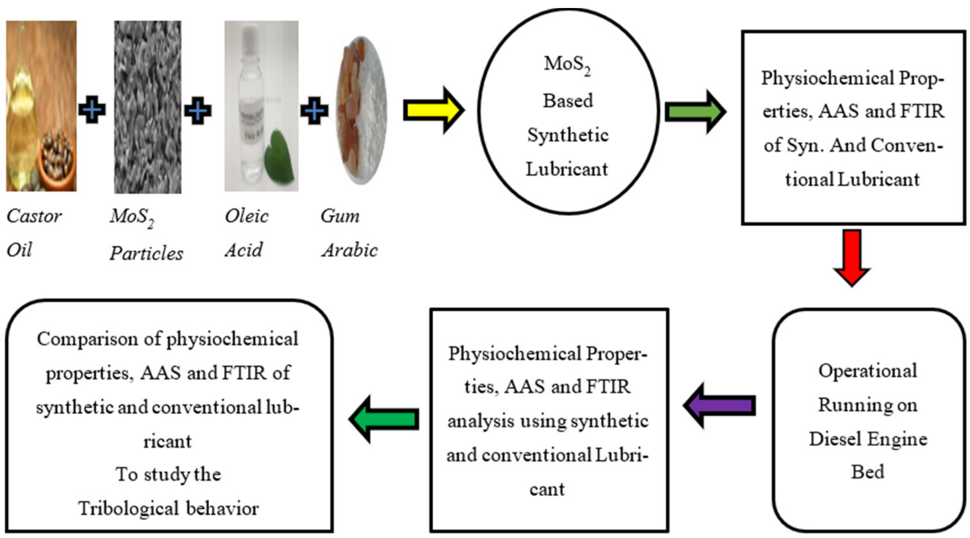

Figure 3. Complete flow chart of methodology.

3. Results and Discussion

3.1. Physicochemial Properties

The physicochemical properties of the MoS_2-based synthetic lubricant and shell-based conventional lubricant were determined by running both lubricants in the diesel engine to check the tribological performance of the former against the latter. Figure 4 represents the comparison of physicochemical properties of fresh and used synthetic lubricant with fresh and used shell lubricant.

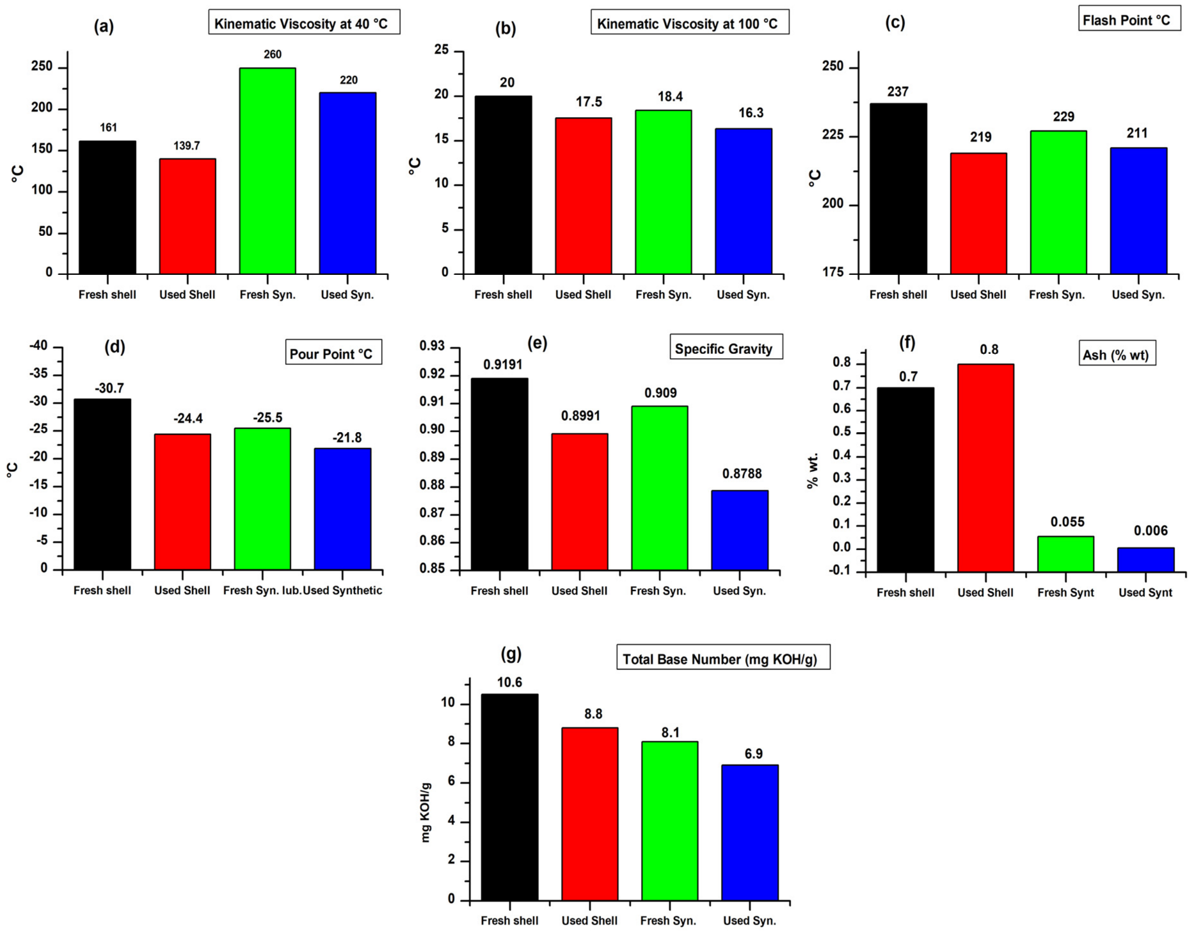

Figure 4. Comparison of physicochemical properties of fresh and used synthetic lubricant with conventional shell lubricant. (**a**,**b**) represent kinematic viscosity at 40 °C & 100 °C respectively. (**c**) represents the comparison of flash points of lubricants. (**d**) represents the pour points. (**e**) represents the specific gravities. (**f**) shows the ash contents of both lubricants. (**g**) indicates the TBN of conventional and synthetic lubricants.

3.1.1. Kinematic Viscosity

Kinematic viscosity is defined as the ratio of the dynamic viscosity to the density of the fluid. The kinematic viscosity decreased with increasing temperature at 40 °C. Figure 4a shows that the shell lubricant kinematic viscosity decreased from 161 cSt to 139.7 cSt, with a relative decrease of 13.6%. On the other hand, the kinematic viscosity of the MoS_2-based synthetic lubricant also decreased from 250 cSt to 220 cSt, with a relative decrease of 12%. It can be seen that the kinematic viscosity of the synthetic lubricant was higher than that of the shell lubricant, with a relative increase of 1.61% at 40 °C. Similarly, the kinematic viscosity of the shell lubricant decreased from 20 mm^2/s to 17.5 mm^2/s, with a relative decrease of 12.5%, as shown in Figure 4b. The kinematic viscosity of the MoS_2-based synthetic lubricant also decreased from 18.4 mm^2/s to 16.3 mm^2/s, with a relative decrease of 11.41%. The results show that the kinematic viscosity of the used synthetic lubricant was decreased marginally compared to the used shell lubricant by 1.2 °C at 100 °C.

3.1.2. Flash Point

Flash point is the lowest temperature at which an ignition source causes the vapors of the lubricant to ignite under specified conditions. Flash point is a very important factor in the physicochemical properties of a diesel engine. The flash points should be higher in order to avoid explosions and for other safety purposes. Figure 4c shows that the flash point decreased with increasing temperature in the diesel engine. The flash point of the shell lubricant decreased from 237 °C to 219 °C, with a relative decrease of 7.59%. On the other hand, the pour point of the MoS_2-based synthetic lubricant also decreased from 229 °C to 211 °C, with a relative decrease of 7.86%. The difference regarding the flash point of the fresh shell lubricant and the used shell lubricant was lower than the difference regarding the flash point of the fresh synthetic lubricant and the used synthetic lubricant, with a 0.27% difference. It is evident that the flash point of the used synthetic lubricant was slightly decreased compared to that of the used shell lubricant by 8 °C.

3.1.3. Pour Point

Pour point is defined as the lowest temperature at which a lubricant can flow under gravity in standard cooling conditions. Figure 4d shows that the pour point also decreased with increasing temperature. The pour point of the shell lubricant decreased from −30.7 °C to −24.4 °C, with a relative decrease of 20.52%. On the other hand, the pour point of the MoS_2-based synthetic lubricant also decreased from −25.5 °C to 21.8 °C, with a relative decrease of 14.50%. It can be stated that the pour point of the used synthetic lubricant decreased compared to the pour point of the used shell lubricant by 2.6 °C.

3.1.4. Ash

The amount of residual substances that are not volatilized from a sample when it is burned in the presence of sulfuric acid is determined in the sulfated ash test. The results are described in the form of graphs. Figure 4e shows that the ash increased with the passage of time in the diesel engine. The concentration of ash in the shell lubricant increased from 0.7 wt. % to 0.8 wt. %, with an increase of 12.5%. On the other hand, the ash of the MoS_2-based synthetic lubricant increased from 0.055 wt. % to 0.06 wt. %, with an increase of 8.33%. The difference regarding the ash of the fresh shell lubricant and that of the used shell lubricant was higher than the difference regarding the ash of the fresh synthetic lubricant and the used synthetic lubricant, with a relative increase of 4.17%. It can be noted that the used synthetic lubricants' ash value was better than the shell lubricant's ash by 0.794 wt. %.

3.1.5. Specific Gravity

The specific gravity is the dimensionless quantity that is defined as the density of the substance to the density of water at a specified temperature and pressure. Figure 4f shows that the specific gravity decreased with increasing temperature in the diesel engine. The shell lubricant's specific gravity decreased from 0.9191 kg/m^3 to 0.8991 kg/m^3, with a decrease of 2.17%. On the other hand, the specific gravity of the MoS_2-based synthetic lubricant also decreased from 0.909 kg/m^3 to 0.8788 kg/m^3, with a decrease of 3.32%. The difference regarding the specific gravity of the fresh shell lubricant and the used shell lubricant was lower than the difference regarding the specific gravity of the fresh synthetic lubricant and the used synthetic lubricant, with a relative decrease of 1.15%. It can be observed that the absolute value of the specific gravity of the used synthetic lubricant was marginally decreased as compared to the used shell lubricant by 0.0203 kg/m^3.

3.1.6. Total Base Number

The diesel engine's total base number is a characteristic that indicates how well the lubricant can mitigate the acidity created by combustion. The total base number actually shows the formation of acidity in the engine and defines the life of the lubricants. This acidity can be caused due to the bad condition of the fuel. Figure 4g shows that the total base number (TBN) decreased with the production of acid during the combustion in the diesel engine. The shell-based conventional lubricant's TBN decreased from 10.5 mg KOH/g to 8.8 mgKOH/g, with a relative decrease of 16.19%. On the other hand, the TBN of the MoS_2-based synthetic lubricant also decreased from 8.1 mgKOH/g to 6.9 mgKOH/g, with a relative decrease of 14.81%. It was revealed that the TBN of the used synthetic lubricant decreased compared to the TBN of the used shell lubricant by 1.9 mg KOH/g.

3.2. Fourier Transform Infrared (FTIR)

FTIR analysis uses infrared light to analyze materials to find organic, inorganic, and polymer-based components. Naturally, changes in the material's composition result from variations in the typical pattern of the absorbance bands. Unidentified materials can be defined and described using FTIR, impurities in a substance can be found, additions can be found, and decomposition and oxidation can be detected. Using Fourier transform infrared (FTIR) techniques, it is possible to determine whether a specimen has various functional groups. Figure 5 shows the comparison of four peaks of lubricants. Two peaks show the absorbance of the shell-based conventional lubricant and the other two peaks represent the MoS_2-based synthetic lubricant. Figure 5a considers the fresh synthetic lubricant and Figure 5b shows the used synthetic lubricant. Similarly, Figure 5c highlights the fresh shell lubricant and Figure 5d represents the used shell lubricant.

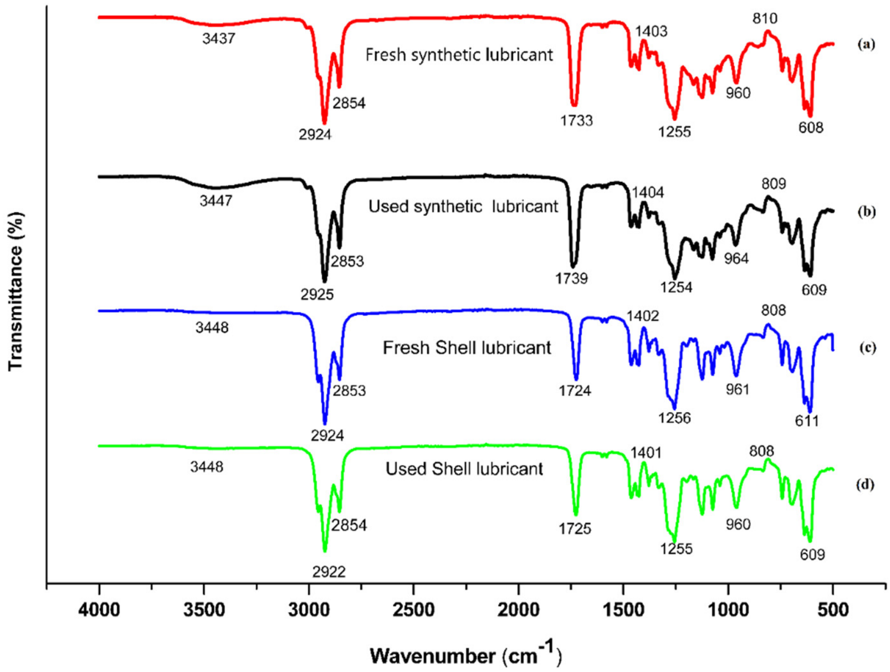

Figure 5. The comparison of peaks of the fresh and used synthetic lubricant with shell lubricant using FTIR to study the tribological behavior and understand their structures. (**a**) represents the FTIR peak of fresh synthetic lubricant. (**b**) represents the FTIR peak of used synthetic lubricant. (**c**) represents the FTIR peak of fresh shell lubricant. (**d**) shows the used FTIR peak of shell lubricant.

There are three spectra of FTIR analysis. First is far IR spectra, with a range of less than 400 cm^{-1}. The second spectra is called the mid-IR spectra, with a range of 400–4000 cm^{-1}. The third spectra is called Near IR spectra, with a range of 4000–13,000 cm^{-1}. Mid-IR spectra have a further four regions. The first region is called the single bond region (4000–2500 cm^{-1}), the second region is called the triple bond region (2500–2000 cm^{-1}), the third region is called the double bond region (2000–1500 cm^{-1}), and the fourth region is called the fingerprint region, with a range of 1500–500 cm^{-1}. Figure 5 shows the different regions of the synthetic lubricant and conventional lubricant. The first region had a narrow peak starting from approximately 3187–3628 cm^{-1}. If comparing this range with the IR chart, then it can be found that the hydroxyl stretch (O-H) functional group was attached to this first peak. The second narrow stretch peak shows that it had an alkanes (C-H) functional group. The third peak, at 2926 cm^{-1}, in the single bond region shows that it also had an alkanes group. The next two peaks, at 2882 cm^{-1} and 2856 $cm^{-1,}$ also contained an alkanes functional group. At the peak of 1733 cm^{-1}, there was a carbonyls (C=O) functional group attached. In the fourth fingerprint region at the peak of 1258 cm^{-1}, an aromatic amines (C-N) functional group was attached. In the last bottom peak, at 609 cm^{-1}, an alkyl halides (C-Br) functional group was attached.

3.3. Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) is for the identification of the different metals in the desired lubricants. For this purpose, an apparatus is used that operates on the flame and also a special wavelength of bulb is used. For the determination of a particular atom or element, the same kind of bulb is attached to the machine. AAS works on the principle of using the light of a specified wavelength at which certain atoms or elements can absorb the light. To perform these experiments, multiple salt solutions were prepared in 50 mL distilled water with 10 mL diluted HNO_3. These salts were ferrous sulfate ($FeSO_4$), chromium nitrate ($Cr(NO_3)_3$), aluminum chloride ($AlCl_3$), zinc nitrate ($Zn(NO_3)_2$), calcium chloride ($CaCl_2$), and cupric sulphate ($CuSO_4$) for iron (Fe), chromium (Cr), aluminum (Al), zinc (Zn), calcium (Ca), and copper (Cu). The calculated quantity of each salt, 0.25 mg, was added to the respective salt solution. Similarly, two samples for each lubricant at 5 ppm and 7 ppm, and 50 mL distilled water diluted with 10 mL diluted HNO_3, were prepared and a calculated amount (0.25 mg) of synthetic and conventional lubricants was mixed in these samples. In this way, for the identification of the desired metal, a separate sample was prepared with the specified salt at 5 ppm and 7 ppm. Then, on the basis of these standards, the mean absorbance of the respective metal in the synthetic and conventional lubricants was detected using the AAS machine, as shown in Table 6. After acquiring the values of the mean absorbance for the fresh and used lubricants, the values of the required ppm were calculated by dividing the sample weight by the volume of sample before digestion and multiplying the resulting value with the respective mean absorbance.

Table 6. Atomic absorption spectroscopy of different elements.

Atomic Absorption Spectroscopy of Different Elements						
Sr.	**Types of Elements**	**Types of Lubricants**	**Before Engine Operation**		**After Engine Operation**	
			Mean Absorbance	**ppm**	**Mean Absorbance**	**ppm**
1	Chromium (Cr)	Synthetic	0.000231	4.62	0.000111	2.220
		Conventional	0.000156	3.12	0.000107	2.14
2	Iron (Fe)	Synthetic	0.000111	2.22	0.000221	4.42
		Conventional	0.000107	2.14	0.000160	3.24
3	Copper (Cu)	Synthetic	0.000221	4.42	0.000280	5.74
		Conventional	0.000162	3.24	0.000160	3.20
4	Zinc (Zn)	Synthetic	0.000287	5.74	0.000122	2.44
		Conventional	0.000016	3.2	0.000120	2.41
5	Aluminum (Al)	Synthetic	0.000122	2.44	0.000329	6.58
		Conventional	0.000120	2.41	0.000123	2.46
6	Calcium (Ca)	Synthetic	0.000329	6.58	0.000111	2.22
		Conventional	0.000123	2.46	0.000107	2.14

To identify the contaminants as a result of wear and tear in the synthetic and conventional lubricants, the atomic absorption spectroscopy (AAS) technique was performed on these six elements: aluminum (Al), copper (Cu), iron (Fe), calcium (Ca), chromium (Cr), and zinc (Zn). Figure 6 shows the behavior of the six elements during the tribological analysis of the synthetic lubricant and the conventional lubricant using the atomic absorption spectroscopy (AAS).

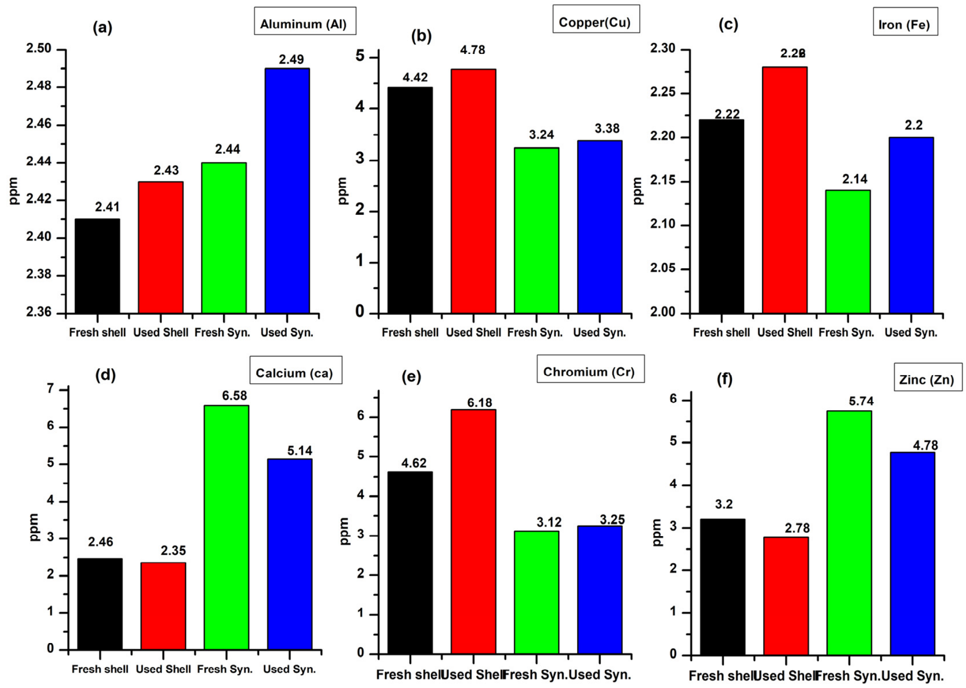

Figure 6. To compare and study the behavior of the different elements during the tribological analysis of the synthetic lubricant and the conventional lubricant using atomic absorption spectroscopy (AAS). (**a**) represents the AAS of Al. (**b**) represents the AAS of Cu. (**c**) shows the AAS analysis of Fe. (**d**) shows the behavior of Ca using AAS. (**e**) shows the AAS analysis for Cr. (**f**) represents the ASS of Zn.

3.3.1. Aluminum (Al)

As we know, aluminum (Al) metal is used for the manufacturing of important engine parts, e.g., pistons and journal jackets. Therefore, due to the wear and tear of engine pistons and journal jackets, their particles can be detected in lubrication oil. Figure 6a shows that the concentration of aluminum metal in the synthetic lubricant increased from 2.41 ppm to 2.43 ppm after 100 h running in the diesel engine. Similarly, the concentration of Al also increased in shell-based conventional lubricant from 2.44 ppm to 2.49 ppm after 100 h engine running. There is also an important point to be noted here: The percentage increase of wear and tear between fresh and used shell lubricant was 0.823%, whereas the percentage increase between fresh and used synthetic lubricant was just 2%. It is evident that synthetic lubricant observed marginally increased wear and tear of 1.1% compared to the shell lubricant.

3.3.2. Copper (Cu)

Copper is used for the manufacturing of engine bearings. The presence of copper particles in lubrication oil is due to the wear and tear of copper-based alloys used in engine parts. Figure 6b shows that the concentration of copper in the shell lubricant increased from 4.42 ppm to 4.78 ppm after 100 h. Similarly, the concentration of Cu also increased in the synthetic lubricant from 3.24 ppm to 4.32 ppm. It can be observed that percentage of increase wear in fresh and used shell lubricant was 7.53% and the percentage increase between fresh and used synthetic lubricant was just 4.1%. The results revealed that 3.39% wear and tear was lowered by using synthetic lubricant compared to shell lubricant in the case of copper.

3.3.3. Iron (Fe)

Iron (Fe) metal is used for the fabrication of piston rings, shafts, valves, bearings, and engine cylinders. Therefore, the presence of these particles in lubrication oil is due to the particles of iron-based alloys. Figure 6c shows that the concentration of iron in the synthetic lubricant increased from 2.220 ppm to 2.26 ppm. On the other hand, the concentration of Fe also increased in the shell-based conventional lubricant from 2.14 ppm to 2.2 ppm. It is very clear to note here that this percentage increase between fresh and used synthetic lubricant was 1.76%, whereas the percentage increase between fresh and used shell lubricant was just 2.72%. That means that the shell lubricant observed more wear and tear and produced 0.96% more Fe impurities than the synthetic lubricant.

3.3.4. Calcium (Ca)

Calcium (Ca) is used for neutralizing acidic-based byproducts produced during the combustion process, and it is known as a detergent additive. Figure 6d shows that the concentration of calcium in the shell lubricant decreased from 2.46 ppm to 2.35 ppm after 100 h experimentation in the diesel engine. However, the concentration of synthetic lubricant decreased from 6.58 ppm to 5.14 ppm. It is evident that the percentage decrease between fresh and used synthetic lubricant was 4.47%, whereas the percentage decrease between fresh and used shell lubricant was 21.88%. An overall deterioration of 17.41% was witnessed in the synthetic lubricant compared to the shell lubricant. We know that calcium is used after running an engine, but even after 100 h of engine running its percentage was higher in the synthetic lubricant compared to the shell lubricant.

3.3.5. Chromium (Cr)

Chromium (Cr) metal is used to make crankshafts, piston rings, and cylinders. The remaining particles of Cr in lubrication oil is due to the wear and tear of these parts. Figure 6e shows that the concentration of chromium metal in the shell lubricant increased from 4.62 ppm to 6.18 ppm after 100 h experimentation in the diesel engine. However, the concentration of chromium increased in the synthetic lubricant increased from 3.12 ppm to 3.234 ppm. The increased percentage of wear and tear between the fresh and used synthetic lubricants was 25.24% and the increased percentage between the fresh and used shell lubricants was just 4.11%. That means that the shell lubricant observed more wear and tear and produced 21.12% more Cr impurities than the synthetic lubricant.

3.3.6. Zinc (Zn)

Zinc (Zn) metal is very beneficial for anti-wear and produces less friction film during the running of an engine to avoid wear. Figure 6f shows that the concentration of zinc in the shell lubricant decreased from 3.2 ppm to 2.78 ppm after 100 h experimentation in the diesel engine. However, the concentration of Zn also decreased in the synthetic lubricant from 5.74 ppm to 3.92 ppm. That means that the deterioration rate of zinc in the shell lubricant was higher than that of the synthetic lubricant by 3.599%.

4. Conclusions

The results show that the flash point and specific gravity of the synthetic lubricant were marginally decreased compared to the shell lubricant by 0.27% and 1.15%, respectively. Some properties of the newly prepared lubricant had better results than the shell lubricant, especially for the cases of ash and kinematic viscosity at 40 °C, with a relative increase of 4.17% and 1.61%, respectively. Other properties like kinematic viscosity at 100 °C, pour points, and total base number were relatively higher than in the shell lubricant, at 1.09%, 6.02%, and 1.38%, respectively, but the absolute values of the used synthetic lubricant were lower than the absolute values of the used shell lubricant. During the start of the running of the engine, the kinematic viscosity of the synthetic lubricant decreased from 250 to 220 at 40 °C, but as soon as the temperature of the engine increased and reached 100 °C the kinematic viscosity decreased from 18.4 cSt to 16.3 cSt. The FTIR analysis shows that all the peaks of the synthetic lubricant and the shell lubricant were overlapping each other in the first three regions of the mid-IR spectra from 4000 to 1500 cm^{-1} and had the same functional groups attached, such as hydroxyl stretch (O-H), alkanes (C-H), carbonyls (C=O), aromatic amines (C-N), and alkyl halides (C-Br). However, in the fourth region, which is called the fingerprint region (1500–500 cm^{-1}), where the wavelengths of electromagnetic radiation (EMR) are very high and the frequency is very low, the peaks fluctuated abruptly—but again, all the peaks had the same functional groups, which means they possessed the same characteristics with minor differences in structure. Atomic absorption spectroscopy (AAS) shows that wear and tear in the synthetic lubricant regarding chromium (Cr), copper (Cu), and iron (Fe) decreased compared to the shell lubricant by 21.12%, 3.39%, and 0.96%, respectively. However, in the case of aluminum (Al), the wear and tear was marginally increased by 1.17%. The concentration of calcium (Ca) and zinc (Zn) always decreased during the operational running of the engine and their values were reduced to 3.59% and 17.41%, respectively. However, even with this decrease, the concentrations of Zn and Ca were greater than those of the shell lubricant before and after engine operation. The overall results indicate that the tribological behavior of diesel engines using MoS_2-based synthetic lubricant produced slight wear and tear in the different parts of the engine due to a lack of in these physiochemical properties, such as kinematic viscosity at 100 °C, flash point, pour point, and specific gravity, compared to the shell lubricant. As a result of this wear and tear, Al metal deteriorated slightly more in the case of the synthetic lubricant. However, wear and tear due to Fe, Cu, Cr, Zn, and Ca particles was decreased compared to the shell lubricant. This shows that an MoS_2-based synthetic lubricant can be used as an alternative because it has higher densities, optimum viscosities, more reduction of friction, and most importantly, is very environmentally friendly.

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