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Specifications of Heavy Diesel Lubricating Oil Improved by MWCNTs and CuO as Nano-additives

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Abstract. In this investigation, the properties of heavy diesel lubricants were enhanced by adding the nano-additives. The purpose of this research is verifying the enhancement of the rheological and thermal characteristics of the lubricating oils by adding the nano-additives, in order to upgrade to the highest level for performance lubricant in the system. The SAE 15W40 (Oil parent) was mixed with two types of nanomaterials (MWCNTs and CuO) at four various concentrations by (0.1, 0.2, 0.5, and 1 % wt.) to prepare the nano-lubricants, studying and comparing their properties with parent lubricants. The results indicated that the thermal conductivity values of (Oil_{MWCNTs}) and (Oil_{CuO NPs}) at 1 wt. % concentration of both additives increased by 23%, 15.3% respectively. Also, the flash point of both nano-lubricants comparison with parent oil increased by (19.54%, 15.9%) respectively. It was concluded that (Oil_{MWCNTs}) showed higher lubricant's specification than (Oil_{CuO NPs}) due to the high surface area of MWCNTs. Hence, the operating properties of lubricating oil much enhanced when scattered the carbon nanotubes and copper oxide NPs.

Keywords: *Heavy Lubricating Oil; MWCNTs and CuO Nano-additives; Thermal & Rheological Properties.*

1. Introduction

Nowadays, petroleum refineries produce many types of lubricating oils with different properties and applications [1]. The main purpose of lubricating oil is to lubricate the moving parts, prevent corrosion, improve performance, and cool the engine. These lubricants must be qualified the requirements engines operation of high performance and long lifetime. Nano-lubricants (or Nanofluids) are the most important application of nanotechnology. Lubricant oils based nanofluids are also called nano-lubricants. Many nanoparticle additives have been investigated in order to improve the tribological performance of the base lubricating oils for diesel engine. Most designers and authors have focused on nanotribology in internal combustion engines as the key strategy for minimizing frictional power losses, excessive heat generation, exhaust emission, combustion, saving fuel, enhance heat transfer rate, reduction of consumed fuel and cost of maintenance [2]. The addition of MWCNTs to lubricating oils can effectively improve the tribological properties through the formation of a protective film on surfaces and creating a rolling effect between friction surfaces [3, 4]. Many authors prepared nano-lubricants containing different nanoparticles and nanomaterials such as BN, TiO₂, SiO₂,



CuO, ZrO₂, Al₂O₃, nano-diamond, and carbon nanotubes [5–8]. In fact, nanoparticles dispersed in base fluids have a significant impact on the rate of increase in the thermal conductivity of nano-fluids, making these liquids highly efficient in heat transfer [9, 10]. For example, carbon nanotubes, due to their high thermal conductivity coefficient, are known as an ideal material for making nanofluids [11, 12]. Hwang et al. studied the heat transfer properties of nanofluids in water base and ethylene glycol base which contain CuO nanoparticles and multi-walled carbon nanotubes [13]. Also, the MWCNTs thermal conductivity nano-lubricants, which contain different nanostructures such as copper and copper oxide nanoparticles with spherical structures and single walled and multi-walled carbon nanotubes with tubular structures, have been studied [13–18]. However, only a few of these published articles have been on other oils' properties including viscosity, flash point and pour point of nano-

lubricants from theoretical and experimental approaches [19, 20, 21]. Indeed, it has been proved that carbon nanotubes have a high thermal conductivity, high electrical conductivity and efficient mechanical properties [22, 23, 24]. The effects of base fluid and concentration on the rheological behavior of MWCNTs were investigated by Chen et al. [25]. Thus, by dispersing CNTs into a liquid phase such as engine oil, water, and ethylene glycol, can improve its thermal properties and transport. Choi et al. stated apparently that nanoparticles in lubricating oils can pad the scar and channels of the friction, and wear surfaces [26] as shown in Fig. 1.

It is important to mention here, that the investigated present work focus on the enhanced of the high-grade lubricating oil such as SAE 15W40 engine oil. Therefore, the main aim of the present work is to study the effect of adding MWCNTs and CuO nanoparticles on the properties of diesel engine oils and will look at their potential in terms of their viscosity, stability, flash point, pour point of nano-lubricants, and also thermal conductivity in heat transfer applications.

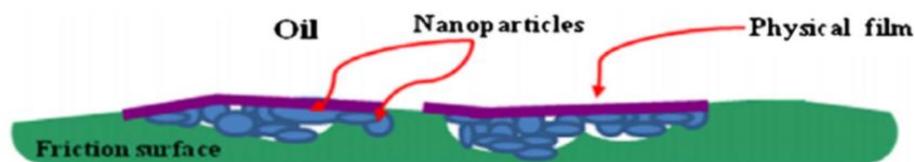


Fig. 1: Mechanism appearing how to reduce friction between oil surfaces when mixed with nanoparticles [26].

2. Experimental work

2.1 Materials

The SAE 15W40 engine oil and diesel fuel were attended from (Al-Dura Refinery, Middle Petroleum Company, Baghdad, Iraq). The SAE 15W40 lubricating oil is used as a parent fluid. **Table 1** shows the specifications of lubricating oil. In the present work the CuO NPs was bought from (Nanjing XFNANO Material Tech Co., Ltd). As for the multi-walled carbon nanotubes (MWCNTs) were manufactured by a new production process. The production process of MWCNTs included the burning of hydrocarbons source fuel in a special combustion chamber unit, under controlled operating parameters of temperature and fuel to oxygen ratio. Tests tribological were conducted on heavy-duty multi-grade diesel engine oils (SAE 15W40). **Table 2** shows main properties of MWCNTs and CuO NPs.

2.2 Measuring and analysing apparatus

A bath ultrasonic (P120 Elmasonic, Germany) was used for homogenizing, dispersing and mixing of CuO and TiO₂ NPs and making so-called nanofluids. The thermal conductivity was measured by KD2-Pro (Decagon Devices, USA) of parent oil and nano-lubricant at different temperatures and concentration. Also, field emission scanning electron microscope (FESEM, Japan, JEOL 7610F), X-ray Diffractometer (XRD, Japan, Shimadzu-6000), and Fourier transform infrared spectroscopy (FTIR-8400S, Shimadzu) was used for characterizing the properties of copper oxide and titanium oxides.

Table 1: Properties of SAE 15W40 engine oil.

Property	Value
Viscosity at 100 °C (cSt)	14.5
Viscosity at 40 °C (cSt)	109.84
Viscosity index	135
Density at 15 °C (kg/m ³)	904
Pour Point (°C)	-27
Flash Point (°C)	220

Table 2: The main properties of MWCNTs and

Specification	CuO	MWCNTs
Color	black	Black
Purity (%)	>99.9	99.1
surface area (m²/g)	263	433
Diameter (nm)	25	11.4
Volume density (g/cm³)	0.20-0.35	0.271
Density (g/cm³)	6.4	3.9
Crystal form	sphere	Tubes

2.3 Preparation of nano-lubricant

The nano-lubricants were prepared by adding MWCNTs, copper oxide and titanium oxides at different concentrations of 0.1 wt. %, 0.2 wt. %, 0.5 wt. %, and 1 wt. %, to parent lubricating oil (SAE 15W40). The required amount of multi-walled carbon nanotubes was carefully weighed using an accurate electronic balance and mixed with the parent oil. In the nanofluids preparation process, the (Two-step method) was used, due to more common, easier and more economical than the (One-step method) for production nanofluids. Due to the high viscosity of the base fluid, the mixing process was achieved by using a mechanical mixer and bath ultrasonic (type, P120 Elmasonic, Germany) method for dispersing of MWCNTs, another nanoparticles CuO inside the base fluid to obtain high desparation for nano-lubricants. The operating conditions parameters of the bath ultrasonic process are shown in **Table 3**.

Table 3: Specifications of Bath Ultrasonic.

The property	Value
Power	100%
Time	2-3 h
Temperature	40 °C
Frequency	20 kHz

2.4 Rheological and Thermal Measurements of Nano-Lubricant

The thermal conductivity of nano-lubricants has been measured, for this purpose, KD2-pro, a laboratory and portable device, was used to increase thermal properties. The device has a probe length of about 60 mm and diameter of 1.3 mm, and the device measures the thermal conductivity based on hotwire technology. The parent oil and Nano-lubricants thermal conductivity that was measured at various concentrations and temperatures. The viscosity of parent oil and nano-lubricants with concentrations from 0.1 wt. % to 1 wt. % concentrations were measured at a temperature of 40 °C and 100 °C. Kinematic viscosity, flash and pour point of the parent oil and nano-lubricants were measured based on ASTM D-445, ASTM D-97, and ASTM D-92 respectively.

3. Results and Discussion

3.1 XRD Pattern and FE-SEM

The XRD pattern in the current investigation indicates the MWCNTs as shown in **Fig. (2. a)**. The result indicated that there were no carbon oxides or other crystalline materials and only pure carbon nanotubes were obtained under applied experimental conditions. The peaks around 26.1° indicated the presence of (MWCNTs)₁, the peaks around 42.9° , indicated the existence of oxygen. The (002) peak indicated the graphitic structure of the MWCNTs presented. More over a comparison between the JCPDS card No. (PDF - C - 00-026-1076) with XRD patterns that the same file data is also confirm, the results that obtained from multi-walled carbon nanotubes are in good agreement with many authors [27, 28] who found that MWCNTs observed at 26.1° with high purity. Additionally, from the XRD pattern in **Fig. (3. a)**, it can be found that the CuO nanoparticles in the current investigation have the same major characterization peaks of pure copper oxide card No. (PDF Card - Cu O - 00-048-1548) at 2θ values of 32.2° , 35.4° , 38.6° , 48.5° , 52.9° , 58° , 61.3° , 65.5° , 67.8° , 72.3° , and 74.5° . Otherwise, in the XRD pattern, no other impurity peak was noticed, observing the formation of the single sample phase of CuO nanoparticles.

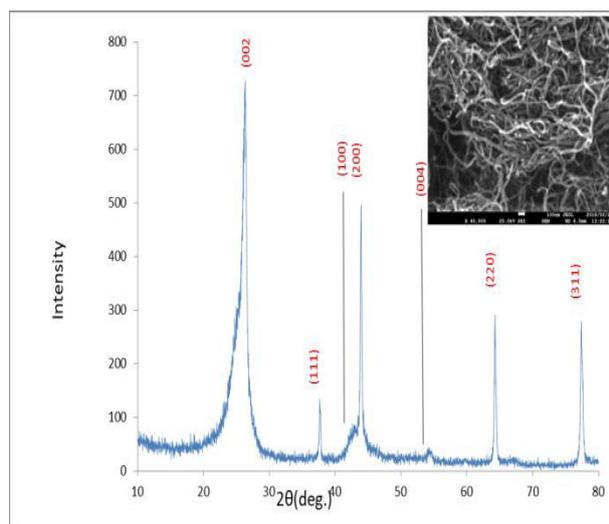


Fig.2: XRD pattern (a) and FE-SEM (b) image of MWCNTs

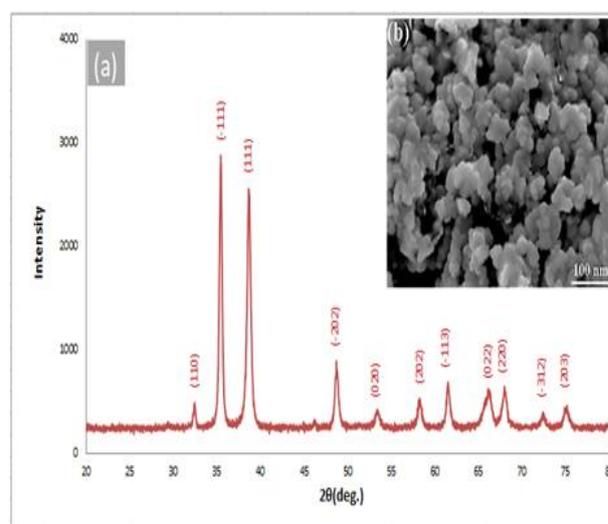


Fig. 3: XRD pattern (a) and FE-SEM (b) image

The FE-SEM pictures in **Fig. (2.b and 3.b)** showed the morphology of the nanoparticles of MWCNTs and CuO respectively. The shape of MWCNTs is generally cylindrical and has helical forms because the inter-molecular force of MWCNTs has various dimensions and sizes are presented in their structure. From the results of FE-SEM, a few impurities were observed on the surface of the tube for the prepared materials which can be removed by the purification process of MWCNTs. The morphology of copper oxide nanoparticles was spherical to some extent, which provided a good rolling mediator inside lubricating oil. The FE-SEM results show that the average particle size of MWCNTs and CuO is about 11.4 and 25 nm respectively.

3.2 Properties of Prepared Nano-lubricants

In fact, the estimating of the suitable concentration is a well important issue to be realized best characteristics [12, 16]. For dispersing MWCNTs and CuO NPs inside the base oil, mechanical methods of bath ultrasonic and magnetic stirrer were used. In the present investigation, it has been observed that samples which prepared by the bath ultrasonic method the NPs are better distribution, not agglomerated, and more uniform dispersed compared with previous samples that prepared from other methods.. All the inside samples were kept in transparent glass containers in a completely stagnant state for about 60 days to assess their own stability conditions as shown in **Fig. 4**.

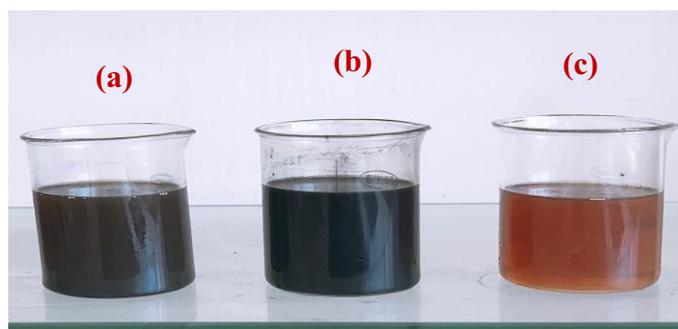


Fig. 4: The stability condition of nano lubricants after 60 days (a) CuO/oil, (b) MWCNTs/oil, (c) base oil.

During this interval, the stability is recorded for all the samples that checked visually. On the other hand, it has been observed that the dispersion of MWCNTs and CuO nano-additives within the base oil was very high through the period of checking; this gives an impression of the high stability of these materials within the lubricants, because of the high dispersion caused by the bath ultrasonic device.

3.3 Viscosity

Fig. (5 and 6) show that the viscosity amount in total has a rising tendency, with increased concentration of (MWCNTs and CuO) NPs at 40 °C. At higher temperature, the viscosity decreased of all the samples significantly. And also it seems, by increasing the concentration of (MWCNTs and CuO) NPs, for each 40°C and 100°C the viscosity increase.

The viscosity relative to the base lubricant increased by 5.38%, 9.97%, 8.93% for each concentration for MWCNTs. And for copper oxide the viscosity increased by 2.42%, 7.1%, 10.88%, which is linked to the nano-lubricant with concentration 0.2 wt.%, 0.5 wt.%, and 1 wt.% respectively and at 40 °C temperature, especially the concentration at 1 wt.% gave the highest ratio of viscosity improvement. The point interestingly with respect to the viscosity of nano-lubricants for both additives nanomaterials with concentration 0.1% at both temperatures is that the amount of viscosity has a little reduction with respect to the base lubricants, but the viscosity gets it an upward direction with increased concentration of multi-walled carbon nanotubes and copper oxide. Nanoparticles take an intermediate position between the oil layers when added, thus facilitating movement between the oil layers and sliding each other.

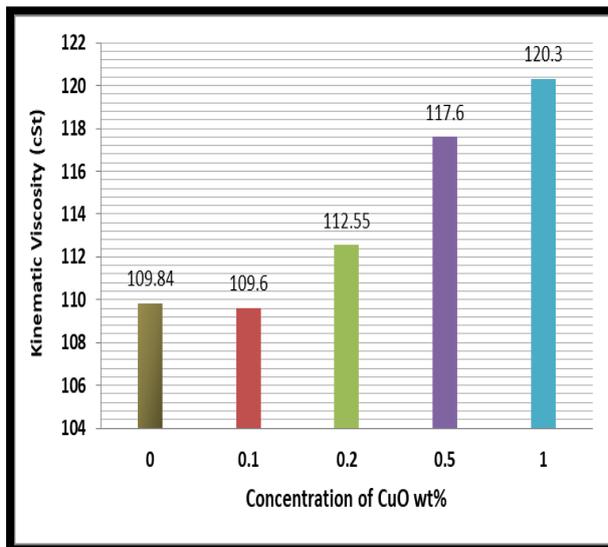


Fig. 5: The kinematic viscosity of nano-lubricants based on MWCNTs at 40 °C and different concentration.

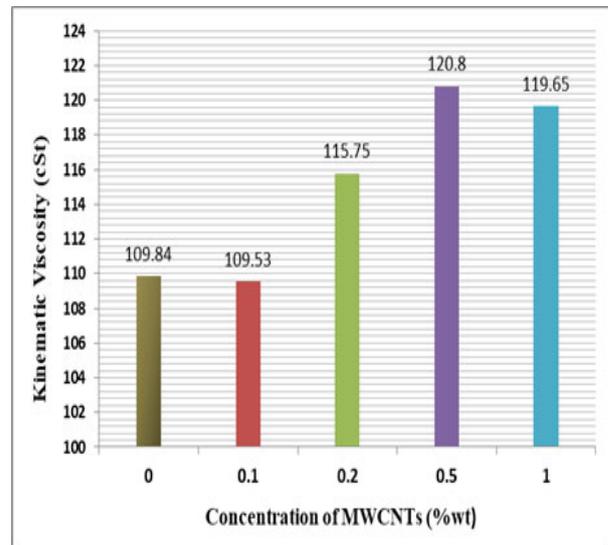


Fig. 6: The kinematic viscosity of nano-lubricants based on CuO at 40 °C and different concentration.

Fig. (7 and 8) show the viscosity of nano-lubricants at 100 °C. In the current work, the lubricating oils viscosity was decreased after adding MWCNTs and CuO NPs at the level by 0.28%, 0.3% at temperature 40 °C at 0.1 wt.%. On the other hand, it can be concluded that the viscosity of the SAE 15W40 base lubricating oil did not undergo any significant changes when adding nanomaterials to a few concentrations. Therefore, the engine oil for the Considered is a function of the concentration of the added nanoparticles.

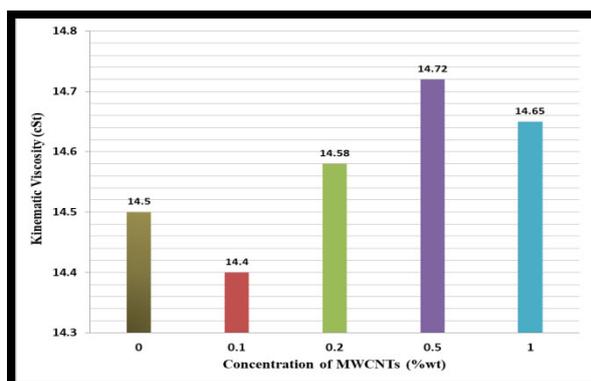


Fig. 7: The kinematic viscosity of nano-lubricant at 100 °C with different concentration of CuO.

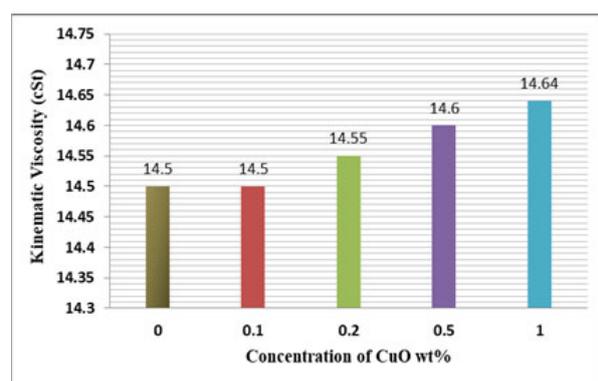


Fig. 8: The kinematic viscosity of nano-lubricant at 100 °C with different concentration of MWCNTs.

3.4 The thermal conductivity measurement

Fig. (9 and 10) show the results for thermal conductivity determined of nano-lubricants after adding nanoparticles to parent oil and in different concentrations and also with different temperatures. It has also been seen, that the results obtained from engine parent oil by the addition of MWCNTs and CuO NPs at specific rates, was the thermal conductivity coefficient of the nano-lubricants much greater than the parent oil without additives.

Based on the results obtained, adding nanoparticles to SAE 15W40 engine parent oil, based on the method which has been done in current work, the amount of thermal conductivity at 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt% concentrations of MWCNTs and CuO NPs had increased 11.4%, 16.76%, 21.48%, and 23.72% respectively with respect to MWCNTs, while CuO had increased 9.85%, 15.2%, 19.73%, and 21.84% respectively. During this research, it can be concluded that MWCNTs has a high impact on the thermal conductivity coefficient of the engine oil compared to copper oxide which have a positive effect of the major, but less than when the addition of MWCNTs to lubricants.

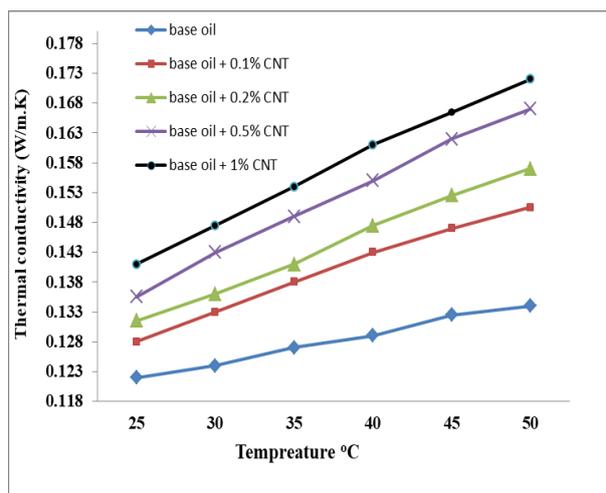


Fig. 9: Thermal conductivity of Nano lubricant (Oil_{MWCNTs}) and base lubricant.

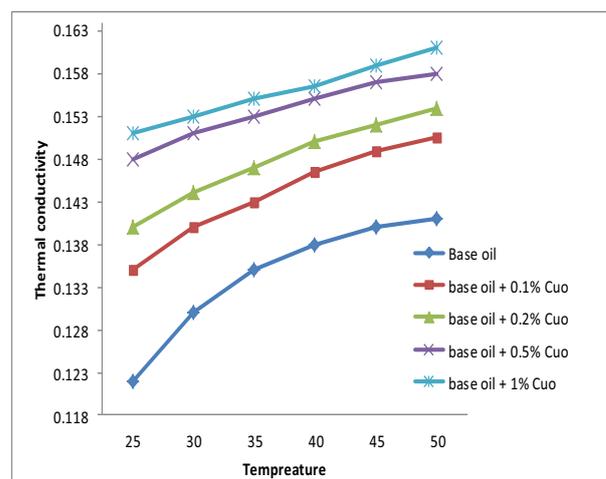


Fig. 10: Thermal conductivity of nanolubricant (Oil_{CuO}) and base lubricant.

As well, it can be observed that, when the temperature increased, the thermal conductivity of the nano-oil increased, this also applies to the concentration of nanoparticles, as the concentration increases, the quantity of thermal conductivity coefficient of the engine oil increased. However, it should be noted that, in the case of different type of basic fluids, the rate of concentration the nanoparticle, kind of nano-additives, the rate of dispersion of nanoparticles within the base fluid, and the method used for dispersion of nanoparticles inside the base fluid. The different parameters resulting from the previous reasons are the effect of the resulting changes in properties.

MWCNTs and copper oxide have greater potential than other nanoparticles to improve thermal conductivity coefficient of engine oils, due to the high thermal conductivity of these materials, especially the MWCNTs. By taking a look at this property, that one of the functions of engine oil reducing the erosion of moving parts, removing some heat generated by friction and combustion between the parts to outside environment, so that helps to cool the engine. Oil works as a cleaner and removes dust and carbon particles between moving parts. Therefore, the using carbon nanotubes structures can be considered as a method to improve the thermal conductivity of diesel engine oils.

3.5 Flash point and Pour point

The flash point is the lowest temperature at which the vapour of the lubricating oil is exposed to the air to ignite; the oil takes the ignition curve in an instant and then turns off quickly in a moment. Therefore, it can be said that the flash point in the lubricating oils of heavy engines is in fact, the main determinant of the maximum temperature limits in the functions of that oil.

Fig. 11 shows the results of the flash point of the nano-lubricant that prepared from MWCNTs and CuO respectively. The increasing of flash point as a function of increasing the concentration of MWCNTs. The high thermal conductivity of carbon nanotubes made the flash point for prepared lubricants significantly higher than base lubricating oil and thus improved remarkably.

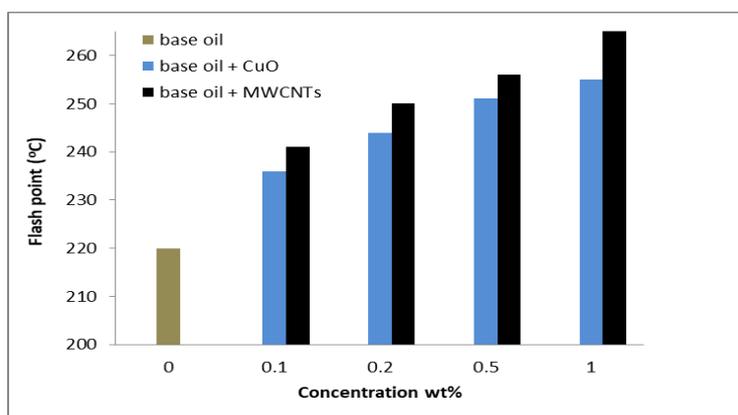


Fig. 11: The flash point values of parent oil and nano-lubricant.

From **Fig. 11**, it has been observed that the flash point of base oil increased by 4.09%, 8.18%, 16.36%, and 24.09% with the value of MWCNTs concentration 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt% respectively. But shows other values of the flashpoint for CuO when the flash point of base oil increased by 3.18%, 6.81%, 11.8%, and 15.45% respectively. It was concluded that the flash point was increased for both types of nano-lubricants concentration, and the highest values of the flash point were 273°C and 254°C for MWCNTs and CuO respectively.

The pour point this property of lubricating oil is appraised as the marginal point of temperature, in which liquid cannot flow at this stage. The moment in which the engine starts working is the greatest rate of wear up to the engine machine. The lubricating oil does not reach all parts of the engine quickly when it is pumped, and to avoid and prevent such a problem and reduce its impact the lubricating oil must be sufficiently viscous stirred to flow easily and fast to reach all parts of the engine. The resulting changes in the rate of the parent oil point were studied under the effect of the addition of nanoparticles MWCNTs and CuO at different concentrations as shown in **Fig. 12**.

Trends in changes in the pour point of oil as a function of the concentration of nanoparticles in oil lubrication with MWCNTs and CuO nanoparticles with a concentration of 0.1% by weight, the spill point was reduced slightly, At 0.2 wt. %, high rate values of pour point were observed at about 7.4% and 3.7% with the addition of MWCNTs and CuO respectively. Yet, when the concentration of nanoparticles increased to 0.5% by weight and 1% by weight, the pour point was reduced again.

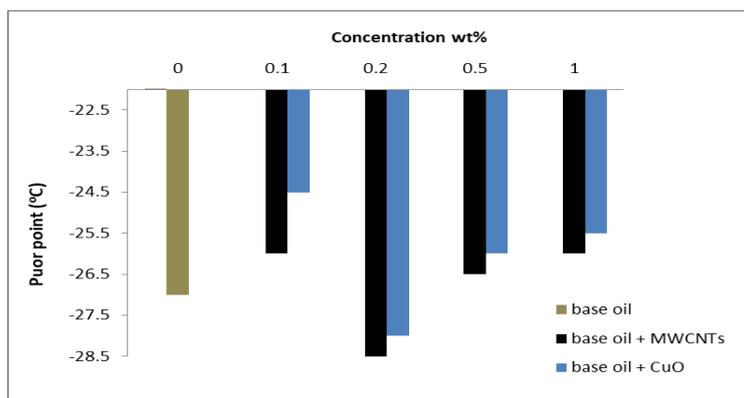


Fig. 12: The pour point values of parent oil and nano-lubricant.

It can be concluded that the increasing thermal conductivity coefficient by adding copper oxide and titanium oxides nanoparticles is due to increased oil resistance against ignition, It can be seen, by estimate the produced change in the rate of pour point and flash point of nano-oil after adding nanoparticles, which were dependence as a function of concentration, the best amount noticed of both parameters have 0.2% by weight concentration.

4. Conclusions

It has been concluded that the dispersing of NPs in lubricating oil to form the nano-lubricant is a very complicated process in high viscosity oil. It has been observed that MWCNTs and CuO have been distributed in different concentrations by using the bath ultrasonic method within the lubricating oil to obtain the best stability, due to the fact that they provide high energy and prevent their aggregation and precipitation again.

The results observed that thermal conductivity and flash point by the effected addition NPs may change for better at a high rate, but the oil properties such as viscosity and pour point have no perceivable concrete changes in the least nanoparticles concentration 0.1% by weight. The thermal conductivity increased MWCNTs/oil and CuO/oil about 11.4% and 9.85% respectively at 0.1 % wt. concentration. Also, a flashpoint for both nano-lubricants prepared increased by about 7.27% and 4.45% respectively.

It can be concluded that the nano-lubricant prepared with 0.2 wt. % concentration of MWCNTs/oil & CuO/oil, it seems that is the better sample for both because in this sample viscosity had unchanged much, this is desirable, thermal conductivity and other oil specifications have been improved. On the other hand, a comparison that observed results from assay the effects of MWCNTs and CuO on the characterizations of engine oil shows that, MWCNTs have a better functionality for improving the characteristics of (SAE15W40) engine oil than CuO NPs.

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