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Physical Properties of New Formulation of Hybrid Nanofluid-based Minimum Quantity Lubrication (MQL) from Modified Jatropha Oil as Metalworking Fluid

Ainaa Mardhiah Sabri[1], Norfazillah Talib[1,*], Nur Syazwani Filzah Mohd Saad[1], Amiril Sahab Abdul Sani[2], Sandip Kunar[3], Said Ahmad[1], Haslina Abdullah[1], Lee Woon Kiow[1], Aslinda Salleh[1]

[1] Department of Manufacturing Engineering, Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia
[2] Faculty of Manufacturing and Mechatronic Engineering Technology, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia
[3] Department of Mechanical Engineering, Aditya Engineering College, Surampalem-533437, India

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ABSTRACT

As a metalworking fluid, vegetable-based crude jatropha oil (CJO) was used in place of petroleum-based oil. The use of petroleum-oil-based metalworking fluids poses significant environmental and health concerns. Furthermore, it has a large amount of free fatty acid (FFA), promoting physical damage. This research targets to substantially evaluate the modified jatropha nanofluids formulation as a metalworking fluid for machining processes. CJO was chemically altered using the esterification and transesterification processes to produce modified jatropha oil (MJO). To make the nanofluids, MJO was mixed with nanoparticles of Hexagonal Boron Nitride (hBN) + Tungsten Disulfide (WS_2) and Hexagonal Boron Nitride (hBN) + Titanium Dioxide (TiO_2) at a concentration of 0.025 wt.%. The viscosity and acid value of MJO nanofluids were assessed using ASTM standards and compared to a synthetic ester (SE). All the data indicates that the physical attributes improved throughout storage. It is possible to conclude that MJO_{hw} (MJO + 0.025 wt.% hBN + WS_2) has the ability as a long-term metalworking fluid for the machining operation. According to the experiment results, MJO_{hw} surpasses non-additive MJO in terms of kinematic viscosity by 5.91% at 40 °C and 15.6% at 100 °C. During a one-month duration of storage time, MJO_{hw} also improve viscosity index (319) by 18.15%. Furthermore, MJO_{hw} has an acid value ranging from 0.34 to 0.58 mg NaOH/g. Finally, the inclusion of additives aids MJO in improving its qualities by 31.1% reduction in acid value and MJO_{hw} demonstrates outstanding lubricating properties across all samples.

1. Introduction

Machining is a manufacturing technique that includes cutting material into a particular form using a cutting tool. Turning, drilling, and grinding are the three basic machining techniques. Lubrication is one of the most important parts of keeping a machine running smoothly and efficiently, hence it is

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[*] *Corresponding author.*
E-mail address: fazillah@uthm.edu.my

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essential that it be available for all machining operations [1]. Lubrication can help the machining process by minimizing friction between two surfaces, protecting against wear and tear, and reducing heat transfer caused by abrasions [2]. Their primary function is to move a fluid film over solid surfaces. Instead, it changes the surface qualities, adjusts the temperature, or removes debris. Nanofluids are liquids with exceptional lubricating and cooling capabilities used as cooling lubricants. Nanofluids enhance thermal conductivity and tribological characteristics by providing superior flow in the cutting zone [3]. As a result, it contributes to improved cutting performance by lowering the coefficient of friction, minimizing tool wear, and enhancing surface quality [4].

Mineral, synthetic, and vegetable base oils are the three base oils used in lubricants. Vegetable oils are rarely employed in industrial applications; mineral oil and synthetic oil are the most used [5]. On the other hand, mineral oil has a low biodegradability and the potential for long-term environmental damage [6]. If utilized for an extended period in metalworking fluids, both mineral oils and synthetic oils can pollute the environment and harm humans due to their poisonous composition. Therefore, vegetable-based oils have been introduced to replace mineral oils and synthetic oils. Bio-based vegetable oils have a high percentage of biodegradation and have improved lubrication efficiency in physical behavior and tribology [7]. The triglyceride structure of vegetable oil confers desirable lubricating properties such as greater lubricity, viscosity index, shear stability, decreased volatility, and increased load bearing capacity [8]. In addition, using vegetable oils can contribute to energy savings and a cleaner environment [9]. Therefore, vegetable oil is one of the best viable alternatives to mineral-based lubricants in promoting sustainable machining [10].

However, in order to address its limits in terms of oxidation stability, high friction, high viscosity, thermal stability, and corrosion resistance, vegetable oil must be modified before use [8]. The physical and chemical properties of raw vegetable oil have several limits, claim Rahim *et al.,* [11]. For them to be employed as MWFs, their properties must be improved. Numerous studies on the alteration of vegetable oil have been conducted. Jeevan and Jayaram [12] chemically modified jatropha and pongamia oil by the process epoxidation. The modified oils then compared with Mineral Oil in terms of physicochemical properties and machining performances. They mentioned that the physicochemical properties of modified oils were comparable with mineral oil and in terms of machining performance, modified vegetables oils are more effective in reducing the cutting force and improved surface finish. Norfazillah *et al.,* [13] make some modification on refined, bleached and deodorized (RBD) palm olein and evaluated the tribological and machining performance of the modified oil. In comparison to the commercial synthetic ester-based cutting fluid, the results showed that the high synergistic effects of the additives being blended in the modified RBD palm olein (MRPOs) demonstrated good tribological behavior and machining performances with high tapping torque efficiency and low cutting force and temperature. They demonstrate a high potential for replacing mineral oil-based metalworking fluids. Rahim *et al.,* [14] investigated several formulations of Modified RBD Palm Olein as a metalworking fluid. Methanol to RBD Palm olein ratios of 3:1, 6:1, and 9:1 was tested. They discovered that the 6:1 formulation has outstanding tribological qualities and that it may be used as an alternate feedstock for metalworking fluid. Talib *et al.,* [15] developed modified Jatropha Oil via transesterification process. Jatropha methyl ester (JME) react with trimethylolpropane (TMP) at the molar ratio of JME:TMP; 3.5:1 with sodium methoxide, CH_3ONa as the catalyst.

According to the published literature on vegetable oils containing single nanoparticles, the physical characteristics of vegetable oil have improved with the inclusion of single nanoparticles [16]. There were various types of nanoparticles used as additives for biobased oil such as activate carbon, hexagonal boron nitrate, graphene, copper oxide and others [17-19]. Previous research looked at the tribological performance of modified jatropha oil with hBN nanoparticles for MWFs. The hBN concentration ranged from 0.05wt.% to 0.5wt.%. They observed that the 0.05 wt.% concentration of hBN outperformed SE in terms of friction and wear [15]. MJO and hBN were also used as additives in another investigation. Additions of hBN were less than those found in the research by Talib *et al.,* (0.01, 0.025, and 0.05 wt.%). The kinematic viscosity and viscosity index of the base oil have been shown to have increased because of the addition of additives. In addition, they discovered that, when compared to Synthetic ester (SE) and its base oil, MJO with additives had a reduced coefficient of friction (COF). Moreover, they determine that hBN's anti-friction properties are a result of its incorporation [8]. Xian *et al.,* [20] studied on the viscosity of Copper Oxide (CuO) nanofluid due to nanoparticles size and concentration. The addition of 0.05 vol.% CuO to base fluid increased viscosity. The particle size influence on the viscosity of nanofluids, on the other hand, was shown to be minimal at low concentrations of CuO nanoparticles (0.025 vol.%). TiO_2 as an additive significantly lesser the surface roughness of the wear scars [21]. Latib and Kamaruzaman [22] found that nanofluid with TiO_2 had higher viscosity compared to other nanofluids. Roselina *et al.,* [23] stated that the visocidty of palm oil increased with the addition of TiO_2. Besides that, the viscosity also increased with the increased of nanoparticle concentration. Zhu *et al.,* [24] used tungsten disulfide (WS_2) as high temperature lubricants. They mentioned that WS_2 formed crystal plane and achieved low friction performance at high temperature. Besides that, the tribological performance of ZnO and WS_2 nanofluids with different presence of surfactants were also investigated. They concluded that surfactants do not affect the stability of WS_2 nanofluids [25]. In this paper, hBN, TiO_2 and WS_2 were chosen as the main lubricating additive to prepare the hybrid nanofluid because of each nanoparticle’s performance in terms of viscosity improver anti friction and anti-wear.

The unique tribological characteristics of each nanoparticle make it worthwhile to investigate their combined performance as an addition to lubricants. Dispersing two distinct nanoparticles into a heat transfer fluid yields a hybrid nanofluid, a novel type of fluid used in nanotechnology. In recent periods, the boundary layer flow formed by hybrid nanofluids has gathered an immerse attention from researchers. The boundary layer is the region where viscosity is dominant and the bulk of the drag experienced by a body submerged in a fluid is formed [26]. Sidik *et al.,* [27] reviewed on different preparation methods and thermal performance of hybrid nanofluids. They discussed on the process of preparation and factors affecting the performance of hybrid nanofluid. They concluded that hybrid nanofluids have good performance in thermal characteristic due to synergistic effect of two different nanofluids. It was also indicated that further experimental research is needed to fully comprehend the fluid's unique properties. Single nanoparticles and SiO_2/MoS_2 hybrid nanoparticles dispersed in deionized water were studied for their tribological performance by Meng *et al.,* [28]. They grind each sample for 30 minutes to see how much the friction coefficient changed. They discovered that the creation of a hybrid lubrication layer, enhanced adsorbing capabilities, and the synergistic interaction between single nanoparticles gave hybrid nanofluids outstanding frictional qualities. Based on the results of this study, incorporating hybrid nanoparticles into a lubricant base is superior to utilizing single nanoparticle additives. Since the shortcomings of one nano-additive may be compensated for by including another, and since various types of nanomaterials tend to interact synergistically to boost friction performance, combining two or more nano-additives is often the best option.

Therefore, this study is to evaluate the physical properties of modified Jatropha based oil as the metalworking fluid for machining processes using hybrid nanoparticles which is Hexagonal Boron Nitride (hBN) + Titanium dioxide (TiO_2) and Hexagonal Boron Nitride (hBN) + Tungsten disulfide (WS_2) nanoparticles as the additives. The physical properties were tested according to the American Society for Testing and Materials (ASTM) standard. For this project, the testing was used to get the desired physical properties of viscosity (ASTM D445), viscosity index (ASTM D4502) and acid value (ASTMD664).

2. Methodology

2.1 Bio-based Lubricant Preparation

The investigation in this study initiated with altering crude jatropha oil (CJO) using a chemical alteration procedure. In this method, CJO was mixed with methanol (CH_4O) in the presence of sulfuric acid (H_2SO_4). To generate the esterified jatropha oil, the combination was heated in a three-neck circular bottom flask for 60 minutes at a constant temperature of 60 °C and sealed with a condenser beneath the magnetic hot plate stirrer (EJO). The transesterification procedure was then carried out by combining EJO with CH_4O to produce jatropha methyl ester (JME) using sodium hydroxide (NaOH) as a catalyst.

The reaction is seen in Figure 1 in the three-neck round bottom flask, covered by the graham condenser and the reaction temperature was kept constant at 105 °C for 24 hours. Finally, as indicated in Table 1, MJO was combined with Hexagonal Boron Nitride (hBN) + Tungsten disulfide (WS_2) and Hexagonal Boron Nitride (hBN) + Titanium dioxide (TiO_2) nanoparticles at a concentration of 0.025 wt.%. The samples are shown in Figure 2 and the properties of nanoparticles are shown in Table 2. The incorporation of nanoparticles enhances the viscosity, viscosity index and improved acid value of the base oil.

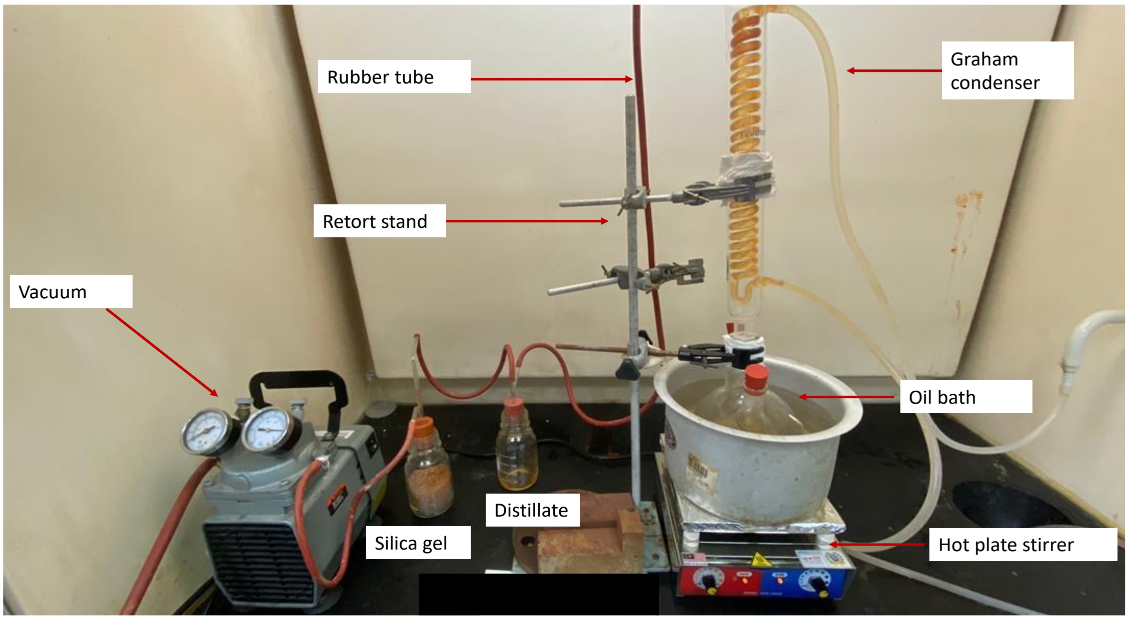

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Fig. 1. Set-up of the transesterification process

Table 1
Sample of MJO with nanoparticles

Symbol	Description	Weight of nanoparticles (wt.%)
MJO_{hw}	$MJO + hBN + WS_2$	0.025
MJO_{ht}	$MJO + hBN + TiO_2$	0.025

(a) (b)

Fig. 2. Samples (a) MJO_{hw} (b) MJO_{ht}

Table 2
Properties of Hexagonal Boron Nitride (hBN), Tungsten Disulfide (WS_2), and Titanium Dioxide (TiO_2)

Properties	hBN	WS_2	TiO_2
Appearance	Colourless crystal powder	Blue Gray powder	White solid powder
Density (g/cm^3)	2.1	7.5	4.23
Size (nm)	6.5	0.8	40
Melting point (°C)	2973	1250	1855
Solubility in water	Insoluble	Slightly soluble	Insoluble

2.2 Physical Testing

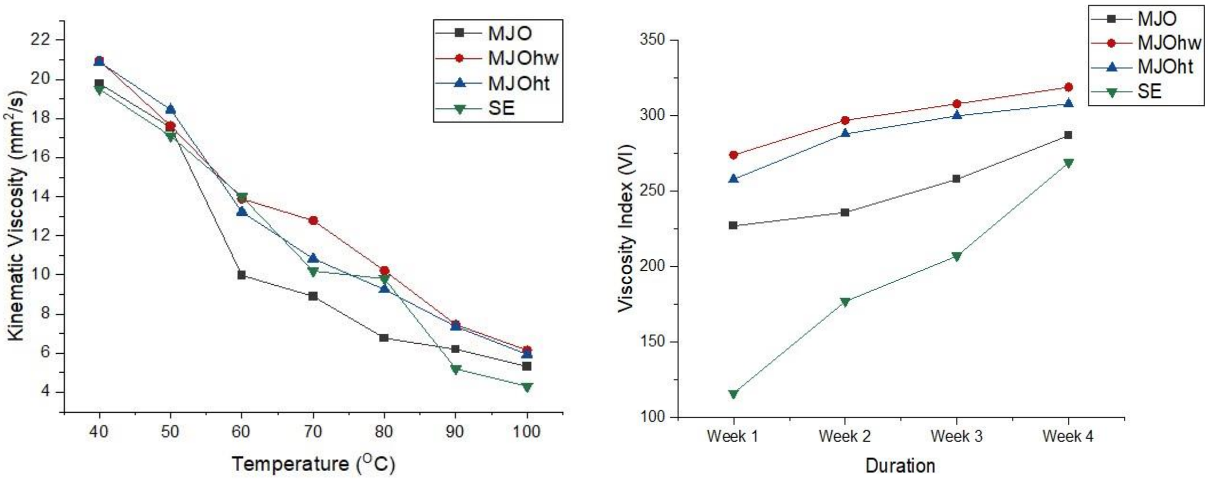
The characteristics of all MJO samples in terms of kinematic viscosity, viscosity index, and acid value were determined by conducting physical testing according to the American Society for Testing and Materials (ASTM), which is ASTM D445, D4502, and D664 standard testing techniques, respectively. The benchmark metalworking fluid for this study was synthetic ester (SE, Unicut Jinen MQL). The kinematic viscosity was measured using a viscometer at temperatures ranging from 40 °C to 100 °C. The hybrid lubricant's dynamic viscosity was measured by dipping a viscometer probe into the fluid. Data analysis involved taking three separate measurements and averaging the results. Dynamic viscosity and density value were then used to calculate the kinematic viscosity. A biobased MWF's viscosity is a measure of its thickness or resistance to flow. The viscosity of fatty acids and vegetable oils is a numerical measure of their flow resistance. The higher the viscosity of biobased MWFs, the thicker it will be, and the more energy will be required to move an item through it. Viscosity is an important element influencing the utilization of biobased MWFs [26,27]. The viscosity index was calculated from kinematic viscosity between temperatures of 40 °C and 100 °C for four-week oil sample storage. A biobased MWF's viscosity index (VI) is a measurement of how the viscosity of the biobased MWF changes with temperature. The viscosity of a biobased MWF is inversely related to its temperature; hence, a machine that operates over a wide temperature range would demand a lubricant with a higher viscosity index. The larger the viscosity index, the less temperature influences lubricant viscosity [19]. The acid values were examined using the titration process by titrating the solution with NaOH. 4g was assigned to each sample of hybrid nanofluid. Samples were then dissolved in 50 ml of methanol (C_3H_8O) by heating them to 60 °C. With the intention of providing a visual cue, 5 drops of phenolphthalein were added to the mixture. The titration was started by slowly adding 0.1 N of NaOH to the solution until the initial pink color became stable and lasted for around 30 seconds. As a final step, the amount of 0.1 N NaOH utilized in the sample titration was determined. When there is an abundance of acidic compounds in biobased MWFs, varnish and sludge are produced, which can erode machine parts and clog oil filters. The total acid value of biobased MWFs is a metric used to assess the acidity of these beverages. The acidity of any given biobased MWFs is established by its additive package, the degree of acidic contamination, and the presence of oxidation by-products [30].

3. Results

3.1 Viscosity and Viscosity Index

The MWF viscosity is a crucial parameter representing flow resistance and influences the lubricating film at the contact areas to reduce friction and wear. The temperature has an impact on the value of kinematic viscosity. It can be proved that increasing the temperature of the lubricant sample causes considerable decreases in kinematic viscosity, as seen in Figure 3(a). This happened because when the temperature was higher, the molecules in the lubricant samples dispersed faster [31]. The graph in Figure 3(a) shows that Synthetic ester (SE) had the lowest kinematic viscosity at 40°C and 100°C compared to MJOs. This result revealed the change in oil's viscosity resulting from intermolecular pressures on hydrogen bonding produced by MJO's chemical alteration via transesterification reaction [31]. MJO_{hw} (20.96 mm^2/s) has the maximum kinematic viscosity, followed by MJO_{ht} (20.89 mm^2/s) and MJO (19.79 mm^2/s). At 100 °C, MJO_{hw} (6.15 mm^2/s) exhibited the maximum kinematic viscosity, followed by MJO_{ht} (5.93 mm^2/s) and MJO (5.32 mm^2/s). The viscosity of non-additive MJOs is lower than that of inventive MJOs. When nanoparticles are added, they take up an intermediate position between the oil layers, making mobility and sliding between them easier [18]. Furthermore, the kinematic viscosity continuously increases for all temperatures throughout one month of storage.

The viscosity index (VI) of MWF assesses how many the fluid's viscosities change with temperature [32]. Figure 3(b) illustrates that the viscosity index (VI) value was calculated using the kinematic viscosity values at 40 °C and 100 °C for four-week oil storage. MJOs samples had higher VI compared to SE. This is due to the chemical modifications made to crude jatropha oil to make MJO. According to Sani *et al.,* [33], the vaster carbon number of MJO (16-18) compared to SE (8-10) affected the viscosity value's stability. The VI of MJO_{hw} and MJO_{ht} was higher than MJO. The addition of hBN nanoparticles improved the VI of MJO by 24% to 27%. This is due to lowest thermal expansion coefficient of hBN 1 × 10-6/°C influenced the thermal stability qualities of the oil and was attributable to a higher level of contact that maintained a bigger thermal network [8]. The VI of the MJO_{hw} (274–319) from one-month storage is higher than that of the other MJO_{ht} (258–308). The greater the VI value, the greater the kinematic viscosity created. The high VI value benefits lubricant stability as temperature increases [34].



(a) (b)

Fig. 3. The viscosity value; (a) kinematic viscosity and (b) viscosity index for 4-weeks storage

3.2 Acid Value

Figure 4 shows the acid value for SE and MJOs from week one until week four. From the graph, the acid value of SE (0.56-0.58 mg NaOH/g) is the highest compared to the MJOs. This is due to the MJO's double bond increasing the rigidity of the fatty acid chain, prohibiting the tight packing of fatty acid chains [35]. The acid value of MJOs with the addition of nanoparticles shows improvement compared to MJO itself. MJO$_{ht}$ has the lowest acid value (0.31 mg NaOH/g), followed by MJO$_{hw}$ (0.34 mg NaOH/g) and MJO (0.45 mg NaOH/g). It can be concluded that the addition of nanoparticles has significantly affected the acid value as the acid value of MJO$_{ht}$ and MJO$_{hw}$ decreased by 31.1% and 22.2%, respectively.

In addition, the acid value of the nanofluids increased significantly as the storage period increased due to the general hydrolysis response of the fatty acid. According to Akowuah *et al.,* [36], the oxidation rate rose as the oxygen concentration grew over the storage period. As a result, after 4 weeks, SE recorded the highest acid value of 0.65 mg NaOH/g. According to the results in week 4, MJO$_{ht}$ has slightly lower acid value values than MJO$_{hw,}$ which is 0.56 mg NaOH/g, and it was the lowest value compared to other MJOs. However, the readings are slightly higher than the maximum suitable acid value for machining, 0.5 mg NaOH/g. Getting the lowest acid levels is critical to increasing lubricant performance since it will provide improved corrosion protection [35].

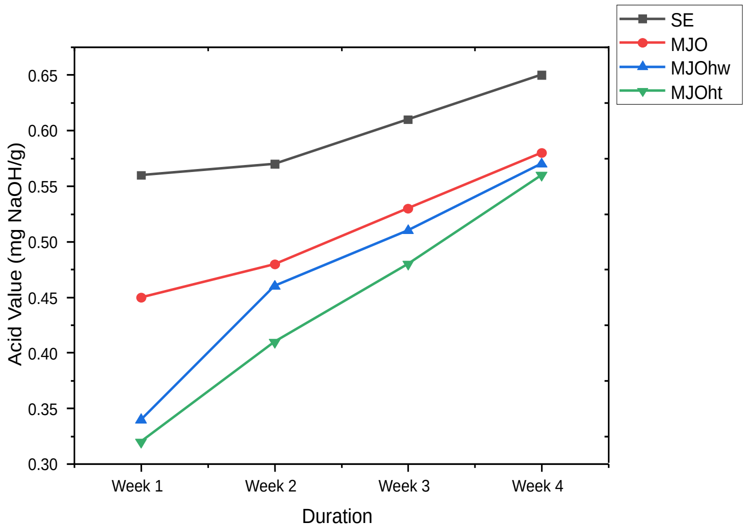


Fig. 4. Graph of Acid values for 4 -weeks storage

4. Conclusions

A novel Modified Jatropha Oil (MJOs) formulation was successfully created. The results revealed that all samples increased as the temperature lowered over time. Furthermore, when the temperature drops, the viscosity of all the samples rises. MJO_{hw} (MJO + 0.025 wt.% hBN + WS_2) (274–319) has the most significant value of VI and due to the presence of additives, the VI increases as storage time increases. Furthermore, the acid value of all samples has increased with time and results showed that MJO_{ht} has the lowest acid values (0.32-0.56 mg NaOH/g) compared to other MJOs. In conclusion, the addition of hBN and WS_2 as an additive to MJO has enhanced its physicochemical properties as a lubricant, and MJO_{hw} performs better than MJO_{ht}.

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