

Evaluation of Physicochemical Properties of Modified Jatropha Oil Blended with hBN and MoS₂ as Future Metalworking Fluid for the Machining Process

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ABSTRACT

The development of metalworking fluids has recently shifted the mineral-based oil with vegetable-based oil as a base stock. This is due to the increase of awareness of the society towards environmentally friendly and sustainable criteria, especially in the machining process. Vegetable-based oil from crude jatropha oil is one of the potential candidates to replace the mineral-based lubricant. However, the process of modification for crude jatropha oil needs to be done because the high composition of free fatty acid (FFA) that exhibit to low and undesirable physical properties. This experimental study aims to evaluate the physicochemical properties of newly formulation from modified jatropha-based nanofluids specifically for metalworking fluid with the inclusion of hexagonal boron nitride (hBN) and molybdenum disulphite (MoS₂) nanoparticles at a concentration of 0.05 wt%. In this study, the properties of MJO nanofluids were analysed in terms of density, viscosity, water content, acid value and corrosion behaviour according to ASTM standard and comparative analysed with the commercial synthetic ester (SE). The findings of this study shows that MJO+0.05 wt.% hBN (MJOh) exhibited excellent physicochemical properties as it achieved better result for kinematic viscosity at 40°C and 100°C. Additionally, the acid value and water content of the MJOh were the lowest among other samples and excellent corrosion resistant by providing the best microstructure at the workpiece's surface. In conclusion, MJOh has the potential of being a sustainable metalworking fluid for the machining process.

Key words: Modified Jatropha Oil, Hexagonal Boron Nitride, Molybdenum Disulphite, Nanofluid, Physicochemical Testing, Sustainable Metalworking Fluid.

1. INTRODUCTION

Machining is an essential process for a wide range of manufacturing and industry. One of the main challenges faced during machining processes is a large amount of heat

generation especially in a dry condition as well as high-speed machining. In that way, lubricants which are also known as metalworking fluids (MWFs) or cutting fluids have a pivotal role by cooling and lubricating the interface between work pieces surface and the cutting tool and help to prevent the chips reach the cutting area. In this case, the minimal friction and tool wear can be obtained as well as prolong the tool life [1]. Generally, the commercial MWFs are predominantly produced from mineral-based oil. The high usage of mineral based MWFs possesses an environmental problem because it is highly damage or disturb environment as well as hard to be disposed. Additionally, the usage of mineral-based MWF causes health problems through the inhalation of MWF aerosols that can give irritation to the nose, throat and lung [2]. Due to the global concern on the environmental issues, the transition from the mineral-based oil to the bio-based oil offers a potential opportunity that can considered as an alternative solution as its high biodegradability and derived from a renewable resource. Vegetable oils consist of triglyceride structure provide qualities desirable in reducing both friction and wear. This related to the high strength of the lubricant film was formed due to the longer fatty acid chains caused the polar tail of the fatty acid able to attached firmly with metallic surfaces [3].

Additionally, there has been renewed interest in nanofluids as a generation of a new type of lubricants due to the inefficiency of common lubricants in reducing friction coefficient, wearing protection of contacting surfaces. Nanofluids are the fluid with colloidal suspensions of nanoparticles either metallic or non-metallic types in which act as transport properties and heat transfer agent to enhance the performance of the lubricant [4]. Interestingly, the potentials of the vegetable-based oils enhanced with nanoparticles and MQL technique had been explored by recent researchers. A recent study by Uysal et al. [5] explored the influence of 1wt.% of MoS₂ mixed with the commercial cutting fluid from vegetable based-oil by performing milling process of AISI 420 martensitic stainless steel using uncoated Tungsten Carbide (WC) as the cutting tool. The inclusion of MoS₂ nanoparticles as additive in MQL cutting fluid significantly prevent from

tool wear and surface roughness to both workpiece and cutting tool. This result proved that the ability of the nanoparticles of MoS₂ to penetrate to the surface of both workpiece and cutting tool, thus prevent friction between the sliding surfaces, thus fewer tool wears were observed.

Previous study by Wang *et al.* [6] performed the friction and wear performance through ball-on-disc tribometer (MPX-1G). The vegetable base stock from castor oil was blended with hBN at concentrations of 1, 2, 5, and 8 wt.%. The finding obtained was demonstrated that the 21.74% improvement of the coefficient of friction achieved by nanofluids with 5 wt.% hBN additive and 55.05% improvement in the wear quantity at low load and high speed due to the higher viscosity and larger thickness of the oil film. The results were observed by Alves *et al.* [7] when running a frictional test to investigate the characteristic of additional of nanofluids in vegetable oil using reciprocating tester improved the tribological properties of nanofluids. The base oil with the inclusion of the nanoparticles had contributed to the anti-wear mechanism because of the deposition of the particle on the sliding surface in which the physical film was formed and provided lower the friction and wear.

Shafi *et al.* [8] performed experimental study by conducting pin-on-disc tribometer to evaluate the effectiveness of the copper (Cu) nanoparticles additive at two different concentration (0.5 wt.% and 1 wt.%) in avocado oil. The experimental findings discovered that there was a significant decrease in frictional coefficient with the addition of Cu nanoparticles in avocado oil in comparison with dry condition and additive-free avocado oil. This proved the improvement in frictional characteristics that were associated to the formation of the thin film as the Cu nanoparticles deposited between the contacting surface. In addition, the effectiveness of nano-additives of avocado oil with 0.5 wt.% copper nanoparticles can be clearly showed comparatively much smoother worn-out surface than another case. Gutnichenko *et al.* [9] evaluated the performance of dispersion of 0.2% vol. graphite nanoplatelets (GnP) in vegetable oil-based lubricant (ECOLUBRIC E200L) through turning process using Alloy 718 and cemented carbide tools. Machining performance results revealed that 0.2% vol. GnP in MQL oil had a significant prolong the tool life, better surface finish and increases the process stability in conjunction with dry machining and pure MQL oil. This proved that the GnP particles provided an important contribution to minimize the friction as well as providing a cooling effect. Therefore, this study aims to develop a new formulation of biodegradable lubricant from vegetable oils with the addition of solid additives to enhance the physicochemical properties of the bio-based MWF.

In this experimental investigation, modified jatropha oil (MJOs) is preferred as a sustainable MWF for the machining process. The effectiveness of the solid additives was evaluated at a concentration of 0.05 wt.%. hBN and MoS₂ nanoparticles. The physicochemical properties of the developed MWF were analysed in respect of density, viscosity, acid value, water content and corrosion test to determine the future prospective of the new developed MWF.

2. MATERIALS AND METHOD

2.1 Preparation of Modified Jatropha Oil

The vegetable-based MWF was developed from crude jatropha oils (CJO) through chemical modification and addition of additives to enhance the lubrication performance in terms of thermal and stability of the oil. The CJO was chemically modified via a two-step acid-based catalyst transesterification process to produce jatropha methyl ester (JME). Next, transesterification process which involved the chemical reaction of JME with TMP (JME:TMP) was conducted in the presence of 1% (wt./wt.) sodium methoxide (NaOCH₃) at a molar ratio of 3.5:1 to produce TMP tribostester, which is also known as modified jatropha oil (MJO) [10],[11]. MJO was mixed with hBN and MoS₂ nanoparticles at the concentration of 0.05 wt.% (based on the weight of the oil sample). Table 1 indicates the prepared sample with and without the addition of hBN and graphene additives.

Table 1: Description of the MJO samples

Name of sample	Concentration and types of additives
MJO	-
MJO _h	0.05 wt.% hBN
MJO _m	0.05 wt.% MoS ₂
MJO _{hm}	0.05 wt.% hBN + 0.05 wt.% MoS ₂

2.2 Physicochemical Testing

The physicochemical testing was performed to investigate the properties of all MJO samples in terms of density, kinematic viscosity, viscosity index, acid value, water content and corrosion testing in accordance with American Society for Testing and Materials (ASTM) standard testing procedure of ASTM D4502, ASTM D445, ASTM D2270, ASTM D664, ASTM D2709 and ASTM D31-72 respectively. Density was measured using the pycnometer to calculate the ratio of the weight to the volume of oil at 15°C. The kinematic viscosity was measured at a temperature of 40 and 100°C by using a portable viscometer. The viscosity index was calculated according to the result of kinematic viscosity obtained at tested temperature. Acid value test of the oil samples was one through the titration process and water content was performed

by using Mettler Toledo C20 Coulometric Titrator. The oil sample was directly injected in the coulometric titrator, and titrated with a hydranal reagent until reaching the end-point. All the testing was repeated thrice to obtain the average value.

The corrosion test was performed to evaluate the performance of the lubricant sample to react to the atmosphere as well as the formation of protective layer on the surface of the workpiece. The material for the workpiece was AISI 1215 steel that has been polished by using sandpaper (400,800 and 1000 grit). The surface roughness of the polished workpiece should be less or equal to 0.3. The oil sample was placed on the workpiece. The corrosion test was carried out at three different times (24 hours, 72 hours and 168 hours), in which the temperature was set at 27°C and 100°C. A digital microscope image analyser was used to observe the microstructure of the surface of the workpiece.

3. RESULTS AND DISCUSSION

3.1 Density

Figure 1 represents the result of the density for all lubricant samples within the storage period from week 1 until week 4. It can be observed that the density of the SE was highest along the storage period in comparison with MJO samples. This finding reveals that the synthetic ester as a commercial MWF consists of various types of additives such as viscosity improver and anti-wear additive. The density of the MJO was the lowest among the other samples. This is because the MJO had passed through a series of chemical modifications such as esterification and transesterification [12]. Nevertheless, the addition of additives had significantly improved the density of lubricant. Moreover, as the storage period increased, the density of lubricant was increased. According to Zulkifli *et al.* [13], the density of lubricant represents the composition and nature in the lubricant, which consists of hydrocarbons as the major component of lubricant and proposed the range of its density between 0.860 to 0.980 g/cm³.

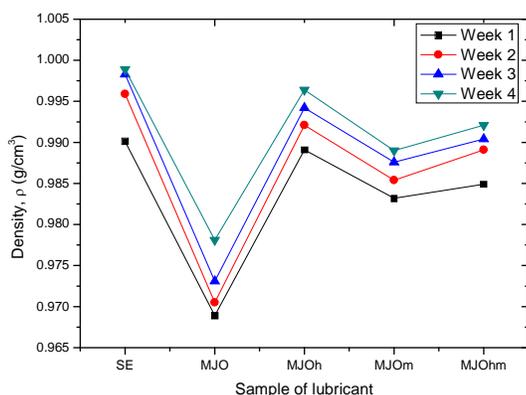


Figure 1: Density for all lubricant samples

3.2 Viscosity

The result of kinematic viscosity at temperatures of 40°C and 100°C is displayed in Figures 2 and 3. The data showed that there is a similar trend of kinematic viscosity at 40°C and 100°C. The kinematic viscosity gradually increased along the storage period which significantly increased with the increased storage period of the lubricant. The SE provided the highest value of kinematic viscosity at 40°C and 100°C in contrast with MJO samples due to the diversity of additives in it. This result proved that SE ester had shorter carbon number between to 8 - 10. The viscosity value of the vegetable-based lubricant increased due to the long carbon chain length [14]. The chemical modification that passed through MJO had reduced its viscosity as the intermolecular forces on the hydrogen bond were weakened [15]. It was also found that the addition of the nanoparticles had improved the kinematic viscosity at temperatures of 40°C and 100°C. Furthermore, MJOh provided a higher value of kinematic viscosity compared to MJOm. This finding proves that the size of hBN nanoparticles was smaller compared to the other additives as it can move easily when the heat is applied [16]. The inclusion of MoS₂ affected the viscosity by decreasing the value because MoS₂ has a strong covalent bond, thus, provided low shear resistance [17]. SE also recorded the highest value of kinematic viscosity at 100°C followed by MJOh, MJO, MJOhm, and MJOm. Surely, the viscosity index depending of the viscosity of the lubricant. Based on the data in Figure 4, SE recorded the lowest viscosity index among MJO samples while the highest viscosity index was provided by MJOh. This finding revealed that the higher of VI provided better lubrication by enhancing the stability lubricity during the increasing of temperature [17]. The presence of additives in MJO improved the viscosity index compared to MJO without additive. However, the MJOh has perceived higher value of the viscosity index compared to MJOm which clearly related to the thermal expansion coefficient of hBN ($1 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) was lower compared to MoS₂ ($(7.4 - 7.6) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) [18].

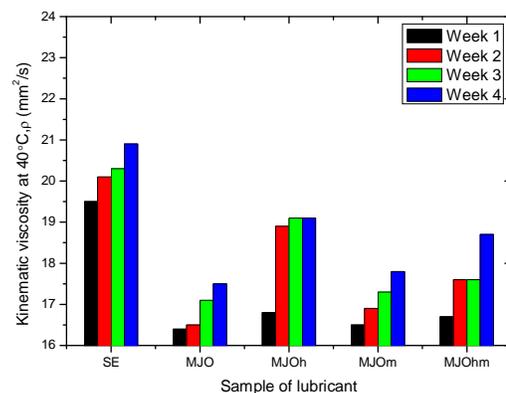


Figure 2: Kinematic viscosity at 40°C for all lubricant samples

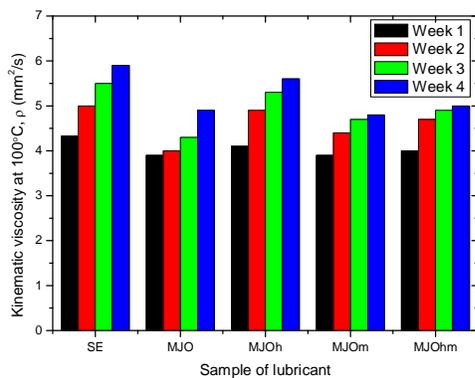


Figure 3: Kinematic viscosity at 100°C for all lubricant samples

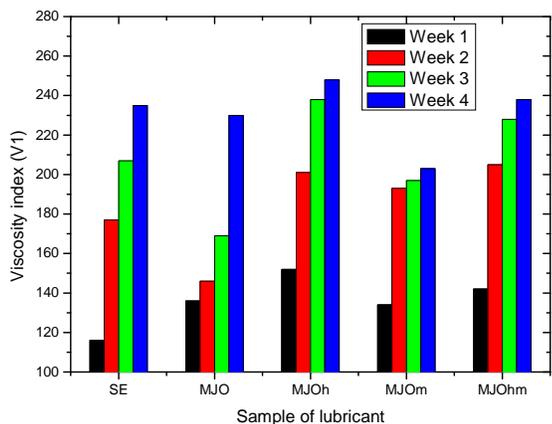


Figure 4: Viscosity index of the lubricant samples

3.3 Acid Value

Figure 5 indicates the variation of acid value of the lubricant samples. The acid value of SE was the lowest compared to the other samples for every week and increased from 28.43% along the storage periods. Among samples, MJO has recorded the higher acid value of 1.58 mg NaOH /g at week 1 and continuously increasing until 1.70 mg NaOH/g at week 4. The acid value of lubricant slightly increased as the longer storage period in view of the fact that the hydrolysis reaction of the fatty acid. The addition of additives positively shown a better result in acid value for the MJOh, MJOm, and MJOhm compared to MJO without additives. The lowest acid value was crucial as it can improve the quality of lubricant by providing excellent prevention towards corrosion and also the formation of hum and sludge [19].

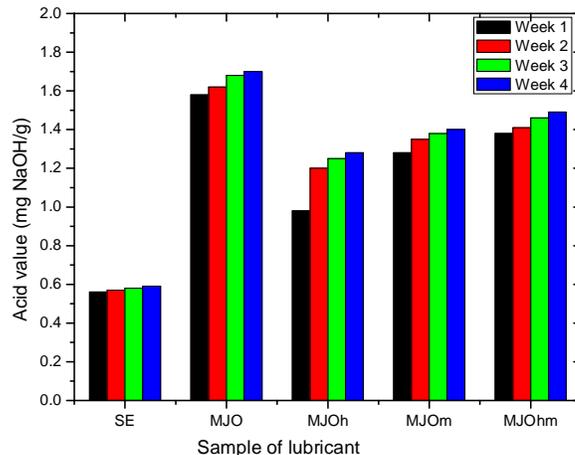


Figure 5: Acid value of lubricant samples

3.4 Water Content

Figure 6 illustrates the result of the water content for various samples of lubricant. The water content for SE was constant from week 1 to week 4 with 0.039 %vol as it did not receive any water or humidity during the storage process. In contrast, MJOs sample had inconsistent water content as it slightly increased along the period of storage. The addition of nanoparticles additives had improved the water content compared to MJO and SE. It was noted that the presence of additives influenced the water content in MJO sample. The free fatty acid in vegetable-based oil was the major factor which speeds up the oxidation process [20]. Moreover, another factor which affects the water content of lubricant was poor handling and non-proper storage condition, for example, the sample was exposed to sunlight. It can be perceived that the result of the water content of all sample excluding SE gradually increases along the storage period. Salimon & Abdo [21] noted that the increase in water content indicated that the sample started to condense. The process of the condensation took place due to the changes of surrounding temperature and the container was closed too tight as no airflow, thus produce water vapor.

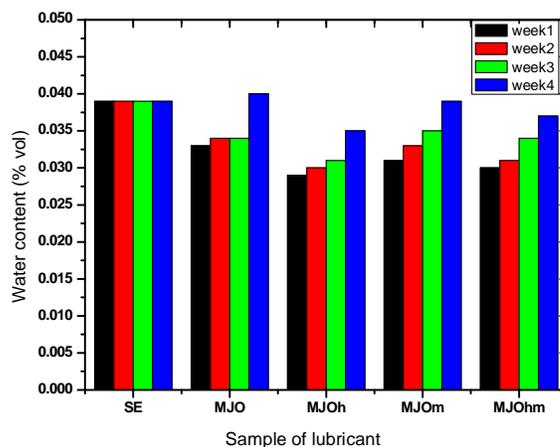


Figure 6: Water content of the lubricant samples

3.5 Corrosion Test

Table 2 presents the result for the workpiece's surface at room temperature (27°C) the workpiece's surface was observed in three storage periods, i.e.; 24 hours, 72 hours and 168 hours. It can be observed that the presence of black spot on the workpiece's surface represents the pitting corrosion. As the black spot reduces, the ability of the sample of lubricant reacts with the workpiece in preventing the pitting corrosion from happening. Based on Tables 2 and 3, MJO samples were compared with SE as the benchmark because it contains various types of additives that provide good protection of corrosion. The workpiece's surface of MJOh at 27°C showed the best surface based on their microstructure due to high resistance to corrosion. Meanwhile the workpiece's surface of MJO presented the worst surface condition. This phenomenon proved that the lower water content of MJOh can provide the high prevention to the chemical reaction on top the workpiece's surface in contrast with MJO which had high water content. The corrosion in storage sample also depends on the acid value as the higher acid value more than 0.5 mg NaOH/g can cause corrosion on the surface of the workpiece. Winter *et al.* [22] stated that poor corrosion protection was affected by the high composition of polyunsaturated acid.

Table 2: Microstructure of the workpiece’s surface at room temperature (27°C)

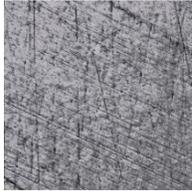
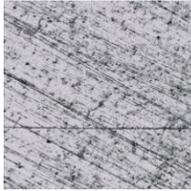
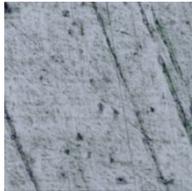
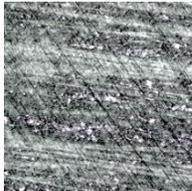
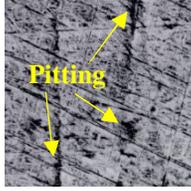
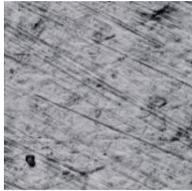
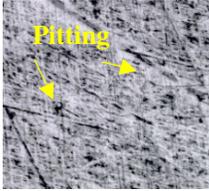
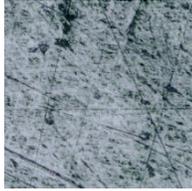
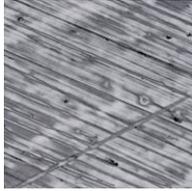
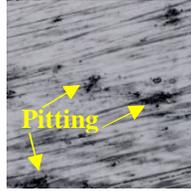
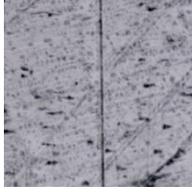
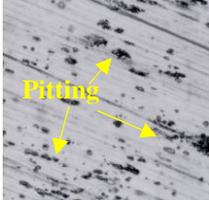
Sample of lubricant	Time (hour)		
	24	72	168
SE			
MJO			
MJOh			
MJOm			
MJOhm			

Table 3: Microstructure of the workpiece' surface at 100°C

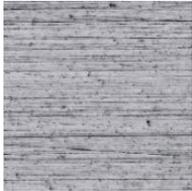
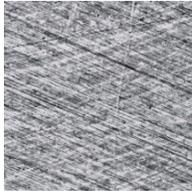
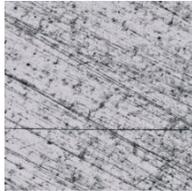
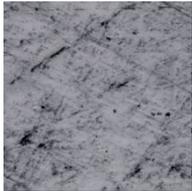
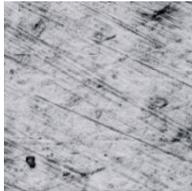
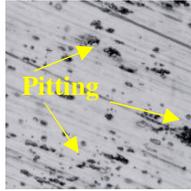
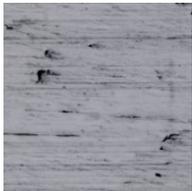
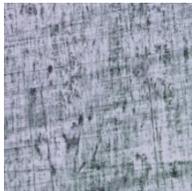
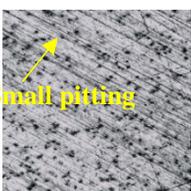
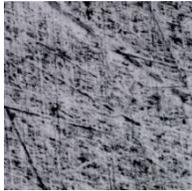
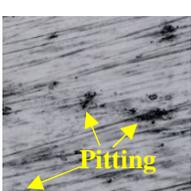
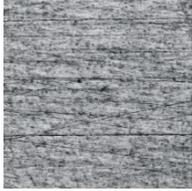
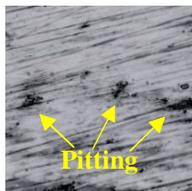
Sample of lubricant	Time (hour)		
	24	72	168
SE			
MJO			
MJOh			
MJOm			
MJOhm			

Table 3 shows the result of the corrosion test at 100°C that was performed at three conditions of 24 hours, 72 hours and 168 hours for all samples. It was observed that MJO had good corrosion resistance compared to MJO. The microstructure of the workpiece's surface was slightly changed due to low humidity as there was no water vapour produced in the oven. The presence of hydrogen and oxygen contributed to the chemical reaction during the corrosion test [23].

4. CONCLUSIONS

In this experimental study, the significant improvements of the physicochemical properties in terms of density, viscosity, acid value, water content and corrosion test were discovered by adding the hBN and MoS₂ nanoparticle. The MJO blended with hBN nanoparticle at 0.05 wt.% concentration was the best combination as it provided better physicochemical properties. The general conclusions of this experimental study can be summarized and listed as below:

- a) MJO provided higher improvement of the kinematic viscosity from week 1 to week 4. This is because hBN nanoparticles have higher molecular weight in comparison with MoS₂ nanoparticles as the result showed that MoS₂ had the lowest density.
- b) The quality of lubricant was affected by both acid value and water content. It can be attributed that the acid value and water content increase along the storage period. The MJO provided the lowest acid value and water content in comparison with all the samples of lubricant.

In terms of corrosion test, MJO provided higher corrosion resistance as compared with SE that acts as benchmark surface condition.

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