THERMAL STABILITY STUDY OF GREASE FORMULATED FROM INDUSTRIAL WASTE OIL

W. Rahman[1], M.A.A. Aziz[1], H. Norasiha[2] and N.S.A. Japar[1]

[1]Faculty of Chemical Engineering & Process Technology, Universiti Malaysia Pahang, Malaysia
[2]Vice Chancellor Office, University College Yayasan Pahang, Malaysia

Email: maizudin@ump.edu.my

ABSTRACT

This is aimed to investigate the effect of additives on thermal stability of grease formulated with waste transformer oil (WTO). One of the key factors of grease functionality is thermal stability. Grease is unsuitable for high-temperature use if the matrix is unable to withstand high temperature. Addition of additive is able to improve the grease thermal stability. In this work, three types of additives (molybdenum disulphide, fumed silica, and polytetrafluoroethylene) were tested as thermal stability additive. The grease was characterized using ASTM International standards and SKF's Grease Test Kit. Based on grease characterization, the addition of additive was found slightly affecting the grease properties. Fumed silica was observed able to improve the grease thermal stability by 3.6%.

Keywords: *Waste transformer oil, thermal stability, sodium grease, molybdenum disulphide, fumed silica, PTFE*

INTRODUCTION

Grease is made of three constituents which are base oil – responsible for lubrication, thickener as base oil carrier, and additive to enhance grease properties. Greases should form in a stable, gel-like structure where there should be chemistry between thickener and the liquid lubricant. To achieve this structure, the particles use must be significantly small and uniformly dispersed throughout the process [1]. According to the National Lubricating Grease Institute (NLGI), in 2016, the production of the grease in the world reached 2.57 billion pounds which is an increase for more than 1.4% from 2015. The year 2015 recorded the value for the global production of grease for 2.54 billion pounds [2]. The primary purpose of getting involved in this field was due to environmental issues. Nowadays, waste transformer oil (WTO), although it is in a small amount compared to other waste oils, is continuously generated without repurposing plan. Most of this waste oil is disposed to sewage or burn by the disposer. The burning of waste oil can lead to the emission of harmful substances that lead to environmental contamination.

Waste oil, although it is a waste, it still valuable since it can be recycled or reused, cheap, and widely available. The utilisation of waste oil will also contribute towards the dependency of the lubricant industry on petroleum resources that are currently depleting and extend the life of these non-renewable resources. The waste oil, however, needs to undergo treatment before it can be utilised due to the presence of contaminants and wear metals. These contaminants can be deleterious to grease structure and affecting the grease performance. Hence, treatment is required to either completely remove the contaminants or reduce it to allowable limit [3].

WTO is an oil that was used as an insulator and coolant in a transformer unit. In general, there was no movement in the transformer unit; hence, chances for the presence of wear metals in WTO that may result from surface friction are repurposing. However, contaminants like water or oxidation products due to exposure to high temperature, are potentially present. The previous study related to grease formulation using WTO was observed to have low temperature tolerant due to the absence of additive that could withstand high temperature [4]. Therefore, this study is aimed to improve the said grease thermal stability by introducing proper additives such as molybdenum disulphide (MoS_2), fumed silica (FS) and polytetrafluoroethylene (PTFE). These three selected additives were a common additive added in grease for high-temperature use [5], [6]. Hence, it was expected for the formulated grease with additive to have high thermal stability.

MATERIALS AND METHODS

Materials

Greases produced in this study were the previous work by Japar et al. [4], which used waste transformer oil (WTO) as grease base oil and sodium stearate as a thickener. Fixed amount (1 wt%) of additives molybdenum disulphide (MoS_2), fumed silica (FS), and polytetrafluoroethylene (PTFE) were added respectively, in the produced grease to enhance the prepared grease thermal stability. WTO was provided by courtesy of XY company, and sodium stearate was purchased from R&M Chemicals (Malaysia). The additives utilised in this study were purchased from Sigma-Aldrich for MoS_2, R&M Chemicals for FS, and Aladdin Chemicals for PTFE. Rotor-stator homogeniser was used to disperse all the grease constituent evenly.

Pre-treatment of waste transformer oil

WTO was contaminated with free water and suspended solids. The WTO was first treated through a settling process to separate WTO and water. Once the water was removed, WTO was vacuum filtered for suspended solids removal using a glass microfiber filter with a pore size of 1.2 µm. Then WTO was removed through the evaporation process at 130-150 °C for two hours with continuous stirring for moisture removal. The characteristics of WTO were analysed before and after treatment, as shown in Table 1.

Production of grease

The composition of sodium grease (base grease) was determined trial and error by varying the weight percent of WTO and sodium stearate until smooth paste resembling peanut butter. The selected grease compositions are listed in Table 2. The percentage of greases was set to be standardised to observe and compare the effect of additive on grease properties. The grease was produced by heating the WTO to 130 – 150°C to remove traces of moisture. Then, sodium stearate was added slowly into the WTO and homogenised at a speed of 4000 rpm for at least two hours until the smooth paste was obtained. Once the grease was ready, it was homogenised for another 15 minutes without the presence of heat. Then the grease was stored in an enclosed container.

Table 1 WTO characteristics before and after treatment

Properties	$WTO_{before\ treatment}$	$WTO_{after\ treatment}$
Appearances	Cloudy amber	Clear yellow
Kinematic viscosity		
at 40°C, cSt	9.89	10.10
at 100°C, cSt	2.58	2.62
Viscosity Index (VI)	85.77	87.22
Density, g/mL	0.926	0.8747
Moisture content, %	0.14	0.05

Table 2 Grease compositions

Type of additive	Additive (%)	Base Oil (%)	Thickener (%)
Base grease	-	75.00	25.00
Base grease + 1% MoS_2	1	74.25	24.75
Base grease + 1% FS	1	74.25	24.75
Base grease + 1% PTFE	1	74.25	24.75

Blending of additive

The one percent of additive was added into the grease after the grease structure was formed. The blending of additive took place for a minimum of one hour to ensure the additive particles were evenly dispersed within the grease with the presence of heat. Once blending completed, the heat was removed, and the greases with additive were homogenised for 15 minutes. Then the grease was stored in an enclosed container.

Characterisation of grease

Consistency

Consistency test is conducted to determine the stiffness of the grease. The decision of a specific consistency for a specific application relies upon many working conditions, for example, temperature, speed, shaft arrangement and pumpability [7]. Ordinary consistency will make the grease remain in the bearing without creating an excessive amount of friction. It is classified according to a scale developed by the National Lubricating Grease Institute (NLGI). The softer the grease, the lower the number. A common grease consistency is between NLGI 1 – 3. The test measures how deep a cone falls into a grease sample in tenths of mm [8].

Dropping point

Dropping point was conducted in accordance with ASTM D2265. The dropping point is the temperature in which grease changes the phase to a liquid state from a semisolid. It is typical of a sodium-based grease to change form from semisolid to liquid. It is very important to test as it helps in identifying types of grease and used for quality control. The dropping point additionally valuable as a sign of the most extreme temperature to which grease can be uncovered without complete liquefaction or over the top oil separation [6], [9].

Oil bleeding

The oil bleeding test was conducted using SKF's grease bleeding kit, and the bleeding percentage was measured by referring to the manual provided in the SKF's test kit [8]. The test for the oil bleeding starts with the fresh grease being heated on filter paper at a temperature of 60°C for two hours. The diameter of the oil spill was then calculated. The grease was then stored in a container for two months and the test was carried out again. The data obtained was then being calculated using Equation 1 and Equation 2, and the two results were compared. The most desirable result was observed at between -15% to 15% of oil bleeding. The positive and negative signs indicate that the grease bleeding was either increased or reduced after used [10].

$$S_{\dots} = 0.785 \times (D^2_{AV\dots} - 100) \quad \text{Eq. (1)}$$

$$\%Diff = 100 \times \frac{(S_{Used} - S_{Fresh})}{S_{Fresh}} \quad \text{Eq. (2)}$$

where $S_{\dots}$ stands for the bled are from a fresh and used sample, D_{AV} is the average diameter of the bled area, and %Diff represents the bled area difference between fresh and used sample.

FTIR characterisation

Fourier transforms infrared (FTIR) spectroscopy identifies the type of base oil, thickener and additive use. FTIR provides information regarding contamination and any changes in comparison to the reference spectrum.

RESULT AND DISCUSSION

Grease appearances

Grease appearance usually depended on the pigment of all grease constituent, either base oil, thickener, or additive. In this study, based on Table 1, WTO is in bright yellow, and sodium stearate is known for its white appearances. Therefore, when base grease was produced, semi-solid beige-coloured grease was obtained (Figure 1(a)). The addition of additives, as shown in Figure 1(b, c, d) displayed different result, especially for grease with MoS_2. MoS_2 was a black powder; hence when it was added into the grease, the resulted grease has black appearances. FS and PTFE was a white powder but, when it was wetted out, it turned transparent. Due to this, grease with either FS or PTFE has similar appearances with the base grease. All greases produced were in semi-solid form resembling peanut butter texture.

Grease consistency

Consistency is defined as the rigidity of the grease. It was favourable for the grease to have consistency ranging between NLGI 2-3 [11]. Based on Table 3, the addition of additives in grease was found to increase the grease consistency; it became firmer. It is because, when the additive was added, the particles attached to the thickener structure, and the structure became denser than before. After all, between the oil to thickener and additive ratio was getting smaller [12]. The value indicates that the grease is in normal condition as most of the industrial grease. However, the consistency test alone was not enough to decide which grease was better; and so further testing needed to be carried out to support the result.

Grease dropping point

The grease dropping point is a test to indicate the temperature at which the grease structure starts to break and flows under its weight. Typically, sodium grease has a dropping point about 175°C, where at this temperature, chances for sodium thickener structure to collapse is high.

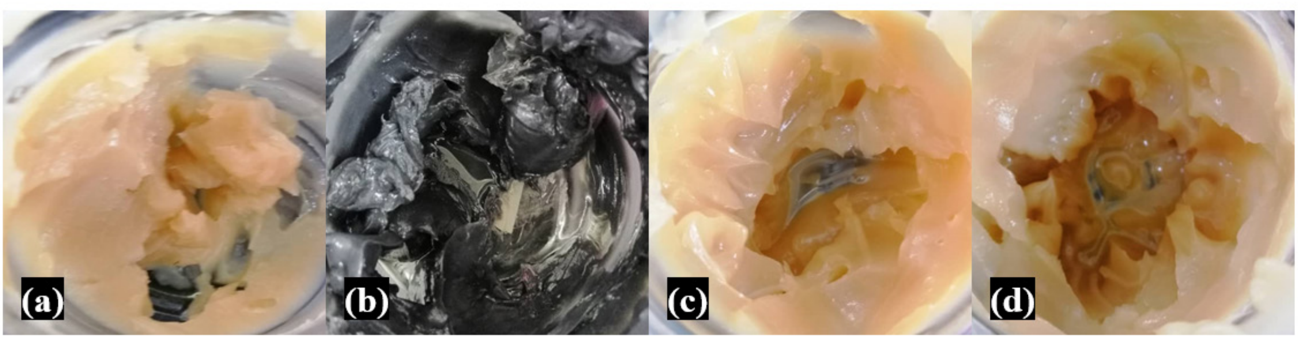

Figure 1 Appearances of base grease (a) and base grease with 1% additive: MoS_2 (b), FS (c), and PTFE (d)

Table 3 Grease NLGI grade consistency

Grease	NLGI grade
Base grease	1 – 2
Base grease + 1% MoS_2	2 – 3
Base grease + 1% FS	2
Base grease + 1% PTFE	2

In this study, the addition of additive in grease was to enhance the base grease thermal stability – its high temperature tolerant. Additive MoS_2, FS, and PTFE was known for their high temperature tolerant and commonly added in grease for high-temperature use [5], [6].

Figure 2 displays the grease dropping point. Based on this test, when compared to the base grease dropping point, the only grease with FS shows significant dropping point improvement by 3.6%. MoS_2 and PTFE were found not affecting the grease dropping point. This finding was in agreement with the work by Mohammed [13], who also saw no significant changes.

As mentioned previously, sodium grease structure is likely to collapse at a temperature of about 175°C. The present work found that at a temperature range of 185 to 200°C, greases started to collapse and flows along the WTO. The enhancement of dropping point of grease with FS was due to the strong interaction between FS-FS particles, forming a new non-melt structure. However, since FS is in a small amount, it was not enough to hold the entire grease structure; hence, it collapses and flows along with the other grease constituent at the temperature of above 190°C.

Grease bleeding

Table 4 and Figure 3 show the oil bleeding result of the formulated greases. It was found that grease

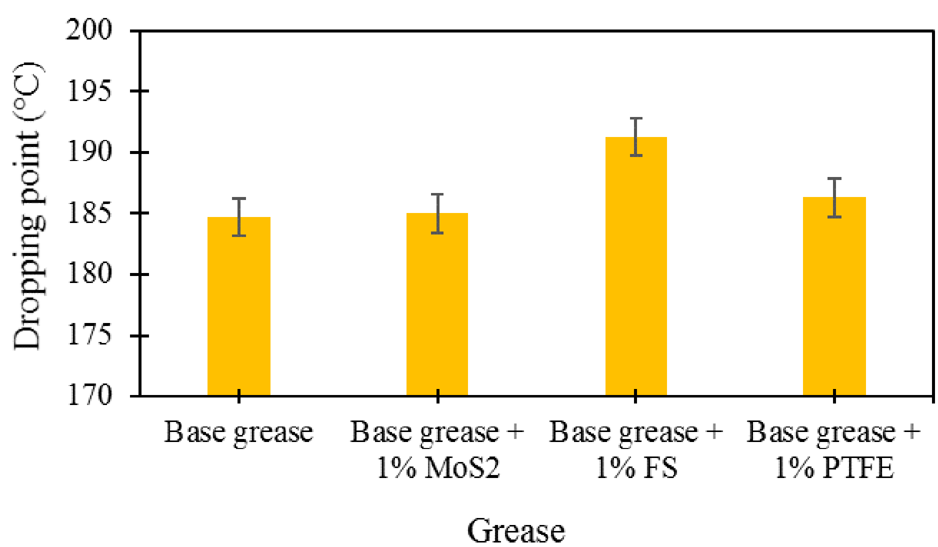

Figure 2 Grease dropping point

Table 4 Oil bleeding different between fresh and used grease

Grease	$D_{av\ Fresh}$ (cm)	$D_{av\ Used}$ (cm)	Different (%)
Base grease + 1% MoS_2	4.700	4.725	-0.3025
Base grease + 1% FS	4.925	4.650	3.476
Base grease + 1% PTFE	5.200	5.050	2.107

formulated with MoS_2 recorded the lowest percentage with -0.3025% bleeding different then followed by grease formulated with PTFE with 2.107% bleeding different. The highest percentage was given by grease with FS with 3.476% oil bleed different. The negative result in the grease formulated with MoS_2 means the used grease bled 0.3025 % less than fresh unused grease.

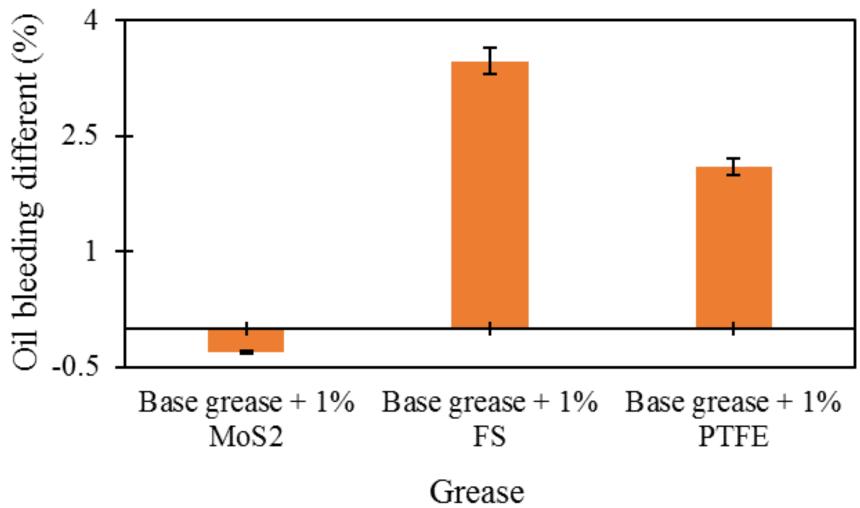

Figure 3 Oil bleeding comparison between greases with additive

The grease that has higher oil bleeding means that the grease cannot keep base oil into its structure due to intensive shearing or vibrations and have poor mechanical stability. The grease formulated from molybdenum disulphide give significant changes to the grease itself due to loss of base oil generally accompanied by an increased consistency. When having a lower oil bleeding, oxidation of base oil leads to base oil viscosity increases due to high temperature. Generally, the base oil viscosity and the molecular interaction between the base oil, thickener and additive mainly determined the oil bleeding percent rate.

FTIR characterisation

FTIR analysis was conducted to detect compounds existed in grease and/or contaminants, oxidation products, additives and unknown material presented the formulated grease. Figure 4 displays the FTIR spectrums of all greases. FTIR spectrums of all greases show not much difference in Figure 4(a). All spectrums have the same strong peaks in the region of 2951 – 2853 cm^{-1}, which indicates C-H stretching of CH_2 and CH_3. Asymmetric stretching vibration of the COO^- group associated with sodium thickener was observed at 1558 cm^{-1} [14]. The functional group of alkane C─H bond stretch of CH_3 bond was observed at about 1376 cm^{-1} [15]. Overlapping of CH_2 rocking vibration at about 721 cm^{-1} also indicates the presence of alkanes [16], [17]. These spectrums are summarised in Table 5.

Figure 4(b) displays the spectrums that indicated the presence of additive in the respective grease. Spectrums (A) with a wavelength between 1219 – 1157 cm^{-1} indicated the presence of PTFE due to the CF_3 and CF_2 group detected by the FTIR. Peaks detected at 1104 cm^{-1} (B) were related to the Si-O-Si stretching vibration representing the FS additive [18], [19]. Peak representing the existence of MoS_2 was detected below 500 cm^{-1} (C) [20]. Based on these spectrums, it was confirmed that all additive added in the formulated grease was found present in the respective grease.

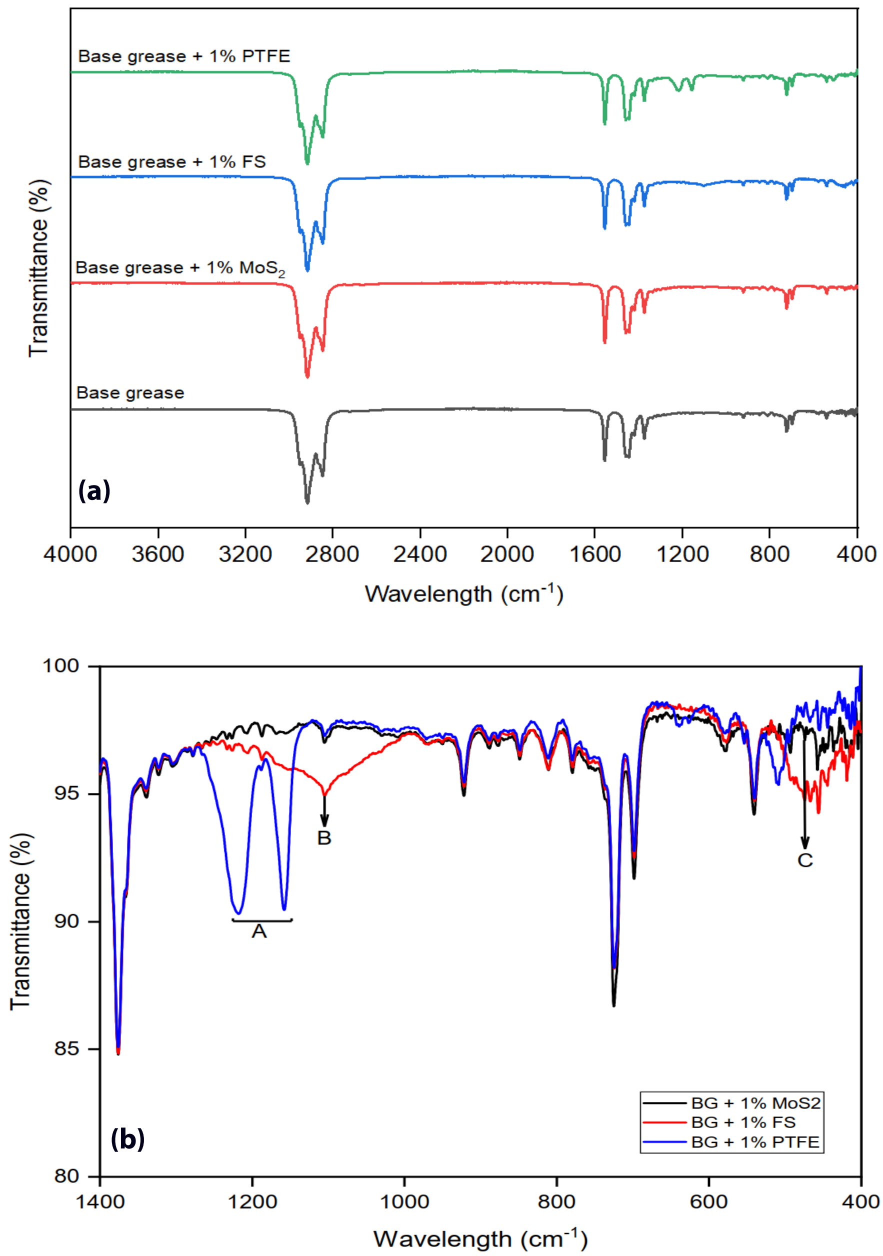

Figure 4 FTIR spectrums of all greases (a) and additive (b)

Table 5 Summary of the FTIR spectrums in Figure 3

Peaks (cm^{-1})	Description	Compound	Component
2951 – 2853	C-H stretching of CH_2 and CH_3	Alkanes	Oil & Thickener
1558	COO^- asymmetric stretching	Carboxylate	Thickener
1441 – 1376	C-H bending/deformation	Alkanes	Oil & thickener
1217 – 1157	CF_3 and CF_2 group	Polymer	PTFE
1104	Si-O-Si stretching	SiO_2	FS
718 – 721	C-H out of plane bending	Single ring aromatics	Oil
470	Mo-S bond	MoS_2	MoS_2

CONCLUSION

This study is aimed to improve the WTO-based grease thermal stability by adding specific additive into the grease and observed the effect of the additive on grease thermal stability. Incorporation of additive MoS_2, FS, and PTFE are only slightly affecting the grease properties. FS is able to enhance the grease thermal stability by improving the grease dropping point by 3.6%. However, due to the selection of sodium thickener in this study, the full potential of additives to improve grease thermal stability is not visible as the thickener starts to collapse below the melting point of additive. Therefore, it recommended for future work that different thickener be used so that the ability of the selected additive to improve the grease thermal stability can be observed. It can be concluded that the addition of FS as an additive will help in improving the grease thermal stability.

REFERENCES

[1] J.G. Speight, *Handbook of petroleum product analysis*, Second Edition, Hoboken, New Jersey: John Wiley & Sons, Inc., 2015.

[2] C. O'halloran, "NLGI spokesman", *NLGI*, 82, 1, Missouri: NGLI, 2018.

[3] Hazardous Substance Division, *Guidelines on standard and specification of recovered waste oil in Malaysia*, Putrajaya, Malaysia: Department of Environment Malaysia, 2010.

[4] N.S.A. Japar, M.A.A. Aziz & M.N. Razali, "Formulation of fumed silica grease from waste transformer oil as base oil", *Egypt Journal of Petroleum*, 28, 1, pp. 91-96, 2019.

[5] V. Stepina & V. Vesely, *Lubricants and special fluids. Tribology V Series,* Elsevier Science, 1992.

[6] M.N. Razali, M.A.A. Aziz, W.N.A.W.M. Hamdan, N.A.M. Salehan & M.Y. Rosli, "Synthesis of grease from waste oils and red gypsum", *Aust. J. Basic Appl. Sci.*, 11, 3, pp. 154-159, 2017.

[7] B.H. Chudnovsky, *Transmission, distribution, and renewable energy generation power equipment: Aging and life extension techniques,* Second Edition. Florida: CRC Press, 2017.

[8] SKF, *"SKF Grease Test Kit TKGT 1: Instruction manual"*, SKF Group, pp. 1–40, 2009.

[9] ASTM D2265-19, *Standard test method for dropping point of lubricating grease over wide temperature range*, West Conshohocken, PA: ASTM International, 2015.

[10] N.W.A. Rahman, N.S.A. Japar, M.A.A. Aziz, A.H.A. Razik & M.Y.M. Yunus, "Sodium grease formulation from waste engine oil,", *IOP Conf. Ser. Earth Environ. Sci.*, 257, 2019. Doi:10.1088/1755-1315/257/1/012018

[11] S.Q.A. Rizvi, *A Comprehensive review of lubricant chemistry, technology, selection, and design*. West Conshohocken, PA: ASTM International, 2008.

[12] D. Gonçalves, R, Marques, B.Graca & A.V. Campos, "Formulation, rheology and thermal aging of polymer greases – Part II: Influence of the co-thickener content", *Tribology Int.*, 87, pp. 171-177, 2015.

[13] M.A.R. Mohammed, "Effect of additives on the properties of different types of greases", *Iraqi Journal of . Chemical & Petroleum Eng.*, 14, 3, pp. 11-21, 2013.

[14] F. Cyriac, P.M. Lugt, R. Bosman, C.J. Padberg & C.H. Venner, "Effect of Thickener Particle Geometry and Concentration on the Grease EHL Film Thickness at Medium Speeds", *Tribology. Lett.*, 61, 2, p. 18, 2016.

[15] H. Kalathiripi & S. Karmakar, "Analysis of transformer oil degradation due to thermal stress using optical spectroscopic techniques", *Int. Trans. Electr. Energy Syst.*, 27, 9, pp. 1-11, 2017.

[16] T.B. Patel, K.D. Panchal & A.S. Shah, "Characterization of WTO (Waste Transformer Oil) & Diesel by Fourier Transform Infrared Spectroscopy & Effect of Additives on Properties of WTO-Diesel Blends", *Int. J. Sci. Res. Dev.*, 3, 11, pp. 747-751, 2016.

[17] J. Pan, Y. Cheng & J. Yang, "Structural degradation of a lithium lubricating grease after thermal ageing", *J. Chem. Eng. Japan*, 49, 7, pp. 579-587, 2016.

[18] K.-M. Li, J.-G. Jiang, S.-C. Tian, X.-J. Chen & F. Yan, "Influence of Silica Types on Synthesis and Performance of Amine – Silica Hybrid Materials Used for CO2 Capture", *J. Phys. Chem. C*, 118, 5, pp. 2454-462, 2014.

[19] M. Rezakazemi, A. Vatani, and T. Mohammadi, "Synergistic interactions between POSS and fumed silica and their effect on the properties of crosslinked PDMS nanocomposite membranes", *RSC Adv.*, 5, 100, pp. 82460-2470, 2015.

[20] T.N. Kumar, N. Chandrasekaran & K.L. Phani, "Structural and electronic modification of MoS2 nanosheets using S-doped carbon for efficient electrocatalysis of the hydrogen evolution reaction", *Chem. Commun.*, 51, 24, pp. 5052-055, 2015.