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A Systematic Study on Composition of Low Viscosity Automotive Lube Oils with an Emphasis on Wear and Frictional Characteristics

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ABSTRACT
In this work the performance of three commercial lube oils and two base oils of different viscosities, composition have been studied for their tribo performance using four ball tribo tester as per ASTM D 4172D and IP 239 and at the end of the test run the steel ball surfaces have been examined under scanning electron microscope (SEM) to assess the wear deformities. The tribo-performance results have been co-related with the physico-chemical properties along with quantity and type of the molecules present in these oils by proton nuclear magnetic resonance (NMR) studies. It has been observed that the lubricant with higher viscosity, higher aromatic molecules containing CH_2 chains shows lower friction and wear behavior whereas the increasing napthenic type molecules have reverse effect which is evident from the results.
Key words- Engine oil, four ball tester, molecular Component, SEM, Tribo-performance,

I. INTRODUCTION

The lubricant formulation primarily involves proper designing of additives to upgrade the base oils. The base oil selection depends on their physical properties such as viscosity, viscosity index, total acid number, residual ash contents etc. It is known that petroleum based lubricant base oil is a complex mixture of hydrocarbons with carbon numbers generally in the range of C20 – C40, depending upon the specific viscosity grade. Base oils contain a variety of molecules, such as paraffins, iso paraffins and napthenes. The properties of the lubricants are dependent upon the types of and the percentage of the individual molecules present in the base oils. Attempts have been made by researchers and lubricant scientist to understand and co relate the properties of the oils for efficient performances along with additive compatibility [1-4]. It is also true that sulphur and phosphorus containing additives are affecting the catalytic converters and filters, thereby degrading the efficiency of the exhaust treatment devices. The International Lubricant Standardization and Approval Committee (ILSAC) proposed the norms of limiting sulphur (0.05% max) and phosphorous (0.08% max), in the finished passenger car engine oils (PCMO) [5, 6]. The most common and universally used additive, zinc di-alkyle di-thio phosphate (ZDDP) is a multifunctional additive, and acts as an antioxidant and anti wear agent [7-10].

Another commercial additive is molybdenum di-thiocromate (MoDTc) or MoS2 [11-14]. All of these are important class of additives enhancing engine oil life and performance. However, as the Sulphur and Phosphorous containing additives possess environmental hazards, extensive research is going on to find their substitutes in new formulations of lube oils. Thakre and Tyagi [15] have studied the variation of tribo-performance of engine oils and correlated the same with their physico-chemical properties and reported varying degrees of performance behavior of commercially available engine oils. However, the performance of the lubricants is also dependent on the type of molecules present in the lube oil. Further, the viscosity of the engine oils have dominating influence on the performance due to which low viscosity engine oils are gaining significant importance. Hence, in the present study attempt has been made to co-relate the physico chemical properties of selected lubricating oils having wide range of viscosities by tribo tests along with quantification of wear scar diameter (WSD) by SEM to co-relate their performance with respect to their molecular composition. However, the presence of the additives in the three commercial lube oils have been quantified and compared to have a trend of the results in synthetic oil vs mineral oil and overall these results have been compared with high and low viscosity base oils.

II. Experimental

Based on the gap of information available in the literature five different lubricating oils have been selected for the study as given in Table 1.

Table 1: Lubricants selected for performance evaluation.

Lubricant	Description
OS-1	Base oil N65
OS-2	Base Oil N150
OS-3	Automotive Lube oil
OS-4	Automotive Lube oil
OS-5	Automotive Lube oil

The physico-chemical properties have been characterized using prescribed ASTM methods.
Further, the Trace metal analysis of the lube oil samples were carried out using ICP AES/AAS technique on DRE, PS-3000UV, LEEMAN Analyzer on lube oil OS-3, OS-4 and OS-5 for indicative presence of metal containing additives. All the five oils were subjected to proton and NMR study for their molecular composition on Bruker Advance - 500 NMR spectrometer.

Fig.1.Four ball tester

The tribological performance of the lube oils have been measured in terms of friction, wear and weld load under point contact geometry. The tribo tester shown in Fig1 utilizes four-ball geometry in a tetrahedral form. The top ball is fixed into the spindle and rotates at the pre-defined speed. The bottom three balls are fixed in a ball pot filled with the lubricant. The four balls make three point contacts. The AISI, standard steel no. E-52100 ball test specimens with a diameter of 12.7 mm and hardness of Rockwell C 64-66 were used for the tests as per ASTM D 4172D.

The test specimens were removed cleaned and analyzed for surface morphological features in a Scanning Electron Microscope (SEM). The weld load tests for lubricants were performed on a four ball EP tester, similar in geometry and operation as shown in figure 1, but with a different experimental protocol IP 239. The lubricant to be tested was filled in the ball pot containing three tightened balls and the top ball held in ball holder secured into the spindle was free to rotate at 1500 rpm. Normal load was applied in increment of 10 kgf starting from 150 kgf till welding/seizure.

III. RESULTS AND DISCUSSION

The physico-chemical properties of the lube oils were determined by using ASTM test methods as given in Table 3. The result includes kinematic viscosity, viscosity index (VI), acid number and pour point. Acid number is negligible in case of base oils due to the absence of any additive component in their formulation, while oil numbers OS-3to OS-5 has comparable acid number.

Similarly, viscosity index of oil OS-1 has lowest Value and oil OS-5 has highest. Viscosity index of rest of the lube oils was observed in between. The density of the five oil samples is also following a same pattern. It is also observed that the pour point of oils OS-3 to OS-5 is below -30ºC and base oil OS-1& OS-2 has pour point -21ºC belonging to group II range.

The trace metal analysis was performed for the quantification of the additives present in the oil OS-3, OS-4 and OS-5 are given in Table 4. Since most of the performance additive contains metals, it will be logical to assess the quantity of various metals in the lube oils. It has been observed that Zn, Mo, Ti are present in all the three commercial lube oils where as oil OS-5 contains highest quantity of these metals, these are the finger prints of ZDDP type additive. Similarly, Na, Ca, Ti type metals identified in these oils is due to the presence of heavy alkali based additives to control pH of the oils. Mg & P type of metal and elements are indicative of presence of multifunctional additive i.e. ZDDP to control wear, frictional and corrosive behavior of the

TABLE.3. Physico-chemical properties of oils.

Properties	Method	OS-1	OS-2	OS-3	OS-4	OS-5
Density @ 15°C g/ml	ASTM D 4052	0.8430	0.8430	0.8559	0.8480	0.8566
K. V@40 °C (mm^2/s)	ASTM D 445	12.41	31.41	68.95	118.34	92.80
K. V @100°C (mm^2/s)	ASTM D 445	3.03	5.56	10.90	13.10	14.61
Viscosity Index	ASTM D 2270	98	115	148	105	164
Total Acid Number (mg KOH/g)	ASTM D 664	0.004	0.002	1.64	1.71	1.64
Pour Point (°C)	ASTM D 97	-21	-21	- 30	-36	-39

oils. Overall these results shows oil OS-5 which is synthetic type is better formulated for higher performance.

TABLE 4 Trace metal analyses

Oil Sample		OS-3	OS-4	OS-5
Elements (mg/l)	Zn	952	939	1210
	Mo	<1.00	100	105
	Ti	<1.00	1.35	1.60
	Pb	<1.00	1.20	1.00
	Sn	6.00	2.00	4.30
	Ca	1760	78.50	2760
	Mg	9.00	1230	105
	P	954	920	1210
	Na	7.95	12.20	11.70

The types of hydrocarbon molecules present in lube oils were estimated using proton NMR and the results are summarized in Table 5. The proton NMR results shows that the presence of terminal CH_3 group is maximum in oil OS-1 while it is minimum in oil OS-5.

TABLE5.Molecular NMR analysis

Structural parameters	**OS-1**	**OS-2**	**OS-3**	**OS-4**	**OS-5**
HCH3	31.4333	29.30	26.4	27.75	25.15
HCH2	58.4333	62.70	66.4	60.58	67.45
Hnaph	10.133	8.60	7.05	11.27	6.16
Halpha	-	-	0.01	0.09	0.10
Har	-	-	0.05	0.14	0.69
Car	0.466	0.53	0.61	0.45	1.46

This indicates that more iso or branching type of napthenic hydrocarbon is present in oil OS-1whereas oil OS-5 which is synthetic in nature contains minimum terminal CH_3 group. Probably it is alpha olefinic oil. It is more evident from the highest presence of CH_2 proton in oil OS-5. Methyl proton and CH_2 proton of other three oils are in between these two oils. Similarly, napthenic proton in oil OS-1 and OS-4 are quite similar & rest three is of the same order. It is interesting to note that aromatic proton is quite high in oil OS-5 which is due to heavy doping with different additives which is also evident from Table 4, where it shows various metal additive content percentages highest. The efficiency of all the five oil samples were evaluated in terms of for their tribological performances i.e. mainly wear and friction coefficient determined on four ball rolling contact machine as per ASTM 4172 B method as explained in experimental section.

TABLE6. Wear performance of the lubricants

Sample Code	Average W.S.D, mm	Coefficient of Friction	OK Load (kgf)	Weld Load (kgf)
OS-1	0.658	0.1362	110	120
OS-2	0.549	0.1294	110	120
OS-3	0.450	0.1260	190	200
OS-4	0.495	0.1294	200	210
OS-5	0.437	0.1192	200	210

The friction and wear characteristics of the lubricants are tabulated in table 6. As predicted previously oil OS-1 has highest WSD followed by oil OS-2 where as oil OS-5 have lowest WSD and coefficient of friction and these results are elaborated in fig. 2. The trend observed for the coefficient of friction is OS-5< OS-3 < OS-4 < OS-2< OS-1. Table 6 also elaborates the extreme pressure performance behavior of the lubricants. The base oils i.e. OS-1 and OS-2 shows lower weld loads of 120 kgf. The lubricant OS-5 which has lowest friction and wear shows the highest weld load.

The used steel ball specimens were investigated for the wear and boundary layer formation using SEM micrographs of6000x magnification are given in fig. 3 along with EDX results in fig 4.

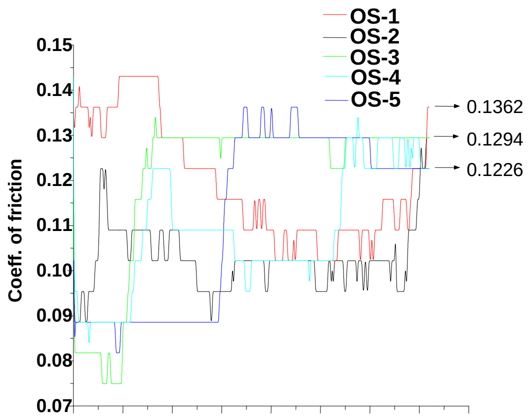
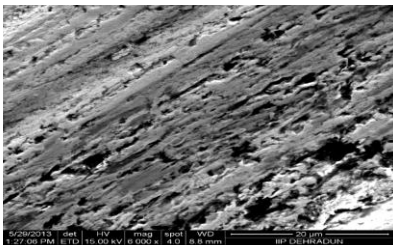
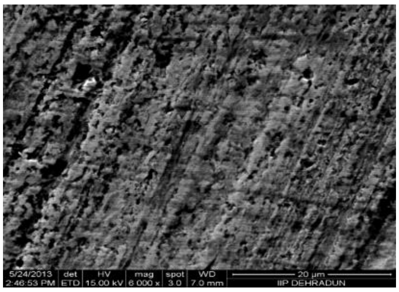


Fig.2 **coefficient of friction vs. time**

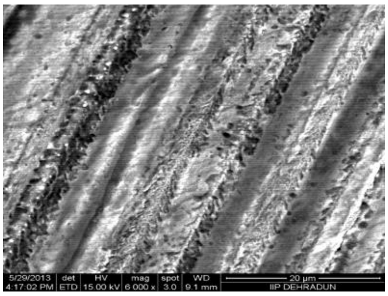
The SEM micrographs reveal impression of wear along the sliding direction for the oil OS-2 to OS-5 lubricated steel ball specimens but oil OS-1 shows random debris instead of any pattern. It is interesting to note that oil OS-2 and OS-4 have deep scars on the specimen with respect to oil OS-3 & OS-5 whereas oil OS-3 & OS-5 scar channels are smoothen enough showing better formulation of lubricant to form thin film on the surface of the steel balls.



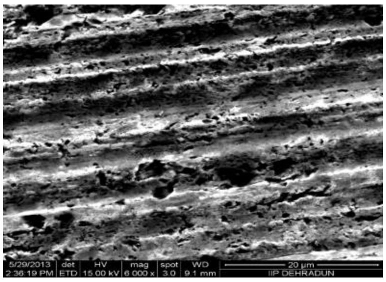
OIL 1



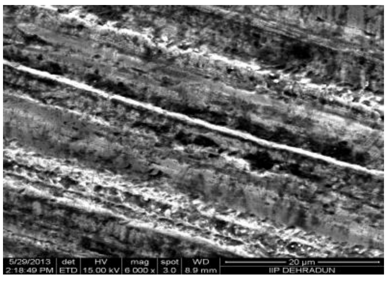
OIL2



OIL 3



OIL4



OIL 5

Fig3. SEM Photographs

The results of EDAX analysis given in fig. 4 shows oil OS-1 and OS-2 contains metal from steel ball only where as oil OS-3 contains Ca, P, Mo, Zn in higher percentage, confirms the results of elemental analysis which have been discussed earlier. Similarly oil OS-4 and OS-5 have similar metal and elemental in different percentages. Interestingly, these embodied on the surface of the steel ball indicating the formation of the thin film of lubricant effectively facilitates the binding of these metal on the surface of the steel ball. It confirms that these metal help to protect the rubbing surface of the metal during course of mechanical operation and reduces the scar and friction of the metal surfaces. Also it shows the effectiveness of ZDDP type additive which reduces the scar and friction of the metal surfaces. Also it shows the effectiveness of ZDDP type additive which contains all those metal and elements mentioned above.

The used steel ball specimens were investigated for the wear and boundary layer formation using SEM micrographs of 6000x magnification are given in fig. 3 along with EDX results in fig 4. The SEM micrographs reveal impression of wear along the sliding direction for the oil OS-2 to OS-5 lubricated steel ball specimens but oil OS-1 shows random debris instead of any pattern. It is interesting to note that oil OS-2 and OS-4 have deep scars on the specimen with respect to oil OS-3 & OS-5 whereas oil OS-3 & OS-5 scar channels are smoothen enough showing better formulation of lubricant to form thin film on the surface of the steel balls.

All of the above findings were correlated to ascertain the influence of physico-chemical properties as well as molecular level chemical composition on the tribological performance and indirectly on the efficiency of lube oil in engine performance as such. Now, if we co-relate primary performance indicators coefficient of friction and WSD with viscosity and different hydrocarbon molecules present in the lube oil we have a definitive pattern which indicates the co relation between all these components and directionally we can evaluate the performance with the basic molecular compositions of the oils. The effect of viscosity on the friction and wear performance of lubricants is shown in figure 5 (a-b). The coefficient of friction and WSD for all the five lube oils shows a definitive pattern i.e. with increasing viscosity, coefficient of friction drops from lube oil OS-1 to OS-2, but in the case of commercial oils it followed nearly same pattern. But it is little distorted due to the presence of different quality of friction improver in the oil itself but it is clear, lube oil OS-5 has best results. The WSD reductions relates to the capability of oil to form thin protective films on the surface.

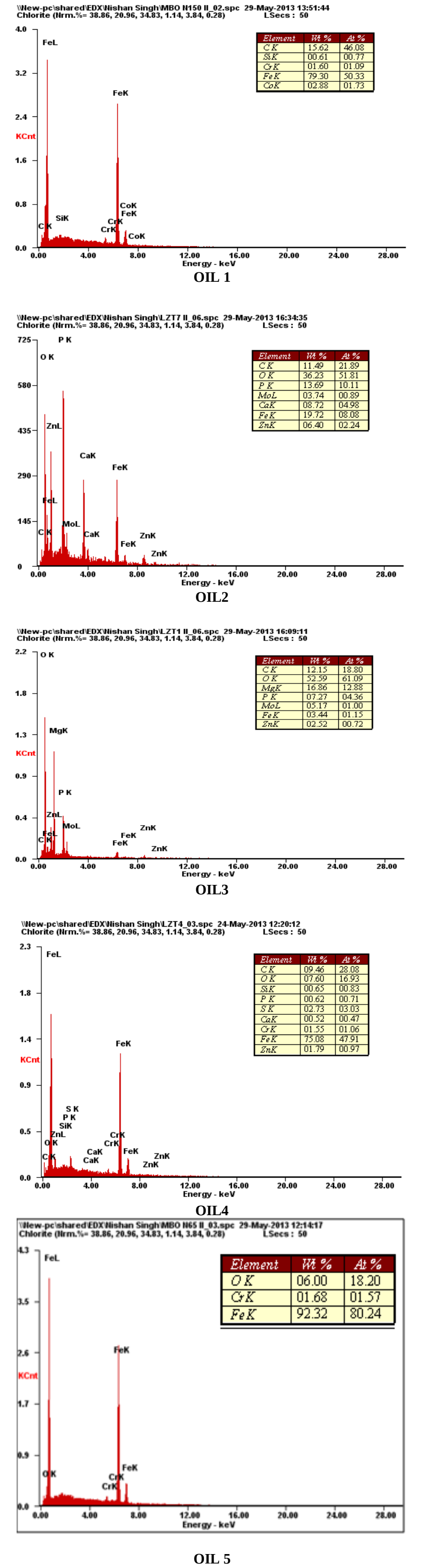


Fig. 4 EDX results

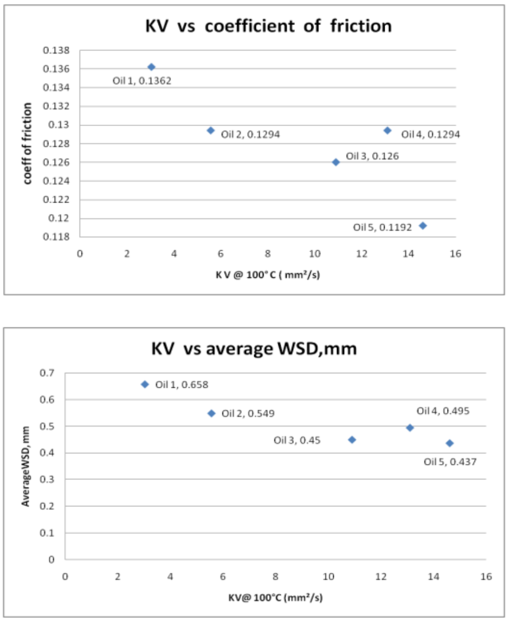


Fig. 5 (a) & (b)

In case of low viscosity oils i.e. oil OS-1 this property is poor, but overall oil OS-3 to OS-5 has not much difference in the performance. A comparative assessment between the presence of aromatic type molecule in the lube oils and coefficient of friction is shown in figure 6 (a). It shows that oil OS-1 having lesser aromatic molecules shows higher coefficient of friction. Similarly the oil OS-5 with higher aromatic molecules shows lower coefficient of friction. The influence of aromatic molecules on wear performance is shown in figure 6(b).

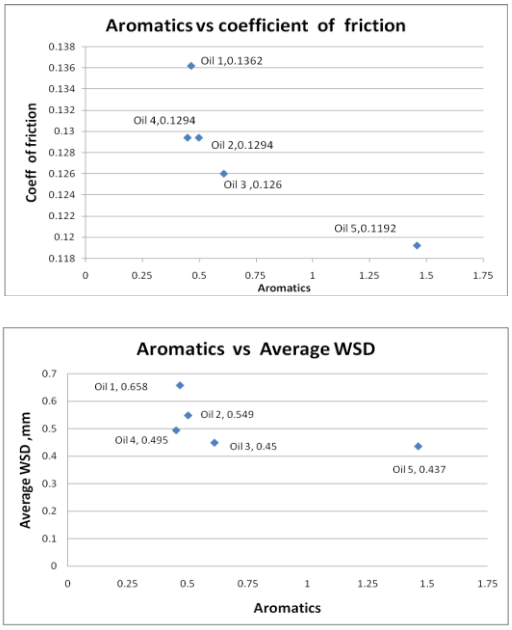


Fig.6 (a) & (b)

It can be seen from the figure that the aromatic molecules do not have significant influence on the wear behavior. In this case the commercial oil with additives shows better anti-wear behavior as compared to the base oils. The influence of average no of CH_2 chain present in oil to the friction and wear behavior is shown in fig. 7 (a-b). It is observed from fig. 7 (a) that the oils with larger no of CH_2 chain present in them shows lower friction and wear. In this case the oil OS-3 and OS-5 with larger CH_2 chains shows better anti-friction and anti-wear performance.

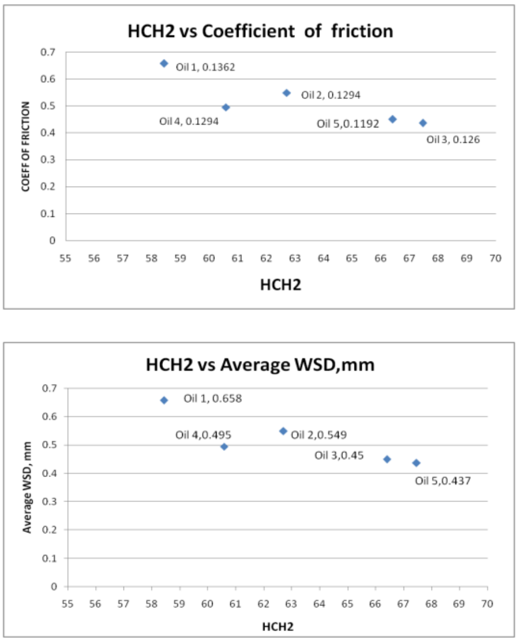


Fig. 7 (a) & (b)

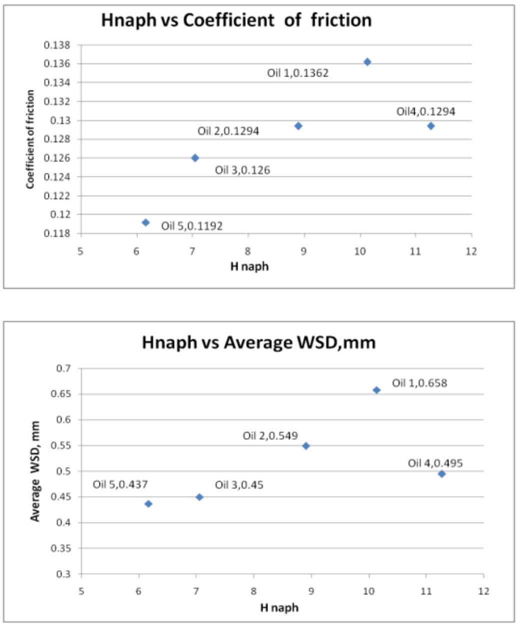


Fig. 8 (a) & (b)

Figure 8 (a-b) shows the effect of quantity of naphthenic type molecule on the friction and wear behavior of the lubricant samples. It is observed that the oil OS-1 and OS-4 with higher napthenic type molecules shows higher friction. The oil OS-5 with lowest quantity of napthenic molecules shows lowest coefficient of friction. Interestingly, oil OS-5 has lowest napthenic proton of 6.16 due to which it shows best results in the improvement of coefficient of friction. Similarly in case of wear, the oils with lower quantity of napthenic type molecule shows better anti-wear performance.

IV. CONCLUSIONS

In the present paper a qualitative assessment on the tribological performance of engine oils have been performed. The tribological performances of the oils have been co-related with their physico-chemical properties and the types of molecules present in them. From the present study following salient conclusions can be derived; the low viscosity commercial lubricants perform better than the base oils due to the presence of P, Zn and Mo based extreme pressure additives. The EP additive is capable of forming the boundary layer, as the P, Zn and Mo are present on the worn out surfaces of the ball test specimens due to which these oils show better tribological performance.

The lubricant viscosity significantly influences the tribo performance, and the oils with higher viscosity show lower friction and wear. The friction decreases with increase in aromatics molecules present in the oil. However, aromatic molecule content does not have significant influence on the wear performance of the oil.

The tribo-performance improves with increase in the average number of CH_2 chain present in the oil. The presences of napthenic type molecules have inverse effect on the tribo performance. The oils with lesser napthenic molecules show better tribo performance. The oil OS-5 with higher viscosity, possessing larger aromatic molecules and CH_2 chain and with lower napthenic molecules shows the best anti-friction and anti-wear performance. Further this oil possesses higher content of EP additives.

V. ACKNOWLEDGMENT

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