Tribological Analysis of Bis(2-Ethylhexyl) Phosphate Ionic Liquid Based Bio-Lubricants at Various Operating Conditions

By

Muhammad Moneeb Butt

(Registration No: 00000330560)

Department of Mechanical Engineering

School of Mechanical and Manufacturing Engineering

National University of Sciences & Technology (NUST)

Islamabad, Pakistan

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Master of Science in
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Supervisor: Dr. Mian Ashfaq

Co-Supervisor : Dr. Rehan Zahid

School of Mechanical and Manufacturing Engineering

National University of Sciences & Technology (NUST)

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Signature: ______________________

Name of Supervisor Dr. Mian Ashfaq Ali

Date: 12th August 2024

Signature (HOD): ______________________

Date: 12th August 2024

Signature (Dean/ Principal) ______________________

Date: 12th August 2024

Email: info@nust.edu.pk Web: http://www.nust.edu.pk

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1. Name: Rehan Zahid Signature:

2. Name: Riaz Ahmed Mufti Signature: R. Mufti

3. Name: Abdullah Jamil Signature:

Supervisor: Dr. Mian Ashfaq Ali Signature:

Emad

Head of Department

Date 12-Aug-2024

COUNTERSINGED

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Student Name: Muhammad Moneeb Butt Signature: ________________

Examination Committee:

GEC Member: Dr. Riaz Ahmed Mufti Signature: R. Mufti
(Professor, SMME, NUST)

GEC Member: Dr. Abdullah Jamil Signature: ________________
(Assistant Professor, SMME, NUST)

Supervisor Name: Dr. Mian Ashfaq Signature: ________________

Name of HOD: Dr. Mian Ashfaq Signature: ________________

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

CSO	Cotton Seed Oil
WCO	Waste Cooking Oil
RJO	Rattan Jot Oil
PAO	Polyalphaolefin
IL	Ionic Liquid
DEHP	Di-Ethylhexyl Phosphate
COF	Coefficient of Friction
WSD	Wear Scar Diameter
VI	Viscosity Index

ABSTRACT

Mechanical components involving surface interaction requires lubrication at all costs to reduce friction and wear in order to avoid mechanical failure. Majority of lubricants used around the world are from mineral based sources. These sources are not infinite and pose danger to the environment due their toxic nature and disposal problems. This awareness has given rise to the formation of environmental friendly lubricants which are obtained from renewable sources such as bio-lubricants. The low thermal stability of bio-lubricants has caused the limitation on it use as compared to mineral based oils. Certain additives are used to increase the thermal stability of these bio-lubricants and further enhance their tribological properties. Ionic liquids are the most common solvents used as an additive to the bio-lubricants. These organic salts are environmentally friendly and have proved to be beneficial to the tribological properties of bio-lubricants. The extent to their effectiveness in enhancing the tribological performance of a lubricants greatly depends upon compatibility and its miscibility. Ionic liquids are generally composed of anions and cations and make strong interaction with polar base oils.

In this research work, Bis (2-Ethylhexyl) phosphate ionic liquid was used an additive to the base test lubricants including PAO and bio-lubricants as Cotton seed oil (CSO), Rattan jot oil (RJO), Waste cooking oil (WCO) at various operating conditions. A four ball tribometer was used to perform the tests for all lubricants with and without the addition of ionic liquid as an additive. To analyze the wear scar diameter on each sample a digital microscope was used. Results were obtained and analyzed, and it was found that addition of ionic liquid has not much improved the performance of PAO but significant effects can be seen for the case of bio lubricants. Where CSO performed best at lower operating loads and RJO performed best at higher operating loads due to its inherent load carrying capacity.

Key Words: Additivation, Polyalphaolefin, coefficient of friction, wear scar diameter, Bio-lubricant, Tribology

CHAPTER 1: INTRODUCTION

1.1 Background

Lubricants is a substance that function as shield to prevent direct metal to metal contact between two interacting mechanical components. One of the main reasons of using lubricant in a mechanical system is to reduce friction and wear. Apart from this, lubricants can also be used to dissipate heat produce during relative motion of two objects, to drive of the wear debris produced, to prevent material from corrosion and decrease the operating temperatures [1]. Lubricants find its use in a wide range of industries, including aerospace industry, automobile industry and any small household industry. In automobile industry use of lubricants is important as almost 17% of the total energy produced by fuel burning is utilized in terms of friction losses [2]. Lubricants are present in all three state solids, liquid and gases out of which liquid lubricants are most used.

Lubricants can be further classified into three subcategories Mineral lubricants, Synthetic Lubricants and Bio- based lubricants. Synthetic lubricants are lubricants that are chemically modified from organic raw material according to the application. Examples of synthetic lubricants are polyalphaolefin and synthetic esters. Mineral lubricants are lubricants obtained from petroleum products and further enhanced with additives. Although mineral lubricants are widely used in industry, researchers are looking into more ecologically friendly and renewable alternatives such bio lubricants due to worries about finite fossil fuel supplies, their effects on aquatic life, hazardous emissions, and growing petroleum prices [3].

Bio lubricants are lubricants that are derived from animal fat or vegetable oils. When compared to mineral lubricants, bio lubricants were found to have better tribological properties [4]. Most of the characteristics needed for lubrication are found to be present in bio lubricants, particularly in vegetable oils. These characteristics include increased thermal stability and viscosity indices, low volatility, low vapor pressure, and higher flash points [1, 5]. Bio lubricants consist of ester bonds that can adhere to metal surfaces forming a protective layer thus enhancing the lubricity [6]. Bio lubricants obtained from vegetable oils when used under high temperature conditions oxidizes, rendering them unsuitable for commercial use [7]. Vegetable based bio lubricants consist of Triglycerides (TAG), which is a glycerol molecule further esterified to produce three fatty acids shown in Figure 1.1: Triglyceride molecule. These glycerol molecule have beta hydrogen atom which oxidizes when expose to high temperature, making these oils unstable under high temperature conditions [1]. Several studies have been done to improve the thermal oxidation properties of these lubricants. This problem can be solved by chemically modifying the lubricants by replacing glycerol with more suitable additive or by using different additives [8, 9].

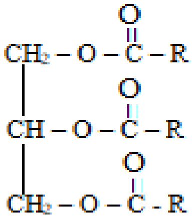


Figure 1.1: Triglyceride molecule

Studies have shown that bio lubricants work best under boundary lubrication regime but to further enhance its tribological properties it can be additivated with additive such as ionic liquid [10]. Ionic liquids are molten salts that exists in liquid state and have very low melting points. Ionic liquids consist of combination of anions and cations [11]. Ionic liquids have higher thermal stability than mineral oils, low volatility, low melting points and higher viscosity indices [12]. Ionic liquids are also referred to as safer solvents because of its environmental friendly nature [13]. Ionic liquids can be used directly as lubricants as well as an additive to other lubricants. Ionic liquids are found to have better miscibility in polar base oils and hence can be used as an additive to vegetable base oils [14]. Ionic liquids can have a variety of combination of ions and so a lot of ionic liquids can be used as an additive to lubricants. Furthermore, ionic liquids with phosphonium cations show in Figure 1.2: Phosphonium Cation [13] are found to have best compatibility with vegetable oils and can be used to enhance its tribological properties [15].

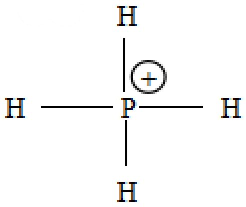


Figure 1.2: Phosphonium Cation [13]

1.2 Objectives

In this thesis a phosphonium based ionic liquid Bis(2-ethylhexyl) phosphate ionic liquid is checked for tribological compatibility with one synthetic oil polyalphaolefin (PAO) and three bio lubricants Cotton Seed Oil (CSO), Rattan Jot Oil (RJO) and Waste Cooking Oil (WCO) using a four ball tribometer (MMW1A) and an electronic microscope Olympus DSX1000. The main objectives of this thesis are:

a) Tribological analysis of Bis (2-ethylhexyl) phosphate (DEHP) ionic liquid (IL) based PAO using four ball tribometer (MMW1A).
b) Tribological analysis of Bis (2-ethylhexyl) phosphate (DEHP) ionic liquid (IL) based bio lubricant using four ball tribometer (MMW1A).
c) Comparison of tribological performance of bio lubricant and PAO.
d) Wear analysis using Olympus DSX1000 microscope.

1.3 General Methodology

In this thesis, a conventional lubricant PAO and three bio lubricants, CSO, RJO, and WCO, both in their pure state and in blends with 1wt% IL, were studied for their tribological compatibility. The frictional properties of each lubricant were studied using a foul ball tribometer (MMW1A), and wear scar analysis was conducted using an electronic microscope Olympus DSX1000. All tests were performed according to the standard ASTM

D4172, with an additional temperature condition of 100°C, which represents the operating temperature of most mechanical systems.

1.4 Scope in Pakistan

Demand for lubricants and oils is an always increasing phenomenon. Majority of the lubricants used are derived directly form petroleum products. Pakistan is a mineral rich country but due to lack of extraction resources the country petroleum need is fulfilled through imports which is a major setback to economy. Since almost all available products are crude oil based the pose a great problem towards environmental stability which is needed to be solved. Pakistan being an agricultural country also have an excess of different plants and seeds which can be used to produce these bio lubricants. Formulation of bio-lubricants with addition of ionic liquids provides a reasonable alternative to mineral lubricants.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Petroleum-based lubricants are most used in machines but are not environmentally friendly. Recently, there has been increasing interest among researchers in bio-lubricants as an environmentally friendly bio degradable alternative [16]. Among bio-lubricants, those derived from vegetable oils are considered better alternatives because of their better lubrication properties and lower changes in viscosity with temperature [4]. Several crops that have seeds that contain oil can be used to make vegetable oils. Vegetable oil feedstocks such as canola, palm, sunflower, cottonseed, jatropha, peanut, coconut, and rapeseed are widely used. There are still a lot of additional plants being investigated as possible sources of feedstock for vegetable oils. A significant obstacle to the manufacturing of bio-lubricants derived from vegetable oil is the higher cost of feedstock, which is approximately 70–80% of the overall production expenses. Both edible and non-edible crops can be used for production of vegetable oils, but nonedible crops are considered better for multiple reasons. Non edible crops are used to derive vegetable oils that cannot be used in food products but are generally used in industrial application such as bio diesel and bio lubricants [17]. In contrast to edible oil crop plantations, non-edible oil plants are considerably less expensive and can be planted on land that is unsuitable for edible oils [18].

Vegetable oils are composed of triglycerides (TAG) and chain of fatty acids. The characteristics of vegetable oils are defined by the type of fatty acids present in them. Chain length and the type of bonds are two factors that are considered important in fatty acids when selecting the vegetable oils. Longer chains typically have higher melting points and viscosities, whereas chains with more double bonds typically have lower melting points, viscosities, and less thermo-oxidative stability [19]. At high temperature the chains of fatty acids oxidizes to form free fatty acids. The triglyceride molecules present in vegetable oils have low thermal stability. The hydrogen atom present on β-carbon atom of glycerol molecule is the major cause of lower thermal stability in vegetable oils. In order to solve this problem a transesterification process is used [20]. Transesterification and is a two step reversible process which is carried out to convert vegetable oils into bio lubricants and is considered to be most effective by researchers [21].

Bio lubricants generally consists of heavy alcohol esters and are considered the best replacement for non-environmentally friendly mineral oils because they have the same lubricating qualities as mineral-based oils [22]. Production of bio diesel from vegetable oil is carried out through two step transesterification process. In the first step the vegetable oils are converted into bio diesels where the TAG present in vegetable oils are converted into Fatty acid methyl esters (FAME) under the presence of a catalyst by chemical reaction with a base such as alcohol. In the second step these bio diesel are than converted into bio lubricants where glycerol in bio diesel is replaced by poly ester [1, 23]. Trimethylolpropane (TMP), neopentyl glycol (NPG) and pentaerythritol (PE) are some compounds that contains ester group and have improved oxidative stabilities [24]. TMP has higher oxidative stability and melting points and lacks β-hydrogen atom and is therefore selected in this study as reagent.

Till date several different TMP based bio lubricants have been synthesized using vegetable oils from different feedstock such as cotton seed, rattan jot, rapeseed, jatropha, canola, sunflower and castor oil etc. Bio lubricants produced from cotton seed oil, rattan jot oil and waste cooking oil have been selected and studied for its Tribological performance in this study. TMP based bio lubricants although have good lubricity, good oxidative stability and low temperature performance but cannot be used under extreme operating conditions [25]. To make these bio lubricants favorable for extreme operating conditions a lot of additives have been studied. Ionic liquid seems to be a potential additive to these bio lubricants which can enhance the Tribological properties of these bio lubricants [2].

2.2 Ionic Liquids

Ionic liquid are salts that exists in liquid state and have very low melting points. Ionic liquids have lower volatility, lower melting points and better thermal properties due to which researcher are investigating ionic liquids as a lubricant for better tribological properties [26, 27]. Ionic liquids are comprised of large cations paired with relatively smaller anions. Due to the vast number of possible combinations of these cations and anions, a wide variety of ionic liquids can be synthesized. They are also known as “Tailored Chemicals” because of the large numbers of combinations of ions [28]. Ionic liquids differ in their properties depending upon the type of ions present in it [29]. Ionic liquids can be further classified into different categories based on the type of ions present in it. On the basis of cations ionic liquids can be further classified into four different categories phosphonium, imidazolium, ammonium or pyrolidinium cations based ionic liquids [2].

Ionic liquids has been investigated for tribological applications with extreme operating conditions [30]. Ionic liquid outperforms all the other conventional lubricants in term of tribological performance. Lu et al. [31] when studying ionic liquids as lubricants for steel/steel contact, found that ionic liquids outperformed conventional lubricants in terms of load-carrying capacity. Although having great tribological properties ionic liquid cannot be used as a lubricant itself because of its high cost. However, ionic liquids at different wt% when used as an additive to other lubricants can enhance its tribological properties [32, 33]. Some researchers have studied using ionic liquids along with other additives in bio-lubricants, and their tribological properties were found to be improved [34-36]. The effect of ionic liquid on tribological properties of base oils depend upon its solubility in that oil. Ionic liquids are found to have best miscibility with polar base oils and perform well when used as additives in it [37-39]. When used as an additive to non-polar base oils, ionic liquids often form emulsions due to their non-miscibility with these oils, resulting in poor performance [38]. Ionic liquids show the best performance when used as additives to polar base oils containing ester groups because of their higher polarity [40]. A. Syahir [41] investigated different ionic liquids as additives to synthetic oil (PAO) and a bio-based lubricant (TMPTO). He found that the ionic liquids enhanced the tribological properties of all lubricants.

Imidazolium and phosphonium-based ionic liquids, when used as additives to lubricants, reduce friction and wear for those lubricants. In many recent studies ionic liquid with Bis (2-ethylhexyl) phosphate (DEHP) anion when used as an additive to lubricants is studied. A. H. Battez [42] studied the effect of two ionic liquids IL1 $(P_{66614})(^{i}(C_8)_2PO_2)$ and IL2

(P_{66614}) (DEHP) as additive to Hydrocracked mineral oil (Yubase4/Group III) at different operating conditions and found that lubricants with 1wt% (P_{66614}) (DEHP) shows the least value of COF and wear. Vibhu Sharma [27] studied the effect of P-DEHP ionic liquid (IL) 2- methoxy-4,4,6-trimethyl-1,3,2-dioxaborinane and Trimethoxyboroxine borate ester (SB1 and SB2) with a group 1 base oil (BO-1) and found out that P-DEHP+BO-1 shows better tribological compatibility than other lubricants. When used as an additive to PAO3, P-DEHP increase the COF values of PAO3 [43]. Weimin Li [44] when investigated the performance of tetraoctyl phosphonium bis (2-ethylhexyl) phosphate (P8888) (DEHP) ionic liquid (IL) with PAO, organic friction modifier and Zinc dithiphosphate (ZDDP) shows that PAO+OFM shows better performance than ionic liquid sample. This study shows that ionic liquid was not compatible with PAO which is a synthetic liquid. In another study [45] when (P8888) (DEHP) ionic liquid (IL) and OFM were used as an additive to a mixture of low viscosity base oil (LVBO) and ZDDP it enhanced the tribological properties of the mixture. Error! Reference source not found. and Figure 2.2: Wear Volume for DEHP based ionic liquid Figure 2.2: Wear Volume for DEHP based ionic liquid shows the tribological properties of (DEHP) anion based ionic liquid when used as additive to different lubricants.

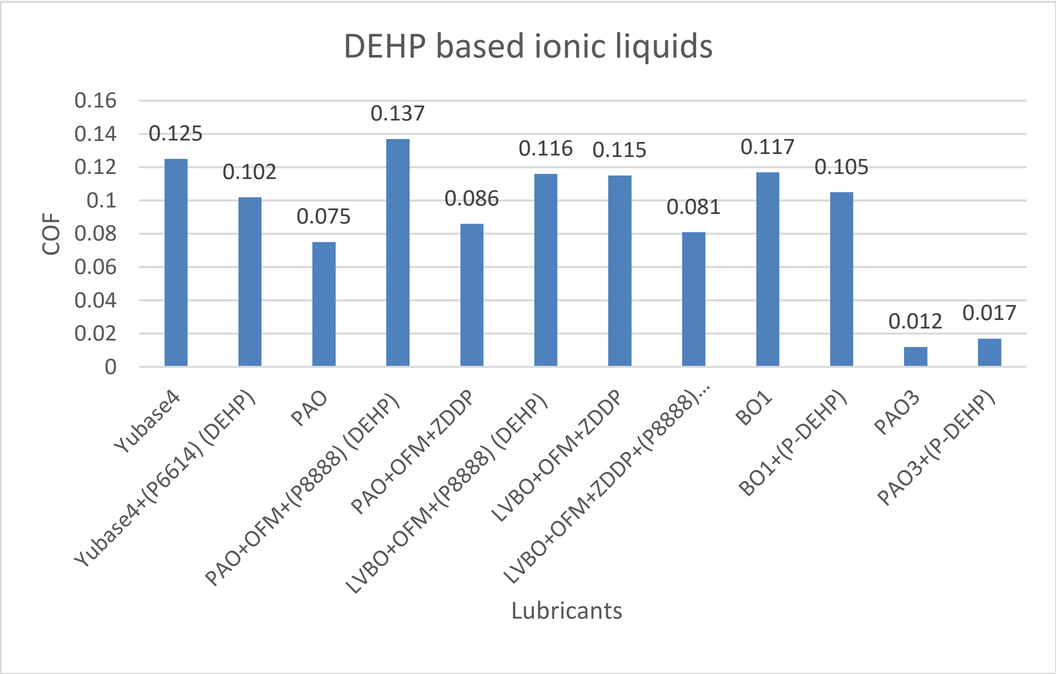


Figure 2.1: COF values for DEHP based ionic liquid

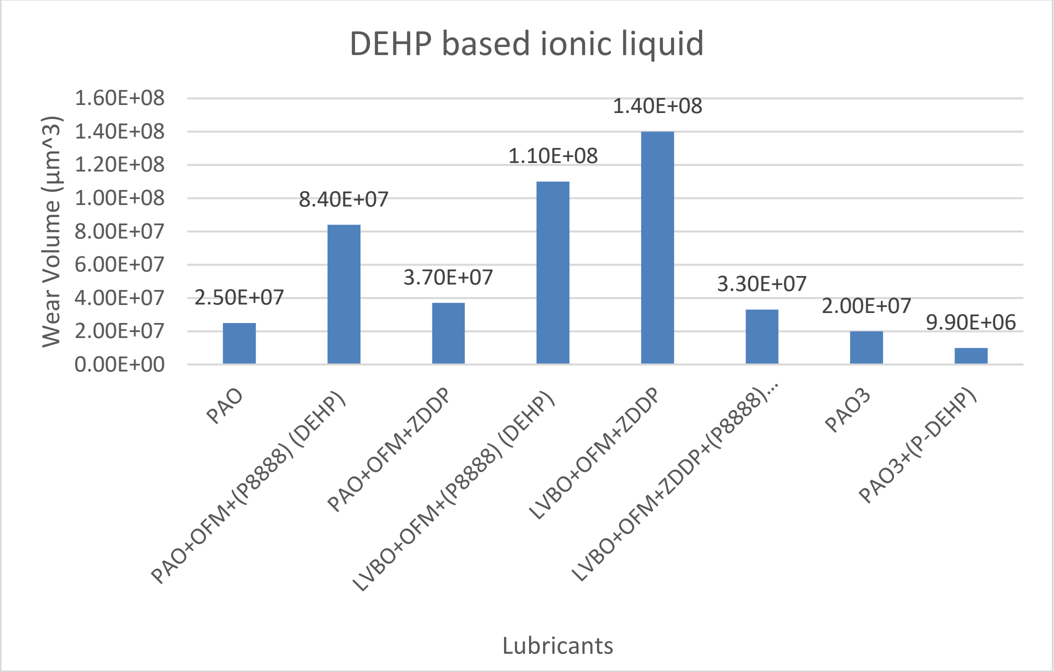


Figure 2.2: Wear Volume for DEHP based ionic liquid

In this study a novel approach is used and ionic liquid with only bis (2-ethylhexyl) phosphate (DEHP) is used as an additive to the lubricants and is shown in Figure 2.3: Chemical structure of bis (2-ethylhexyl) phosphate **.**

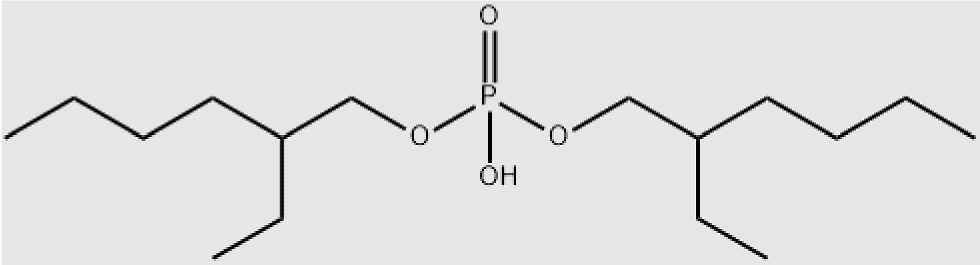


Figure 2.3: Chemical structure of bis (2-ethylhexyl) phosphate

2.3 Lubrication Mechanism of Ionic Liquid Based Lubricants

Lubricants used in industry are usually present in all three forms of matters. Most of the mechanical system use liquid lubricants because it can flow easily and can be used for cooling of parts. Lubricants properties can be further enhanced using different additives. Ionic liquids have excellent lubrication properties and hence are used as an effective additive to lubricants [46]. In case of mixed and boundary lubrication ionic liquids present in the lubricants form a lubrication layer between the asperities [47, 48]. Ionic liquids are charged particles consisting of ions due to which they form covalent bonds with metal surfaces [46]. Due to these covalent bonds the ionic liquids form a protective layer over the metal surfaces which help in distributing the load among asperities as well as protect the metal surfaces from effects such as corrosion. The formation of tribofilm over the metal surfaces by ionic liquid occurs as a result of chemisorption [49]. Ionic liquid consisting of phosphonium ions are considered to be the most effective because of their ability to rapidly form tribofilm over metallic surfaces [43].

CHAPTER 3: PRODUCTION OF IONIC LIQUID BASED BIO LUBRICANTS

3.1 Introduction

Vegetable oils are composed of triglycerides (TAG) and fats. These vegetable oils are converted to bio lubricants by performing esterification reaction twice. The first esterification reaction is done to convert the TAG to bio diesel, which is composed of fatty acid methyl ester (FAME). This esterification reaction happens in three phases under the presence of a catalyst. In the first phase, TAGs are reacted with alcohol molecule to yield FAME and diglyceride. The diglyceride than further reacts with alcohol molecule to yield another FAME and a monoglyceride molecule. In the third phase this monoglyceride molecules react with alcohol and produce FAME and glyceride. So, in total an esterification reaction produces three FAME and on glyceride molecule [23]. This reaction is shown in Figure 3.1.

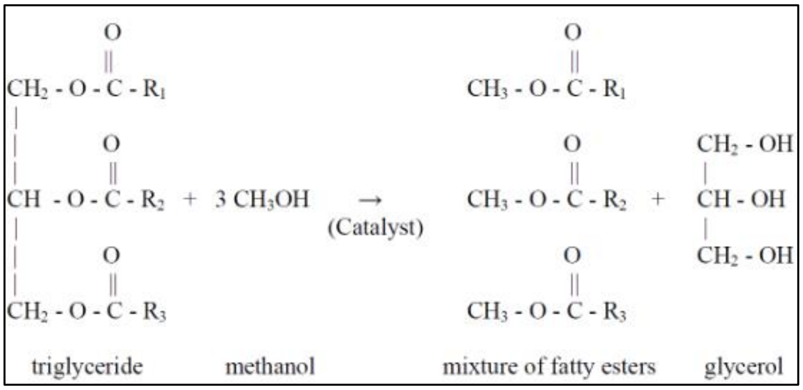


Figure 3.1: Chemical structure of bis (2-ethylhexyl) phosphate

The efficiency of esterification reaction depends upon a lot of factors such as catalyst used, concentration of catalyst and ratio of alcohol to oil [50, 51]. Best results of esterification reaction are achieved when a base is used as a catalyst. Study [52, 53] shows that potassium hydroxide was used as a catalyst in methanol with oil to alcohol ratio of 1:6 and 100℃ temperature, the reaction produce 90% yield at 45-60% of reaction time. The properties of bio diesel produced from transesterification are defined by the quality of vegetable oil used and method of its extraction. TAGs are generally composed of three fatty acids. These fatty acids are either saturated or unsaturated. Unsaturated fatty acids results in poor oxidative stability due to the high amount of double bonded carbon atoms present in it. Study [54] that the transesterification reaction maintains the favorable properties of base oil whereas increases its thermal stability and decreases its pour point.

Bio diesel produced through esterification reaction further undergo esterification reaction to produce bio lubricant. The esterification reaction occurs between biodiesel and trimethyl propane (TMP) in the presence of a catalyst sodium methoxide ($NaOCH_3$) to yield TMP based monoester with chain of fatty acids [19]. TMP due to its high thermal stability are best for esterification process. The conversion of bio diesel to bio lubricant happens with 3:1 ratio of methyl ester to TMP and in presence of $NaOCH_3$. This reaction is shown in the Figure 3.2.

$$3CH_3 - COO - R \quad + \quad TMP \quad \xleftrightarrow{NaOCH_3} \quad R'COO - R \quad + \quad 3CH_3 - OH$$

Methyl Ester (bio diesel) **TMP triester (bio lubricant)** **methanol**

Figure 3.2: Conversion of bio diesel to bio lubricant

3.2 Lubricant and Equipment Used

Cotton Seed Oil (CSO), Rattan Jot Oil, Waste Cooking Oil (WCO) are used as a feedstock for bio lubricants. RJO and WCO were procured from market whereas WCO was collected from home. The chemicals used were Methanol, TMP, KOH, $NaOCH_3$ and propanol. A synthetic lubricant PAO was used for comparison. PAO and all chemicals were procured from Sigma Aldrich [55]**.** The equipment used during this study are listed in Table 3.1.

Table 3.1: List of Equipment used during study.

Sr. no	Equipment Used	Location
1	Ostwald Viscometer	DME, NUST
2	Viscosity Index	Kluber Online Calculator
3	Pour point Tester	SCME, NUST
4	Flash point Tester	USPCASE, NUST
5	Titrating Equipment	DME, NUST
6	Tribometer	DME, NUST
7	DX 1000 Microscope	DME, NUST

3.3 Production of Bio-Diesel:

A layout to produce bio diesel from vegetable oil is shown in the

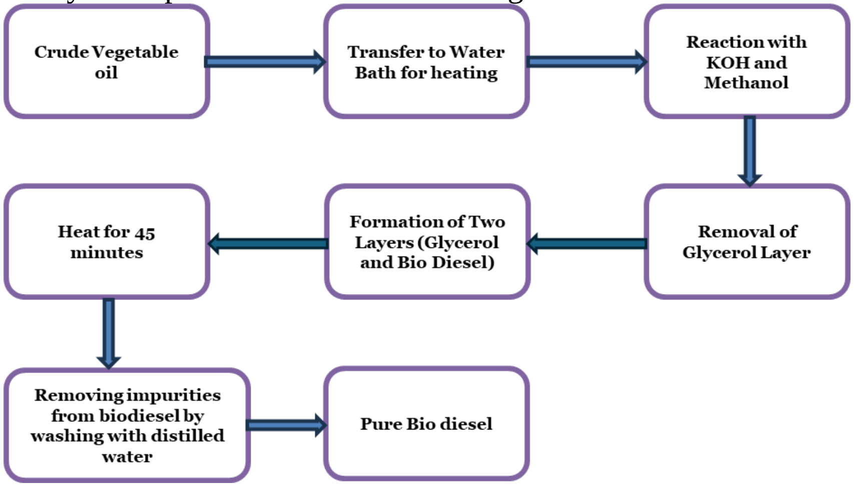


Figure 3.3. Bio diesels are derived from raw vegetable oil and are used to run diesel engines. Bio diesel consists of FAME derived by reaction of fatty acids of vegetable oil with alcohol usually methanol or ethanol. This process is called transesterification process. The bio diesel produced with reaction of vegetable oil with methanol are known as methyl esters whereas that derived from reaction with ethanol are known as ethyl esters.

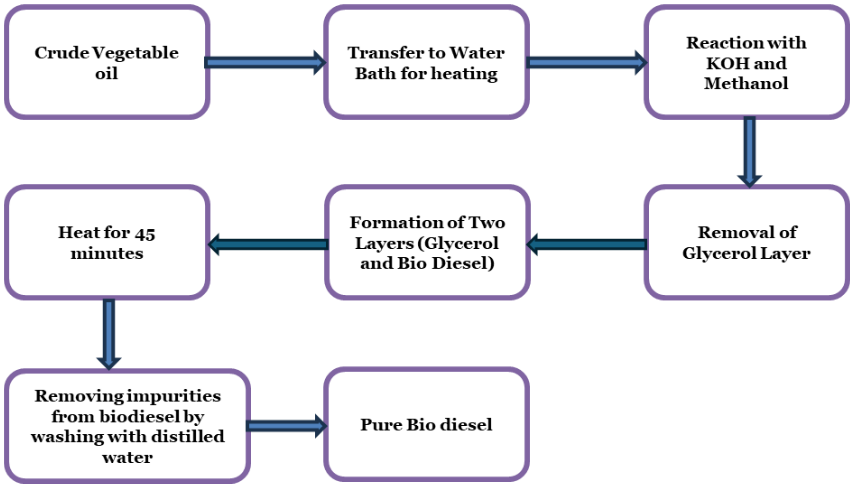


Figure 3.3: Flow chart for production of bio diesel.

A molar ratio of 6:1 of vegetable oil to alcohol is generally used to produce bio diesel. Base catalysts such as KOH or NaOH are used in the reaction and these catalysts are consumed during the process and removed through the separation of the glycerol layer.

3.3.1 Procedure

Take 250g of vegetable oil in a beaker and measure its weight using a measuring balance. Transfer this vegetable oil to a round bottom flask fitted with thermometer. Raise the temperature of oil to 60°C through a magnetic hot plate. Take 4.25 gram of catalyst potassium hydroxide (KOH) in a conical flask, add 56g of methanol to it and cover the flask to avoid escape of methanol vapors. The weight of methanol is in accordance to 6:1 molar ratio of vegetable oil to alcohol. A homogeneous mixture is obtained by heating the solution with constant stirring until whole KOH is dissolved. This solution is than transfer to round bottom flask containing heated vegetable oil and a reflux condenser is attached to it for condensation of methanol vapors.

The reaction is allowed to happen for 45 minutes and then the mixture is allowed to cool down for 8 hours in a separating funnel. Two layers are formed, the upper layer is impure bio diesel and the lower one is glycerol. Some methanol that was not utilized in the reaction are present in the lower layer. The glycerol layer is than removed and impure bio diesel is obtained. This is shown in **Figure 3.4**

Figure 3.4: Formation of two layers impure biodiesel and glycerol [55]

The impure biodiesel obtained has some impurities and methanol in it. To purify this bio diesel, it is than washed thoroughly three times with water. 250 g of water is added to the separation flask containing impure biodiesel and is shaken until all impurities from biodiesel is dissolved in water. Water being heavier in weight than biodiesel set at the bottom of the funnel and is removed as shown in

Figure **3.5**. This whole process is repeated three times until all the impurities are removed from bio diesel. The obtained purified bio diesel is than heated to a temperature of 110℃, so that any water present in bio diesel is removed through evaporation.

Figure 3.5: Biodiesel and water layers after three washes [55]

3.4 Production of Bio-lubricant from Bio diesel

After production of biodiesel, this biodiesel is than converted to bio lubricants by further esterification with TMP in presence of $NaOCH_3$. Figure 3.6 shows a layout for production of bio lubricants from bio diesel. Normally, a 3:1 molar ratio of methyl ester (bio diesel) to TMP is required for the reaction but methyl ester is used in excess to avoid any backflow during the reaction.

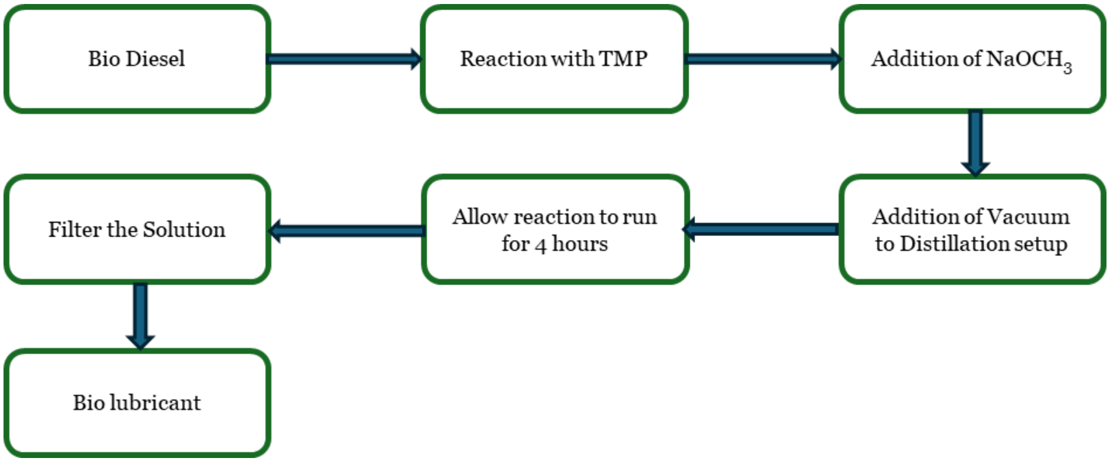


Figure 3.6 : Flow chart for production of bio lubricant from bio diesel

3.4.1 Procedure

250 g of bio diesel is taken in a rounded flask and added to an oil bath where it is heated to a temperature of 60°C. 37g of TMP is added to the bio diesel and is further heated to a temperature of 140°C and maintained until the TMP is melted. After this 2.5 g by weight $NaOCH_3$ is added to the solution and the temperature is maintained at 140°C. A distillation setup is installed to the reaction flask to lower the pressure. Bubbles start to form and methanol along with FAME is collected. The reaction takes almost 4 hours to complete and formation of bubbles stop. The mixture is allowed to cool and filtered to remove any impurities. The filtrate obtained is TMP based bio lubricant. The reaction setup is shown in Figure 3.7.

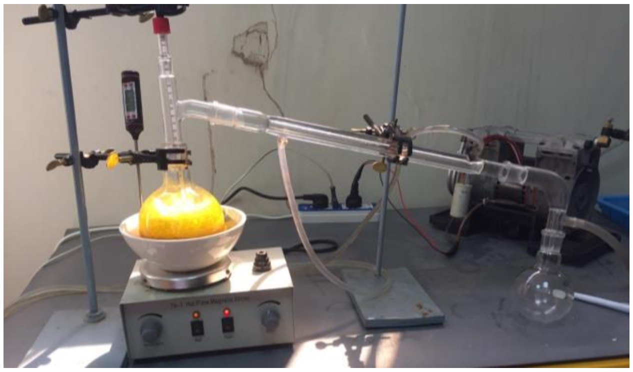


Figure 3.7 : Production setup for bio lubricant

3.5 Production of Ionic Liquid Based Bio-Lubricant

Ionic liquids are added to bio lubricant in different wt% ranging from 0.5% to 3%. Studies have shown that ionic liquid produce best results with ionic liquid when added at 1wt% to bio lubricants. In this study the selected ionic liquid is added at 1wt% to lubricants and its effect on their tribological properties is studied. The samples are prepared by simply mixing the ionic liquid into the lubricants.

3.5.1 Procedure

247.5g of lubricant is taken in a beaker and heated to a temperature of 80℃. In another beaker around 2.5g of ionic liquid is taken and heated to a temperature of 60℃. The weight of ionic liquid was decided based on its wt%. When both the ionic liquid and lubricant achieved the required temperature, lubricant is poured into ionic liquid and is constantly stirred until a homogeneous mixture is obtained. This procedure is repeated for all lubricants.

CHAPTER 4: PRODUCTION OF IONIC LIQUID BASED BIO LUBRICANTS

4.1 Introduction

Lubricants are widely used in industry to reduce frictional losses in mechanical equipment as well as to dissipate heat from the system. Mineral lubricants produce toxic emissions and are dangerous for the environment. Bio lubricants are considered as best alternative to these mineral based lubricants as they are renewable and are unharmful to the environment. Bio lubricants have lower thermal stability and hence other additives are used in it to enhance its tribological performance. Ionic liquids have been proved to be an effective additive to lubricants as they are halogen free, nonflammable, nonvolatile and tailored compounds [56].

Physiochemical properties of lubricants before and after addition of ionic liquid was measured using ASTM standards and are studied in this chapter. Major physiochemical properties like Total Acidic Number (TAN), Total Base Number (TBN), flash point, pour point, viscosity, viscosity index and density are studied.

4.2 Methodology

The physiochemical properties were measured according to ASTM standards and are presented in this chapter.

4.2.1 Density

Density is defined as mass per unit volume. It shows how much space is taken by a substance as compared to its mass. Density of bio lubricants is less as compared to vegetable oil. This is because of the transesterification reaction. Less density of bio lubricant makes it easy for its transport. Density of all lubricants with or without addition of ionic liquid is measured according to ASTM D1480 in bio lubricant lab at SMME NUST.

For finding density of lubricants, sample of each lubricant was added to a pycnometer with known volume. The pycnometer is heated until the required temperature is achieved. Weight of pycnometer is measured. This weight is than divided with the volume of pycnometer to find density of that liquid. The setup is shown in Figure 4.1.

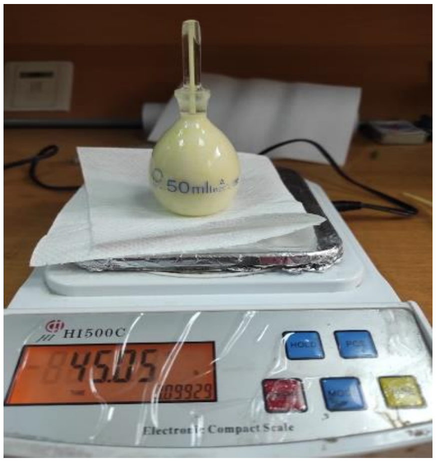


Figure 4.1: Pycnometer [55]

4.2.2 Kinematic Viscosity

Viscosity defines the fluid ability to flow under gravitational force. The viscosity of a lubricant tells us about its load carrying capacity. Lubricants with lower viscosity forms a thin film over metal surfaces relative to higher viscosity lubricants which doesnot effectively separate the asperities, hence resulting in increased wear. Bio lubricants generally have higher values of viscosity index due to their branched structure.

Ostwald viscometer present in bio lubricant lab at NUST H-12 Islamabad shown in Figure 4.2. Kinematic viscosity values were measured according to standard ASTM 445. The lubricant is allowed to move under the influence of gravity in a calibrated capillary viscometer. At first the kinematic viscosity of PAO was known to us and kinematic viscosities of all other lubricants were measured by comparing them with kinematic viscosity of PAO. To find the viscosity of lubricant, the Ostwald viscometer is filled with lubricant to the bulb of U-shaped tube. The lubricant is than heated to a desired temperature and a pippet sucker is placed on top of tube to suck the lubricant to top mark. Time taken by the lubricants to move to the top mark is noted and then compared with that of PAO. This comparison gives us the value of kinematic viscosity. Kinematic viscosity of all the lubricants was measured at the operating temperature of 40℃ and 100℃.

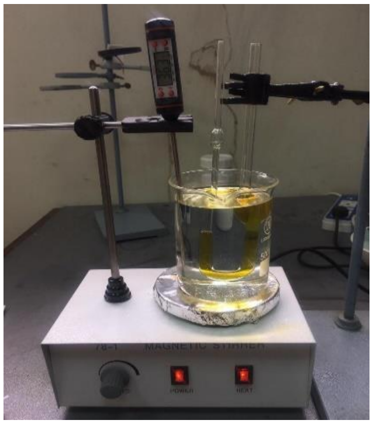


Figure 4.2: Ostwald Viscometer [55]

4.2.3 Viscosity Index

Viscosity index value tells us the how much the value of viscosity will change with increase in temperature. Viscosity Index values for all lubricants were measured according to the standard ASTM D2270

4.2.4 Flash Point

Flash point defines the lowest temperature at which lubricant will ignite. Lubricants normally have flash points less than 40℃. Flash point of lubricants is measured with a flash point tester show in Figure 4.3 present at USPCASE NUST H-12 Islamabad according to ASTM D92.

To find the flash point of lubricant, 5 ml of each lubricant was added to cup of flash point tester and its temperature was raised at a slow rate. After small interval of time a flame is passed through the cup and the temperature at which that lubricant ignites is noted as its Flash Point.

Figure 4.3: Flash Point Tester [55]

4.2.5 Flash Point

Pour point is defined as the lowest temperature at which the lubricant will flow under gravity and possess fluid like properties. The pour point of a lubricant is important as it tells us about the lowest temperature at which lubricants can be transported through pipelines. Pour point of lubricants was measured using Koehler’s cloud and Pour Point Tester present at SCME NUST H-12 Islamabad shown in Figure 4.4 according to standard ASTM D97.

Figure 4.4: Koehler’s cloud and Pour Point Tester [55]

4.2.6 *Total Acid Number (sTAN) and Total Base Number (TBN)*

Total Acid Number (TAN) is defined as the number of mg of KOH required to neutralize acid present in 1g of lubricant. Lubricants with high acid content can cause corrosion and increase friction and wear between components. TAN of all the lubricants is measured using titration with KOH in bio lubricant lab at DMME NUST H-12 Islamabad.

Total Base Number (TBN) is the number of milligrams of Hydrochloric acid (HCl) required to neutralize 1g of lubricant. TBN of lubricants is measured using titration with 0.1 mg of HCl in bio lubricant lab at DMME NUST H-12 Islamabad. The titration setup is shown in Figure 4.5.

Figure 4.5: Titration Burettes [55]

4.3 Results

The physiochemical properties of all lubricants were measured using ASTM standards and are listed below in Table 4.1**.**

Table 4.1: Physiochemical Properties of Lubricants

Property		Density	Kin. Vis. @ 40°C	Kin. Vis. @ 100°C	Viscosity Index	Pour Point	Flash Point	Total Acid no (TAN)	Total Base no (TBN)
Unit		**kg/m^3**	**cST**	**cST**	**-**	**°C**	**°C**	**mmKOH/g**	**mmHCl/g**
Standards		**ASTM D1298**	**ASTM D2500**	**ASTM D2500**	**ASTM D2270**	**ASTM D97**	**ASTM D4206**	**ASTM D664**	**ASTM D4739**
Standards Lubricants	**Bare PAO**	827.6	65.1	9.8	133	-41	230	0.21	0
	Bare CSO	904.6	27.7	5.94	167	-10.2	175	0.25	0.14
	Bare RJO	906.4	29.9	5.43	118	-13.2	150	0.29	0.15
	Bare WCO	907.8	36.8	7.9	194	-12.8	155	0.3	0.1
	PAO + IL	853	65.30341	10.96542	160	-39.6	215	Neutral	Neutral
	CSO + IL	937	26.20266	4.844939	106	-10	175	Neutral	Neutral
	RJO + IL	925	34.06716	7.801088	211	-12.2	190	Neutral	Neutral
	WCO + IL	933	25.6071	5.737776	177	-11.8	185	Neutral	Neutral

4.4 Analysis

Physiochemical properties of all lubricants are calculated and compared with that of PAO. Since all bio lubricants varies in type and size of TAG therefore they7 have differences in their chemical properties.

Densities of PAO and bio lubricants CSO, WCO and RJO as well as their blends with ionic liquids is shown in Figure 4.6. Densities of lubricants and their blends are shown in proportion to each other. PAO has lower density as compared to vegetable-based bio lubricants. This higher value of bio lubricants is because of their strong intermolecular interaction due to the presence of strong intermolecular forces between them.

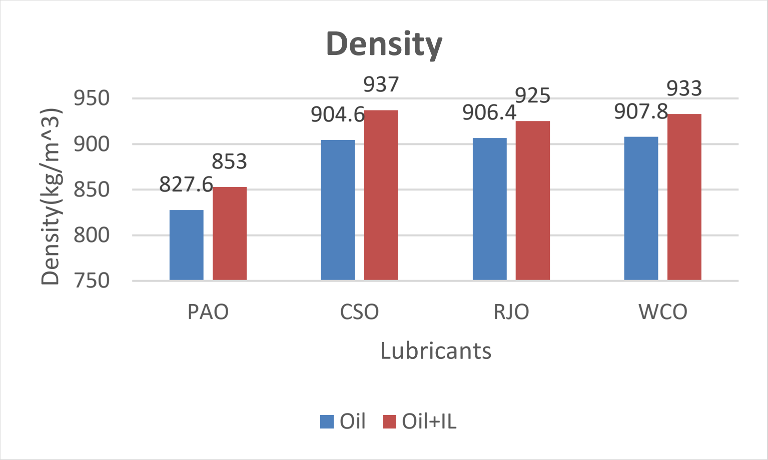


Figure 4.6: Densities of all lubricants

Viscosity of lubricant is one of the most important physiochemical property of a lubricant as it defines the thickness of lubricating film between asperities in contact. The viscosity of all lubricants as well as their blends with ionic liquids at 40℃ and 100℃ is shown in Figure 4.7 and Figure 4.8. Viscosity of all bio lubricants are found to be like that reported in literature [57-60]. It can be seen that addition of bio lubricants have no significant effect on the viscosity values at 40℃ temperature whereas at 100℃ there is a significant change in viscosity values. This change in viscosity values can be because of higher thermal stabilities of these lubricants [36].

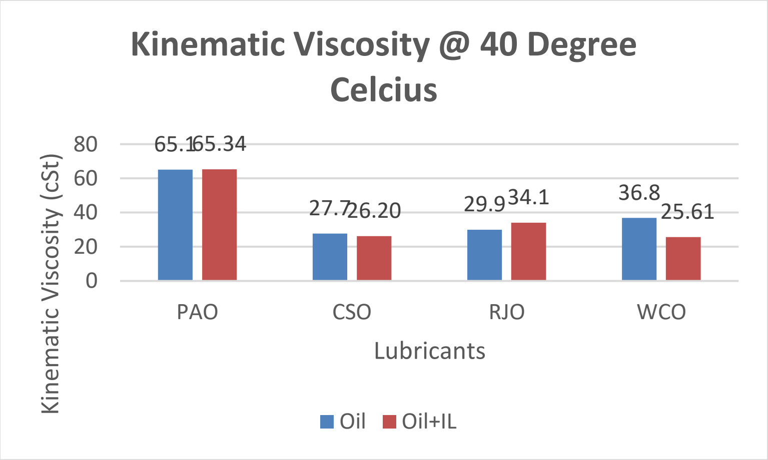


Figure 4.7: Viscosity at 40̊C for all lubricants

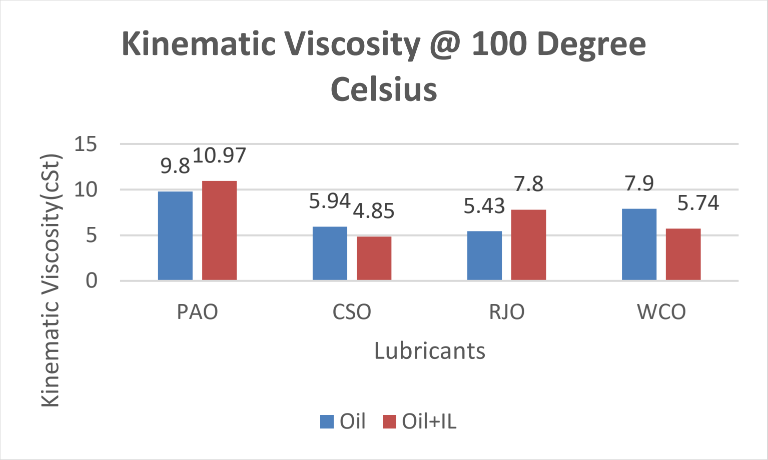


Figure 4.8: Viscosity at 100̊C of all lubricants

Viscosity index of a lubricant defines how the lubricant is going to behave under conditions with variable operating temperatures. In IC engine, as lubricants are exposed to a very high temperature it is important for lubricant to maintain its protective film at higher temperature. Under such conditions lubricants with higher viscosity index are considered suitable. The viscosity index of all lubricants is shown in Figure 4.9. As can be seen from the figure, when incorporated with ionic liquid WCO and CSO shows the highest values of viscosity index and hence is best suitable for tribological applications. From the figure, viscosity index of all lubricants increases after the addition of ionic liquid. These results are in accordance with literature [59, 61, 62].

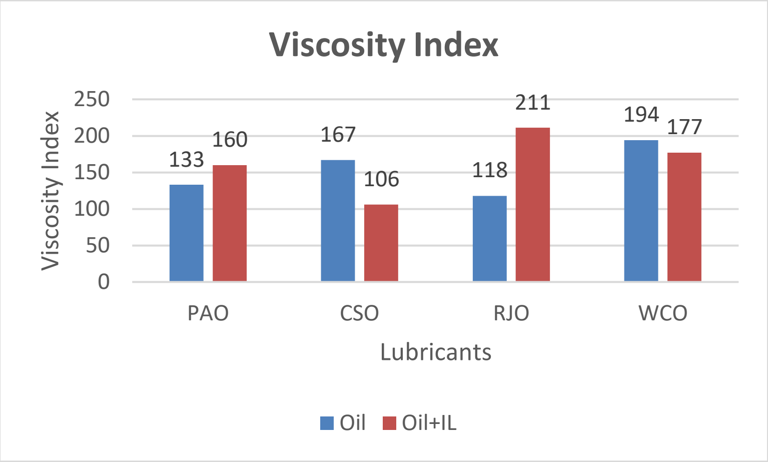


Figure 4.9: Viscosity index of all lubricants

Pour point of all lubricants is shown in Figure 4.10. The pour point of lubricant defines the flow ability of a lubricant. For PAO, the pour point was provided to us by manufacturer i.e, -41℃ and the pour point of other lubricants were found by comparing them to it. The pour point of all lubricants is in accordance with literature except for WCO. The difference in pour point value for WCO is because of presence of unsaturated fatty acids of vegetable oil present in it [63]. Generally, the addition of ionic liquid doesn't have much effect on pour point value of bio lubricants.

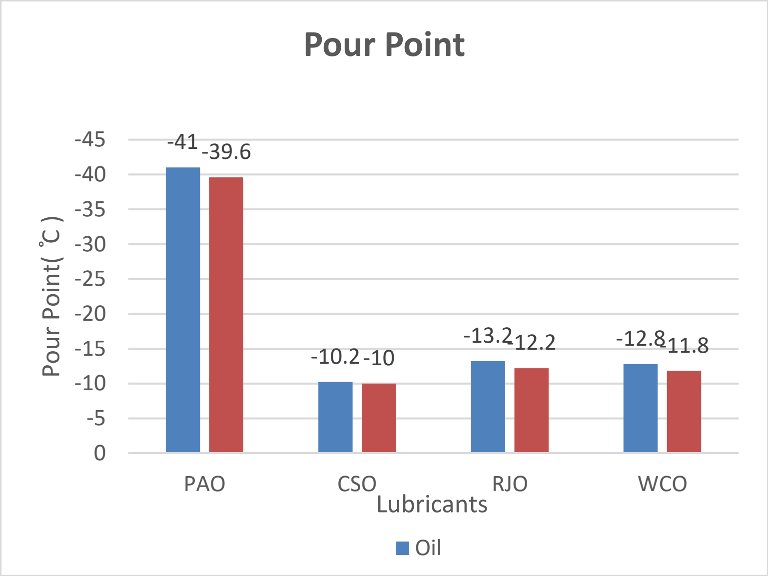


Figure 4.10: Pour Point of all lubricants

Flash point of all lubricant is shown in Figure 4.11. IC engines normally operate at high temperatures and hence the flash point of lubricant is a very important parameter for lubricants operating in such applications. Flash point of PAO is higher both in pure state as well as along its blend with ionic liquid as can be seen from Figure 4.11. Flash point of ionic liquid samples is higher as compared to pure lubricants; this is because of the nonvolatile nature of ionic liquid.

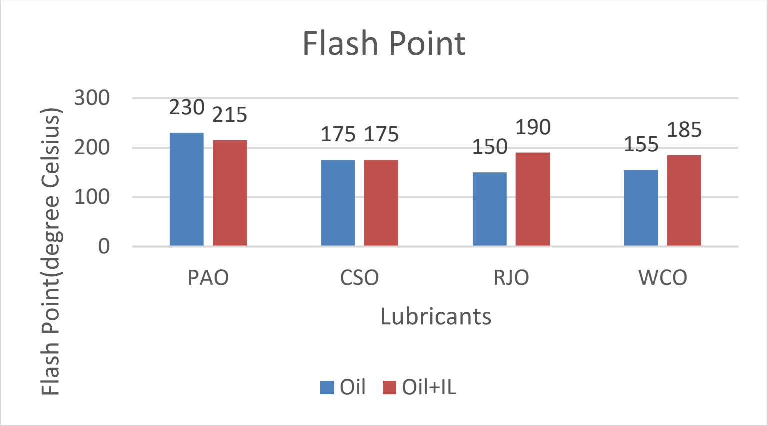


Figure 4.11: Flash Point for all lubricants

Total acidic number (TAN) and Total base number (TBN) of all lubricants can be seen in Figure 4.12 and Figure 4.13. All ionic liquids are neutral in nature and hence their TAN and TBN values are not shown.

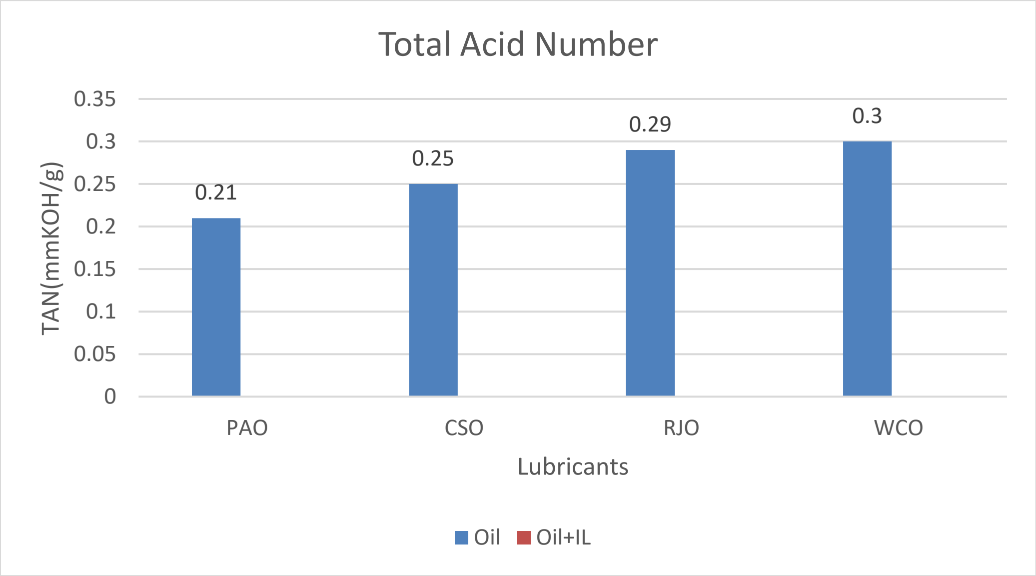


Figure 4.12: TAN for all lubricants

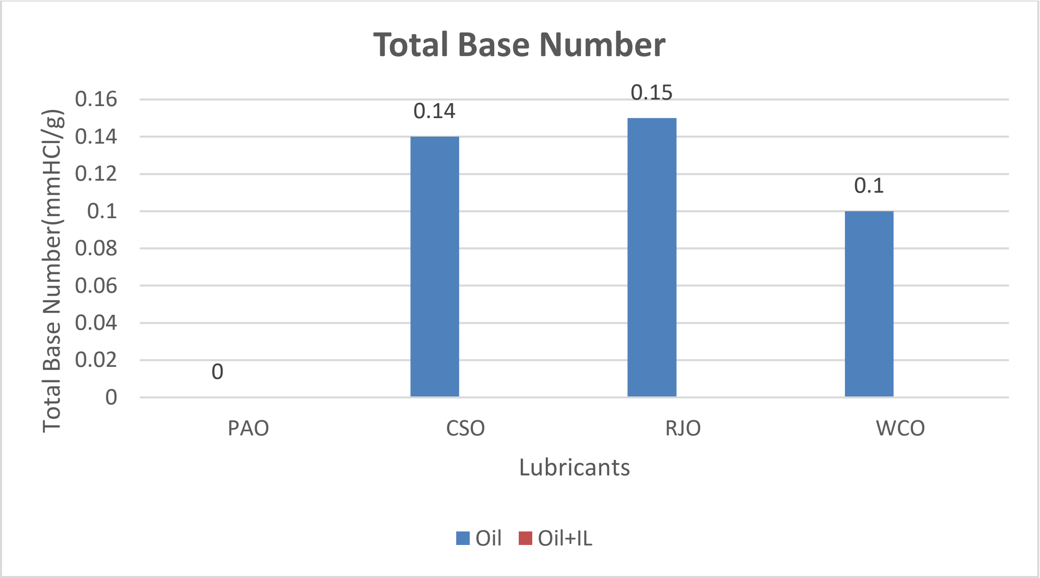


Figure 4.13: TBN for all lubricants

CHAPTER 5: RESULTS & DISCUSSION

5.1 Introduction

As discussed earlier the purpose of this research work was to analyse the performance of lubricants such as PAO and bio-lubricants at different operating conditions with selected ionic liquid as additive. Different type of test configurations are used in order to determine tribological performance of test lubricants. These test setups generally include a four-ball setup, ball on disk and pin on disk configurations. Customized engine test rigs designed for specific applications are sometimes also used to determine the tribological performance of lubricants. In this research work a four-ball test configuration is used to determine the tribological performance of PAO and bio-lubricants at different operation conditions with and without addition of ionic liquid. It is to be mentioned that all tribological tests required to analyze the performance of lubricants were performed at Four-ball Tribometer available in Tribology Lab, SMME, NUST.

5.2 Experimental Setup

Vertical Universal Friction Testing Machine (MMW-1A) as shown in Figure 5.2 was used to perform Four Ball tests for all lubricants. Test configuration includes the use of four AISI 52100 steel balls (Dia 12.7mm). Among these four balls, three are held stationary inside a cavity containing fixture/cup. The lubricant under test is poured inside the cavity. The fourth ball is not stationary and is fixed inside a rotating spindle as show in Figure 5.3. ASTM D4172 was adopted to perform the tribological tests on lubricants. All lubricants were tested at varying operating conditions. Two different loads 147N and 392N along with two different operating temperatures of 75℃ and 100℃ with the spindle rotating at a speed of 1200 rpm. All test conditions are summarized in Table 5.1**:** Four Ball Test Conditions. Test procedure starts with the use of acetone to clean the working equipment including the fixture, spindle and steel balls. Steel balls are then held stationary inside the fixture with a lock nut. After making sure that there is no foreign contaminant at the contact point, 9 mL of test lubricant is poured carefully inside the fixture containing steel balls. To start the test, the cavity containing the steel balls and test lubricant should be at a homogenous temperature. The fixture is then placed on the heating element and a PID controller is then used to control and monitor the increase in temperature of oil inside the cavity. The test temperature was achieved by increasing the set temperature at intervals of 5℃. After the required test temperature was achieved, the system was left untouched for about 20 minutes so the steel balls and oil inside cavity are at homogenous temperature. A load cell was then used for the application of required test load at the contact point. After confirming that the setup has achieved both the required temperature and load the test was started by using the command given on the user interface on the machine. The test was allowed to run for 60 minutes. During the test, the software provided with the equipment was able to record the real time values of co-efficient of friction and upon the completion of test all the data was stored for further analysis. After completing the run time of 60 minutes, the test setup is then un-loaded by using the "quick unload" command on the user interface. The steel balls inside the fixture are then removed carefully. Visible signs of wear in terms of small wear scar at the surface of each ball. The location of this wear scar is marked for further analysis and all the steel balls are then stored in a container and each container is then labeled as per test details. Figure 5.1 summarizes all the steps involved and required for this experimental setup. A digital microscope named OLYMPUS, model number as DX-1000 was used to analyze the wear scar on each steel ball.

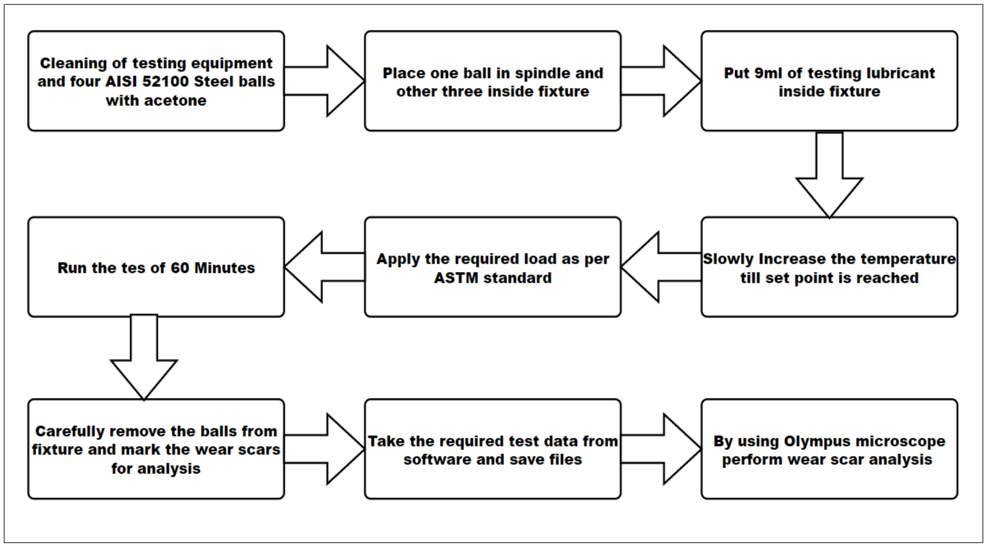


Figure 5.1: Steps involved in the experimental setup.

Figure 5.2: Vertical Universal Friction Testing Machine (MMW-1A).

Figure 5.3: OLYMPUS DX-1000

Table 5.1: Four Ball Test Conditions

Operating Condition	Value
Speed of Spindle	1200 Rpm
Temperature	75℃ and 100℃
Load	147N and 392N
Soaking Time	20 Minutes.
Run Time	60 Minutes

5.3 Results

All lubricants under consideration including PAO and bio-lubricants along with their blends with ionic liquid were tested using a four-ball tribometer at two different operating loads and temperatures. The values for co-efficient of friction were obtained from real-time data collection of user interface of tribometer and values for the wear scar diameter for all experiments were obtained using digital microscope OLYMPUS DX-1000. All the results obtained are listed in the Table 5.2 and Table 5.3

Table 5.2: Tribological Properties of Lubricants at 75℃

OILS	COF @75℃		WSD @75℃ (μm)		Surface Roughness@75℃(μm)	
	147N	392N	147N	392N	147N	392N
PAO	0.059	0.069	609.7	839	0.453	0.405
PAO+IL	0.074	0.085	604.5	873.5	0.245	0.234
CSO	0.042	0.056	595.1	770	0.330	0.310
CSO+IL	0.078	0.051	639.4	710	0.394	0.419
RJO	0.057	0.039	602.7	740.7	0.262	0.319
RJO+IL	0.039	0.049	545.1	609.7	0.316	0.298
WCO	0.067	0.049	550.4	685	0.358	0.485
WCO+IL	0.041	0.049	539.8	627.2	0.499	0.476

Table 5.3: Tribological Properties of Lubricants at 100℃

OILS	COF @100℃		WSD @100℃ (µm)		Surface Roughness@100℃(µm)	
	147N	392N	147N	392N	147N	392N
PAO	0.068	0.072	632.4	683.1	0.113	0.48
PAO+IL	0.065	0.077	522.3	807.1	0.39	0.43
CSO	0.042	0.052	700.5	707.5	0.278	0.24
CSO+IL	0.042	0.031	506.6	607.9	0.274	0.322
RJO	0.052	0.037	711	738.9	0.25	0.397
RJO+IL	0.043	0.039	265.4	569.5	0.29	0.445
WCO	0.038	0.055	335	690.1	0.35	0.103
WCO+IL	0.039	0.056	466.4	882	0.402	0.101

5.4 Coefficient of Friction Results

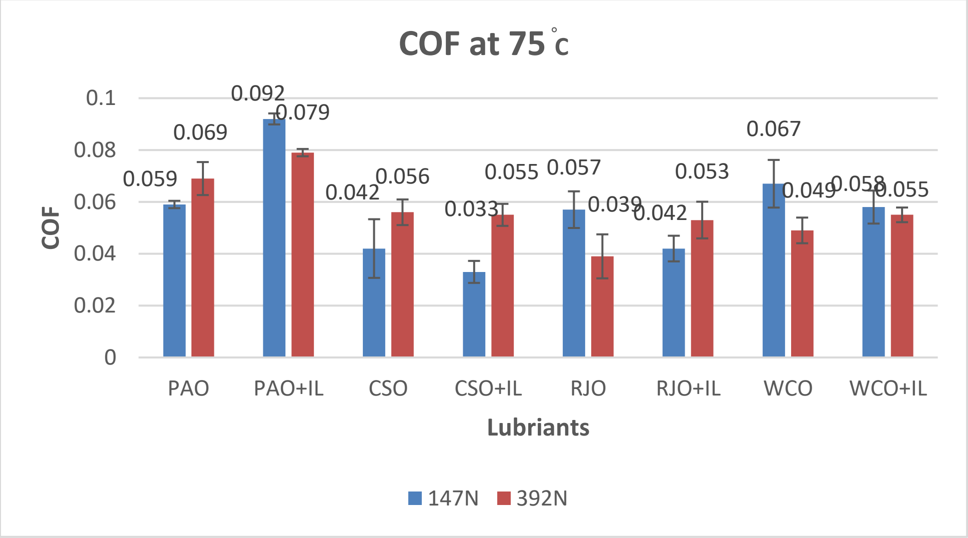


Figure 5.4: Average COF of Lubricants at 75℃

Results for the coefficient of friction at both operating loads of 147N and 392N at temperature of 75℃ are presented in Figure 5.4. At a load of 147N for the case of lubricants without the addition of ionic liquid, it is evident from the results that the highest value of the coefficient of friction is shown by WCO at 0.067 whereas CSO shows the least value at 0.042. On different occasions, increased values of friction are observed for the samples relating to waste cooking oil which could be related to the presence of saturated fatty acids [63]. This explains the higher values of the coefficient of friction for the case of WCO during the experiments. On the other hand, CSO showed the least COF values, which can be attributed to the presence of monosaturated fatty acids i.e. oleic acid in their mix [64]. Figure 5.4 also shows that at operating conditions of 392N and 75̊C, RJO performed best by portraying the least value of COF at 0.039 where as PAO showed the highest value at 0.069 can be explained by its inability to make strong interactions with steel surfaces due to its non-polar behavior unlike bio-lubricants [65].

After the addition of ionic liquid in all lubricants under consideration, a change in the coefficient of friction results can be seen in Figure 5.4. It is evident from the results that additivation with ionic liquid at both operating loads of 147N and 392N has caused an increase in values of coefficient of friction value for PAO by 54.8% and 14.4% respectively. This change in results can be attributed to the non-polar base oils incompatibility, in this case, PAO with the selected ionic liquid bis (2-ethylhexyl) phosphate [45]. Looking at the results for bio-lubricants under consideration, at the operating load of 147N, CSO, RJO and WCO showed decrease in the values of co-efficient of friction by 21.42%, 26.31% and 13.43% respectively. This decrease in COF value for the case of CSO+IL, RJO+IL and WCO+IL could be due to the rapid generation of tribofilm at the contact point at these operating conditions. The formation of tribofilm helps the idea of asperities being separated at contact point hence reducing the friction. For operating load of 392N, CSO+IL showed an decrease in value of coefficient of friction by 1.78% unlike RJO+IL and WCO+IL that showed an increase in coefficient of friction values by 35.89% and 12.24%. This increase in values of COF could be explained by the inability of these samples to main a protective tribofilm at the contact point for higher operating loads i.e 392N.

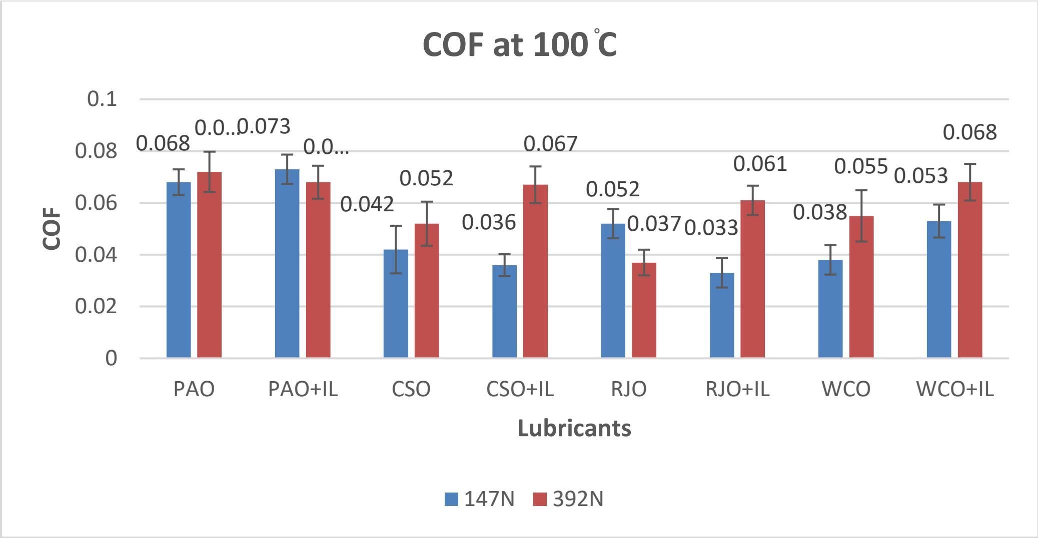
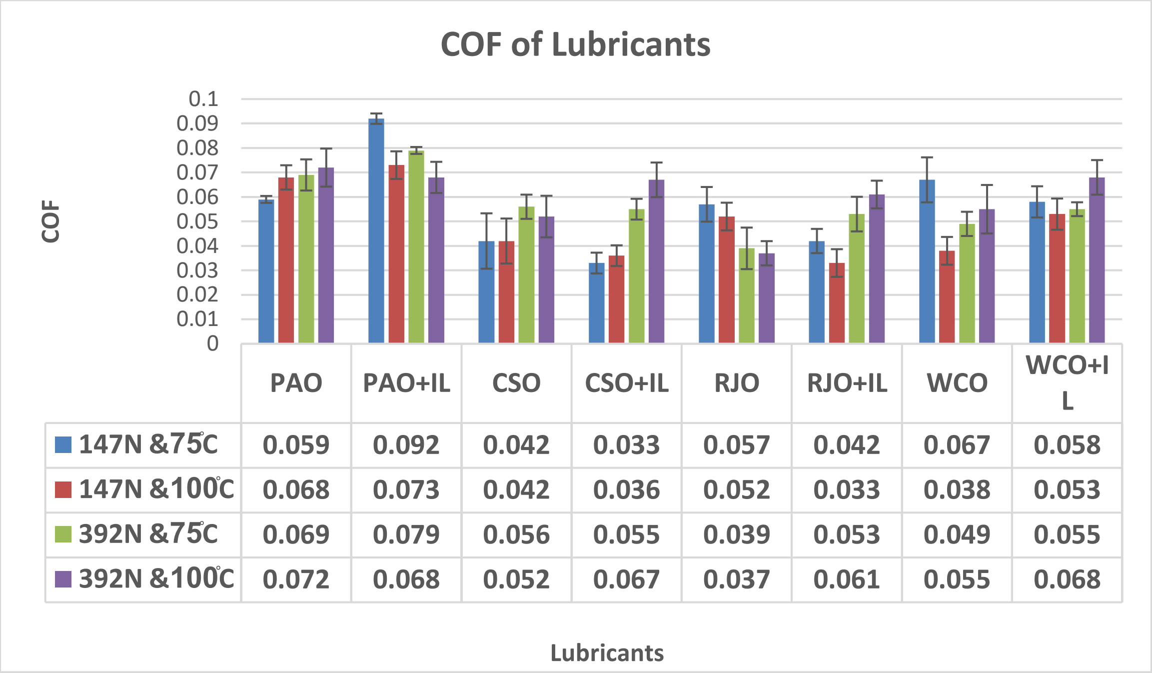


Figure 5.5: Average COF of Lubricants at 100̊C Temperature.

Results for the coefficient of friction at both operating loads of 147N and 392N at a temperature of 100̊C are presented in Figure 5.5. At both loads for the case of lubricants without the addition of ionic liquid, it is evident from the results that the highest values of coefficient of friction are represented by PAO as 0.068 and 0.073 respectively. The fact that PAO has a relatively lower viscosity index as compared to bio-lubricants under consideration could be the reason for increased COF values as shown in **Table 5.2**. For the case of bio-lubricants WCO showed the least value of coefficient of friction (0.038) at 147N whereas for the operating load of 392N, RJO showed least value of coefficient of friction (0.037). upon reviewing the COF values obtained at 147N, it can be said that the results are in accordance with the viscosity index of lubricants. Since greater the viscosity index, lesser will be the value of the coefficient of friction. For the case of RJO, an argument of better load carrying capacity at loads of 392N can explain the decrease in the COF values.

After the addition of ionic liquid in all lubricants under consideration, a change in the coefficient of friction results can be seen in Figure 5.5. It is evident from the results that additivation with ionic liquid at both operating loads of 147N has caused an increase in the COF values of PAO+IL and WCO+IL by 7.3% and 39.4% respectively. Contrary to that CSO+IL and RJO+IL showed a percentage decrease in the value of COF by 14.2% and

36.5%. At the operating loads of 392N, PAO+IL showed a 5.5% decrease in value of COF as compared to bare PAO. Unlike bio-lubricants, where CSO+IL, RJO+IL and WCO+IL showed an increase in COF values by 28.84%, 64.86% and 23.63% respectively. This varying behavior in terms of COF values for the case of bio-lubricants can be explained the in-effectiveness and incompatibility of chosen ionic liquid additive as per temperature and load.



	PAO	PAO+IL	CSO	CSO+IL	RJO	RJO+IL	WCO	WCO+IL
🟦 147N &75℃	0.059	0.092	0.042	0.033	0.057	0.042	0.067	0.058
🟥 147N &100℃	0.068	0.073	0.042	0.036	0.052	0.033	0.038	0.053
🟩 392N &75℃	0.069	0.079	0.056	0.055	0.039	0.053	0.049	0.055
🟪 392N &100℃	0.072	0.068	0.052	0.067	0.037	0.061	0.055	0.068

Figure 5.6: Average COF of all lubricants

Coefficient of friction values for all the lubricants with and without the addition of ionic liquid at all operating conditions are represented in the Figure 5.6. Upon increasing the operating load from 147N to 392N at a fixed operating temperature of 75℃, a decrease in the values of coefficient of friction can be seen for PAO+IL, RJO, WCO, and WCO+IL. This decrease in COF values can explained by the increased amount of wear debris at contact point due increased surface roughness [66]. The direct contact between asperities was eliminated due to wear debris acting as a filler in between. It is also visible from the Figure 5.6 that upon increasing the temperature from 75℃ to 100℃, a decrease in the coefficient of friction values can be seen for most lubricants under consideration except for the case of CSO+IL at both operating loads and WCO at an operating load of 392N [67].

5.5 Wear Scar Diameter Results

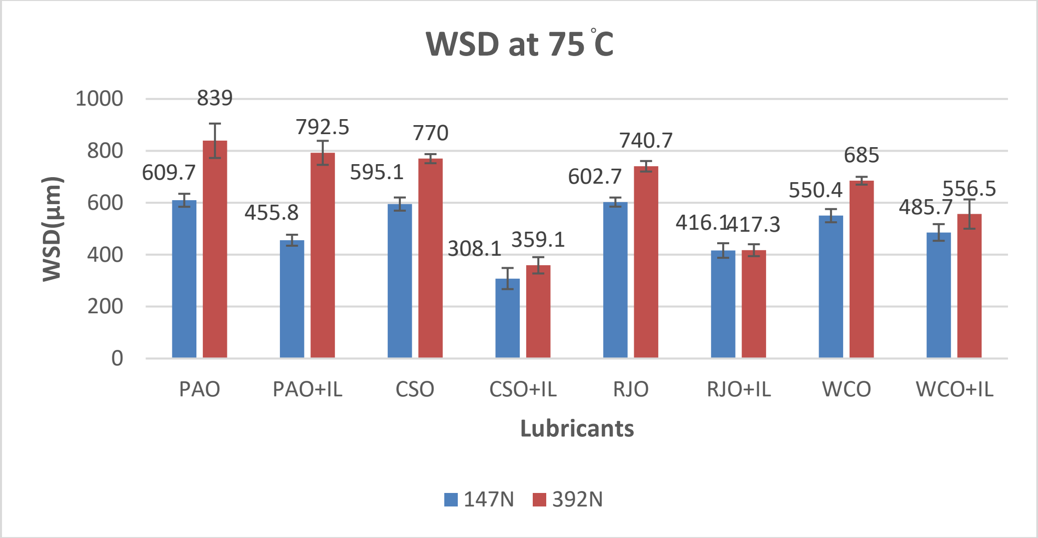


Figure 5.7: Average WSD of Lubricants at 75̊C Temperature.

Results for the wear scar diameter (WSD) at both operating loads of 147N and 392N at a temperature of 75̊C are presented in Figure 5.7. As evident from the results, PAO shows the highest value of wear scar diameter among all lubricants under consideration without the addition of ionic liquid at both operating loads of 147N and 392N. Hence, it can be said that bio-lubricants performed better than PAO in terms of wear results. This can be explained due to the presence of fatty acids for the case of bio-lubricants. Reacting with the metal surfaces hence give rise to formation of a low shear strength tribo-layer at the contact point [41]. Among lubricants without additivation of ionic liquid, WCO performed best with least wear scar diameter values at both operating loads.

At 75̊C, after addition of ionic liquid, CSO+IL showed the best results with least values of wear scar diameters at both operating loads. For the case of PAO+IL, a percentage decrease can be seen in the values of wear scar diameter by 25.24% and 5.54% respectively for both operating loads of 147N and 392N. In the case of bio-lubricants at operating load of 147N after ionic liquid additivation, CSO+IL, RJO+IL and WCO+IL showed reduction in the wear scar values by 48.22%, 30.96% and 11.75% respectively. At operating load of 392N, CSO+IL, RJO+IL and WCO+IL showed percentage decrease in the wear scar diameter values by 53.36%, 43.6% and 18.7% respectively. This overall trend of reduction in wear scar diameter for most lubricants can be explained by the enhancement of load carrying capacity after additivation with the selected ionic liquid.

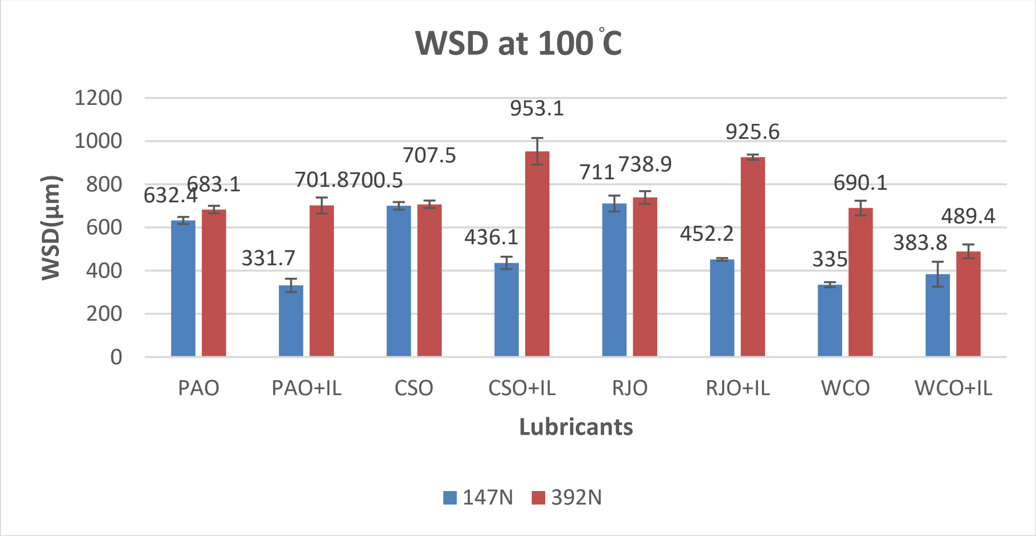
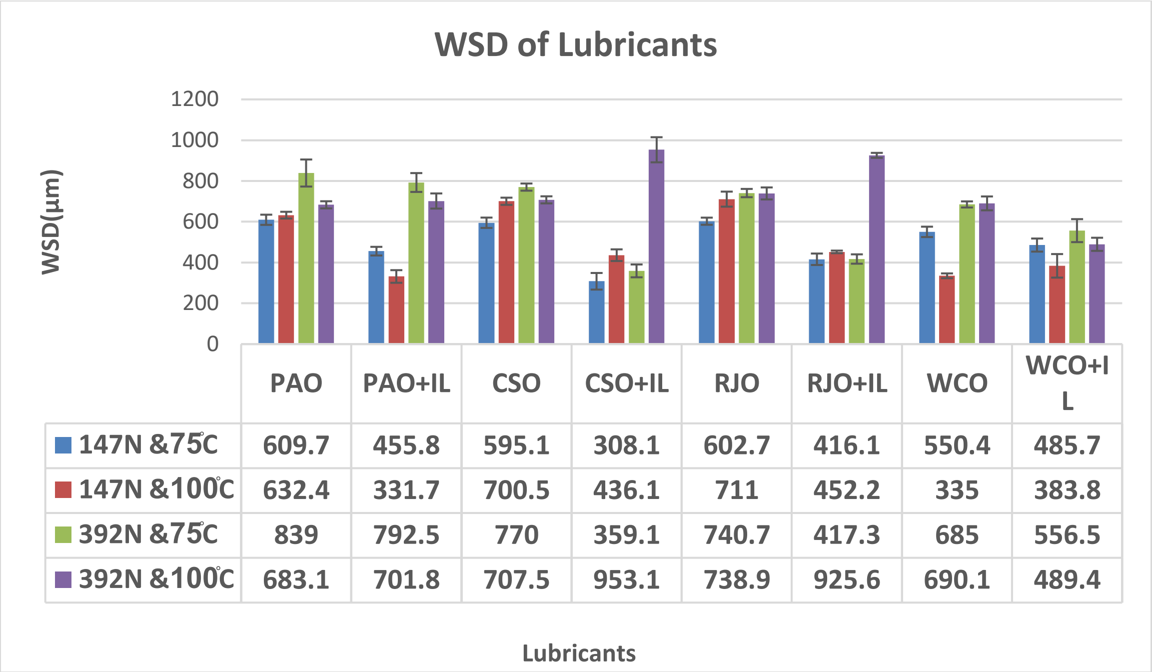


Figure 5.8: WSD of Lubricants at 100°C Temperature.

Results for the wear scar diameter (WSD) at both operating loads of 147N and 392N at a temperature of 100°C are presented in Figure 5.8. As evident from the results, for the case of lubricants without additivation of ionic liquid, RJO showed the highest values of wear scar diameter at both operating loads of 147N and 392N. This behavior of RJO can be explained by its thermal instability as compared to other lubricants under test as a jump in wear scar value is evident from the data upon increasing the temperature up to 100°C. PAO depicts the least value of wear scar diameter at operating load of 392N whereas at operating load 147N, WCO shows the least value of wear scar diameter.



	PAO	PAO+IL	CSO	CSO+IL	RJO	RJO+IL	WCO	WCO+IL
🟦 147N &75°C	609.7	455.8	595.1	308.1	602.7	416.1	550.4	485.7
🟥 147N &100°C	632.4	331.7	700.5	436.1	711	452.2	335	383.8
🟩 392N &75°C	839	792.5	770	359.1	740.7	417.3	685	556.5
🟪 392N &100°C	683.1	701.8	707.5	953.1	738.9	925.6	690.1	489.4

Figure 5.9: WSD of all Lubricants

Wear scar diameter values for all the lubricants with and without the addition of ionic liquid at all operating conditions are represented in the Figure 5.9. It is evident for the data that, wear scar diameter values for all lubricants increases with increase in operating load from 147N to 392N [68]. This behavior of increased wear scar values with increase in operating load is corresponded to the decrease in the material strength. With increase temperature and loading condition, heat is generated at the contact point causing plastic deformation [66]. It can been seen that with increase in operating temperature from 75°C to 100°C for the same operating load, the wear scar values decreases for some cases except for PAO, CSO,CSO+IL, RJO, RJO+IL at operating load of 147N and CSO+IL,RJO+IL,WCO at operating load of 392N.

5.6 Surface Roughness Results

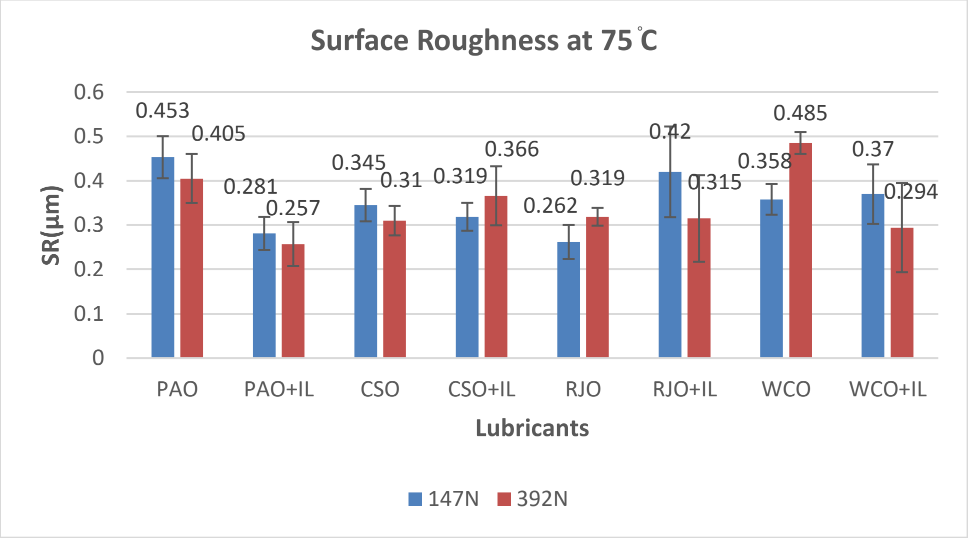


Figure 5.10: Surface Roughness of Lubricants at 75̊C Temperature.

Results for the surface roughness on both operating loads of 147N and 392N at temperature of 75̊C are presented in Figure 5.10. It is evident from the results that upon increasing the operating load from 147N to 392N an increase in surface roughness values is seen for this case of CSO+IL, RJO and WCO. This is found to be true for some cases where an increase in surface roughness was noted with increase in operating loads [66]. Whereas for the remaining lubricants a decrease in the surface roughness values can be seen. Hence it can be said that, unlike coefficient of friction, surface roughness has an inverse relation with load variation.

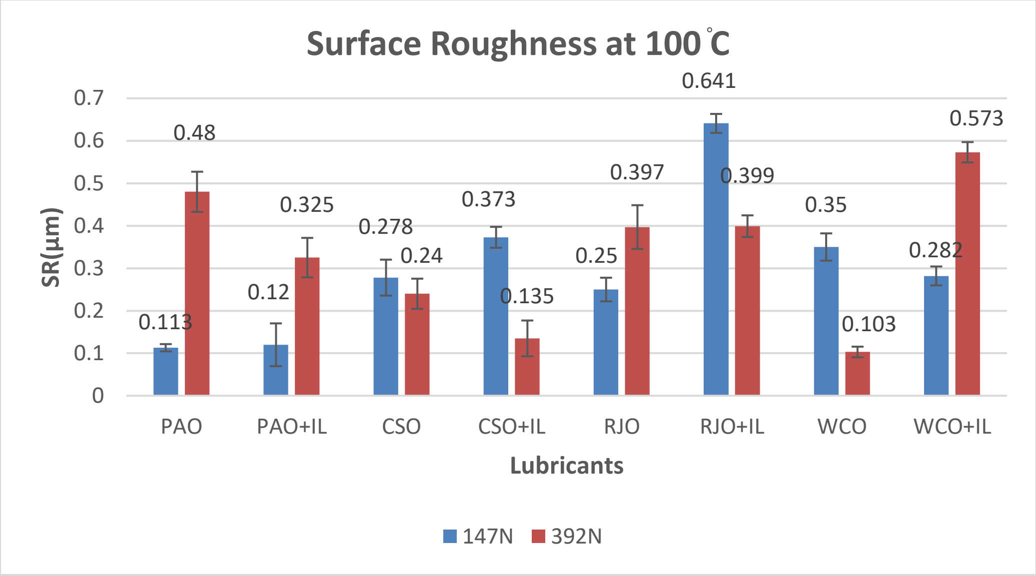


Figure 5.11: Surface Roughness of Lubricants at 100℃

Results for the surface roughness on both operating loads of 147N and 392N at temperature of 100℃ are presented in Figure 5.11. Upon increasing the operating load from 147N to 392N, an increase in value of surface roughness can be seen for PAO, PAO+IL, RJO and WCO+IL. Contrary to that a subsequent decrease in the value of surface roughness can be seen for CSO, CSO+IL,RJO+IL and WCO. This values for surface roughness indicates the influence of operating conditions, and how it impacts the values of coefficient of friction.

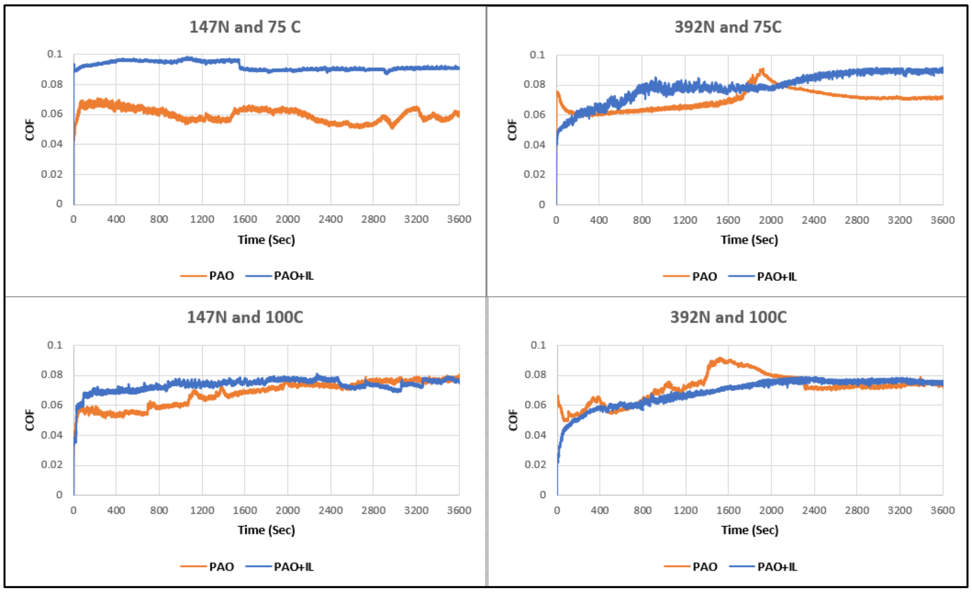


Figure 5.12: COF graph of PAO and PAO+IL

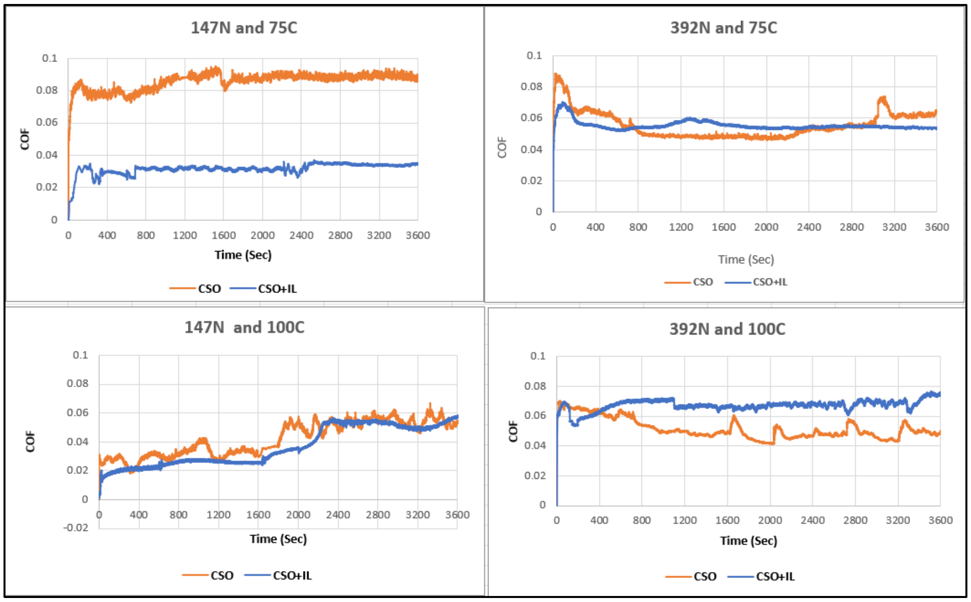


Figure 5.13: COF graph of CSO and CSO+IL

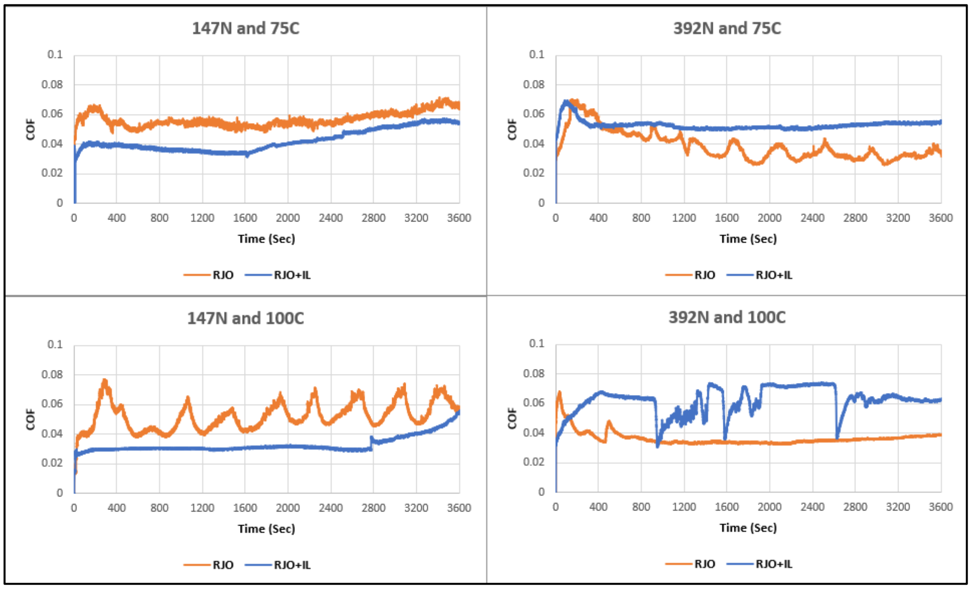


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Figure 5.14: COF graph of RJO and RJO+IL

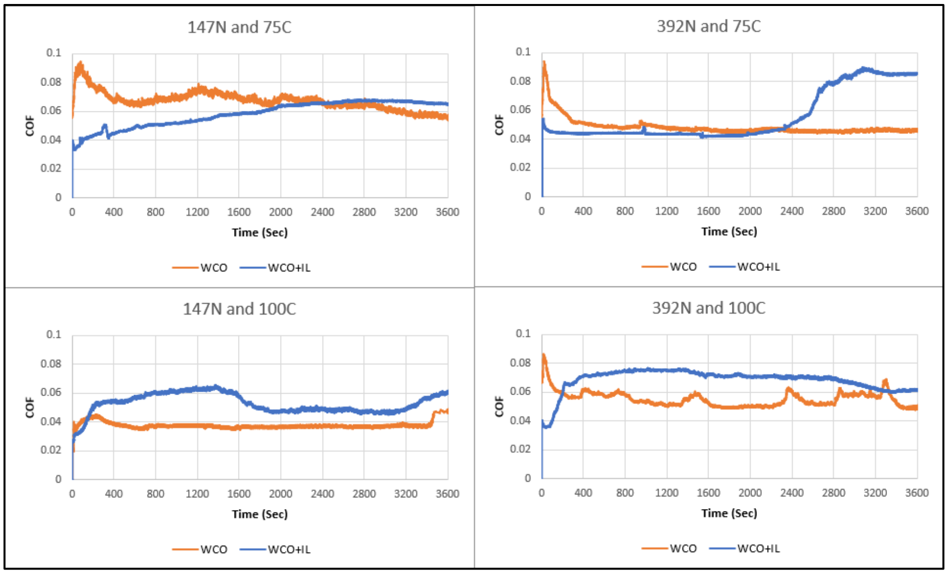

Figure 5.15: COF graph for WCO and WCO+IL

As discussed earlier in the thesis, the user interface provided with the four-ball tribometer had the capability of recording the real time data during each performed test. The data was stored, and COF graphs were plotted for lubricants under consideration with and without addition of ionic liquid as shown in Figure 5.12, Figure 5.13, Figure 5.14 and Figure 5.15. Upon inspection during start of each test, a slight increase/spike in the value of COF can be seen for all lubricants. Which is then stabilized at lower steady state value indicating the running-in state. As evident from the results, for a complete run time PAO depicts a more stable coefficient of friction value as compared to other test lubricants. This could be explained by the rapid formation of a tribo-layer at the contact point. Considering the bio-lubricants, the least stable pattern was displayed by RJO for a complete test run. Especially for the operating temperature of 100̊C. This could be due the lubricants inability to separate or maintain a distance between interacting surfaces at high temperatures. Additivation with ionic liquid, generally enhanced the tribological performance of lubricants to exhibit stable coefficient of friction values. Which is credited to the formation of tribo-layer at the contact point but this not true for the case of CSO+IL that showed extreme variation in results at higher temperatures pointing towards the incompatibility of ionic liquid with the selected bio-lubricant at higher temperatures.

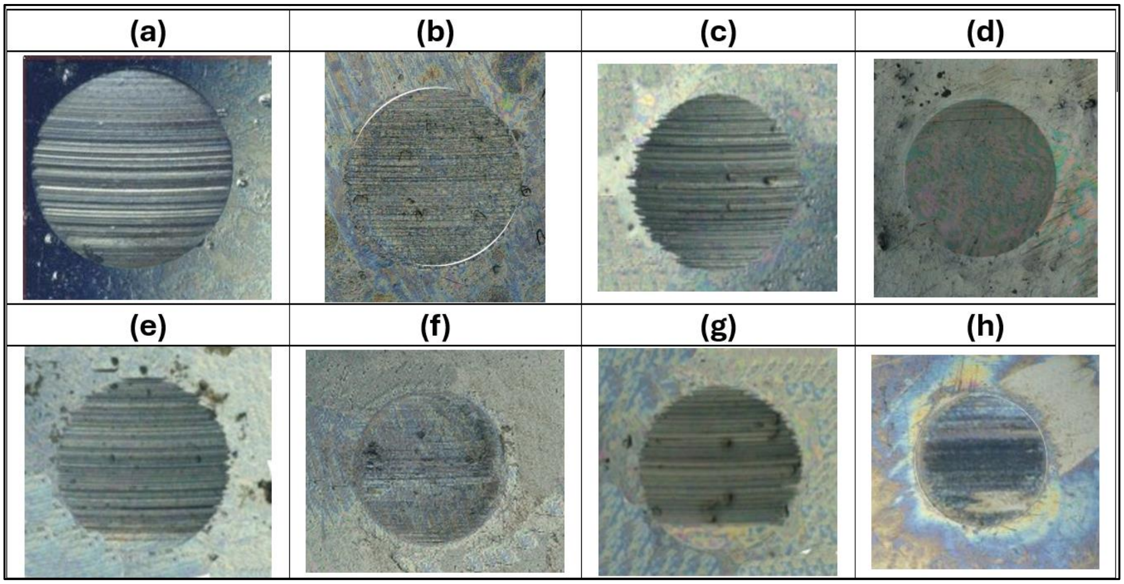

Figure 5.16: WSD at 147N and 75 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

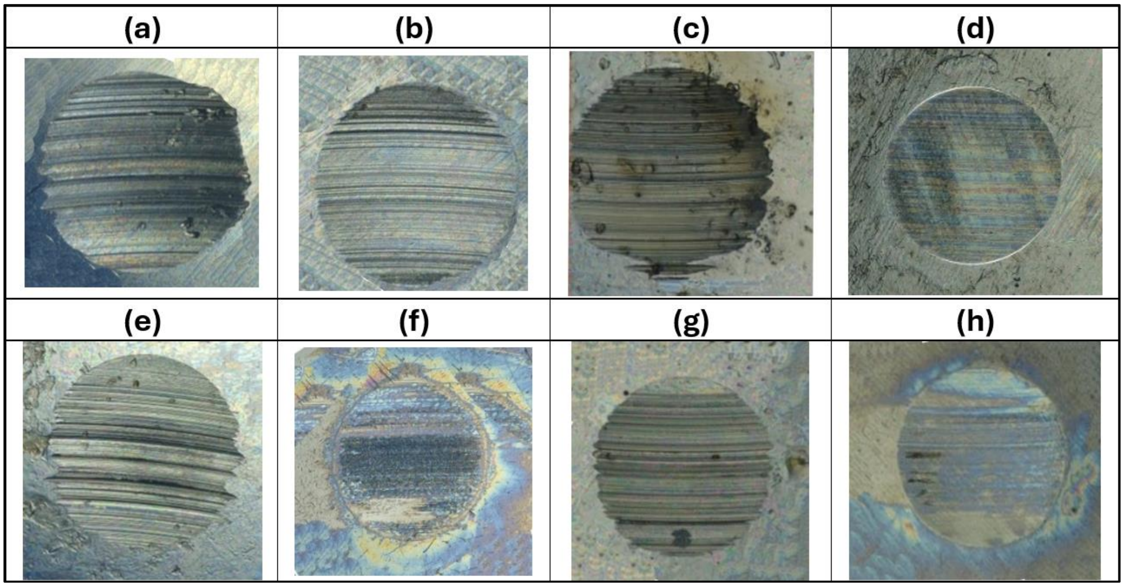

Figure 5.17: WSD at 392N and 75 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

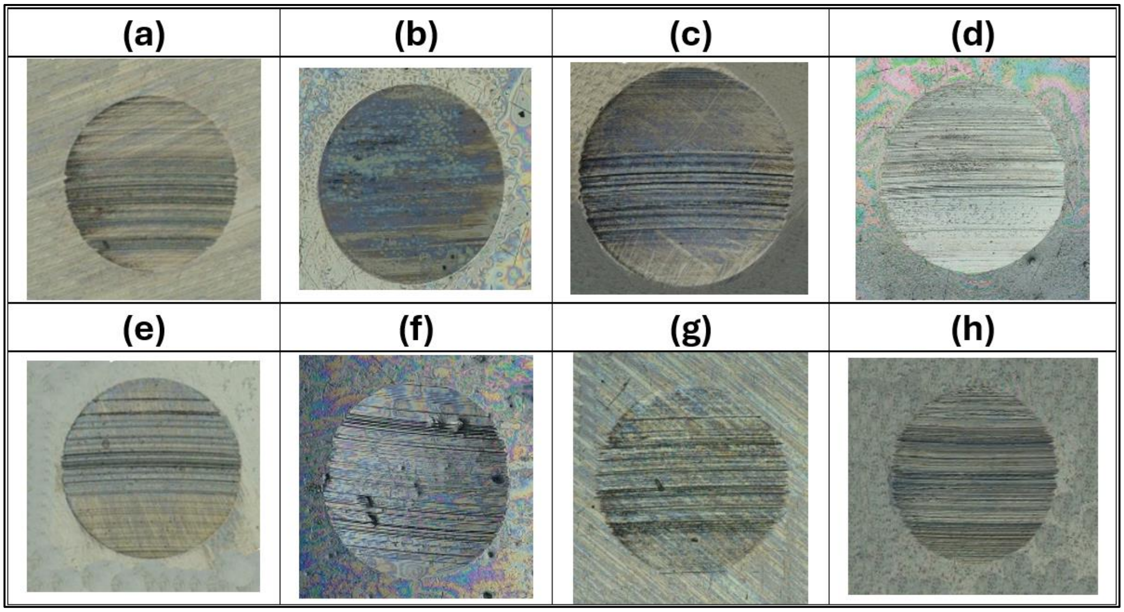

Figure 5.18: WSD at 147N and 100 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

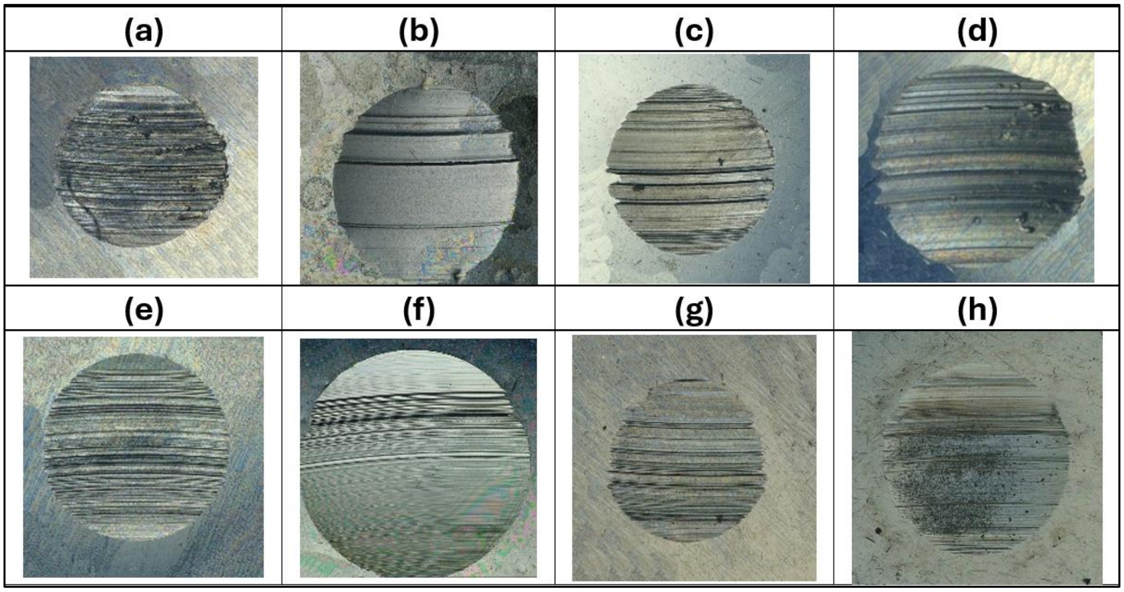

Figure 5.19: WSD at 392N and 100 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

Figure 5.16 to Figure 5.19 shows the wear scar images obtained by inspecting steel balls from each experiment under a digital microscope, OLYMPUS DX-1000. The set magnification level on the equipment was 200x. As evident from the images, each sample faced abrasive wear to some extent. Upon increasing the operating load from 147N to 392N an increase in abrasive wear at the contact point can be seen for most cases. This is due the heat generated at the contact point causing removal of material which inevitably reduces the strength of material. Another visible trend is the increase in abrasive wear with increase in operating temperature especially for the case of lubricants without the addition of ionic liquid. Contrary to that, an improved pattern can be seen for lubricants with addition of ionic liquid showing decrease in abrasive wear. This could be related to the enhanced thermal stability of bio-lubricants with ionic liquid as an additive caused by presence of concentrated oleic acid in them [69]. As compared to other bio-lubricants, both CSO and RJO showed better performance in COF and WSD values. Where CSO+IL performed better at lower operating loads and RJO+IL performed better at increased operating loads.

CHAPTER 6: CONCLUSIONS

As per results obtained from tribological testing of bio-lubricants and PAO, a number of conclusions can be obtained relating to changes in operating conditions and with addition of ionic liquid. As evident from the results, for all cases bio-lubricants outperformed PAO. In addition to that, it can also be observed that additivation with ionic liquid did not much improve the tribological performance of PAO because of its incompatibility with non-polar base oils. During experiments, it was observed that the addition of ionic liquid in base bio-lubricants has increase their tribological performance with reduced friction at the contact point and decreased wear scar diameters with some lubricants performing better at higher loads and some at lower loads. This is due to the lubricant's compatibility with ionic liquid and ability to maintain tribo-film at higher lower loads and temperature. During this study, it was found that among bio-lubricants CSO and RJO both showed better tribological properties as compared to other test lubricants where CSO performed better at lower loads, RJO performed better at higher loads due to its inherent load carrying capacity. Contrary to that, PAO did not show much improvement in terms of co-efficient of friction and wear scar diameter.

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