Tribological Analysis of Trihexyltetradecylphosphonium bis(2,4,4-trimethyl pentyl)phosphinate ionic liquid based Bio-Lubricants at variable operating conditions.

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A thesis submitted to the National University of Sciences and Technology, Islamabad,

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MS Mechanical Engineering
Supervisor: Dr. Rehan Zahid
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SCHOOL OF MECHANICAL & MANUFACTURING ENGINEERING
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ISLAMABAD

March 2024

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Abstract

All mechanical systems require lubrication between interacting surfaces to avoid failure of mechanical components and to decrease the losses due to friction, especially for the interacting bodies that operate in boundary lubrication regimes. Due to the decrease in the reserve of mineral oils, increasing environmental concerns, and difficulties in the disposal of non-biodegradable conventional lubricants, a trend is increasing amongst researchers to produce more environmental friendly lubricants. The use of bio-lubricants as an alternative to mineral based oil is limited due to its low thermal stability. Ionic liquid are molten salts which are environment friendly and can be used as additive to bio-lubricants to enhance its physiochemical properties. The effectiveness of ionic liquid in bio-lubricants depends upon a lot of factor amongst which its miscibility with that particular lubricant plays an important role. Ionic liquids make strong interaction with polar lubricants and hence can be effectively used as additives to bio-lubricants. Among ionic liquids phosphonium based ionic liquids are found to show best results with lubricants and hence is used in this study.

In this thesis tribological performance of phosphonium-based ionic liquid Tri hexyl tetra decyl-phosphonium bis (2, 4, 4-trimethylpentyl) phosphonate when used as an additive to Cottonseed oil, Rattan Jot oil, Waste Cooking oil and Polyalphaolefin (PAO) will be studied at different operating conditions and results will be compared with conventional PAO base oil. The physical properties of these oils were already investigated by a previous student Tehreem Naveed[1] and their tribological analysis is done in this study. Tribological performance of all lubricants were studied using a four ball tribometer and its wear scars were determined using an electronic microscope OLYMPUS. From this study it was found that with the addition of ionic liquid, tribological performance of all bio-lubricants enhanced. Ionic liquid does not have much effect on the tribological performance of PAO. Rattan Jot oil was found to have the best tribological properties with and without addition of ionic liquid into it.

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Nomenclature

PAO	(Polyalphaolefin)
CSO	(Cotton Seed Oil)
RJO	(Rattan Jot Oil)
WCO	(Waste Cooking Oil)
IL	(Ionic liquid)
FAME	(Fatty Acid Methyl Ester)
TAG	(Triglycerides)
FA	(Fatty Acids)
TMP	(Trimethylopropane)
COF	(Coefficient of Friction)
WSD	(Wear Scar Diameter)
VI	(Viscosity Index)

CHAPTER 1: INTRODUCTION

1.1 Background

In machines, the major cause of mechanical losses is friction which can be decreased by the use of lubricants[2]. Lubricants introduce a thin film between two interacting bodies that helps reduce friction and wear between them. Apart from reduction of friction and wear, lubrication also has other applications such as releasing the heat produced during the sliding of two bodies, removing wear debris, transmitting forces between two bodies, decreasing operating temperature and preventing materials from corrosion[3]. In a passenger car use of lubrication is important as almost one-third of the total energy produced from the burning of fuel is used by friction[4].In an IC engine, almost 17% of the total energy produced by burning fuel is utilized in terms of friction losses[5]. Lubricants find its use in many fields such as automobiles, machine components, the pharmaceuticals industry, bearings, gears, hydraulic systems, and even in our daily life for example in cooking lubricant is used in form of cooking oils. Lubricants exist in all three forms solids, liquid and gases but most of the time lubricant is used in liquid forms in form of oils.

Lubricants are generally classified into three categories: synthetic, mineral, and bio-lubricants. Synthetic lubricants are mostly generated from organic raw material by tailoring the reactions to get the required product examples of synthetic lubricants are synthetic esters, silicon and polyalphaolefines. Mineral lubricants are derived directly from crude or petroleum reserves such as aromatic oils. Contrary to these bio-lubricants are derived from animals and plants and are more environmental friendly[6]. In the automobile industry mineral oils which are obtained from chemical modification of crude oil are mostly used as lubricants. Due to limited resource of petroleum reserves, toxic emissions which include noxious metals, problems in the disposal and overly increasing prices of petroleum products these conventional oils are being replaced by biodegradable and nontoxic vegetable oil[7].

Bio lubricants are lubricants that are derived from animal and plants feedstock. Bio lubricants have good chemical properties and can be used for lubrication purposes. Bio lubricants especially plant oils possess most of the properties that are required for lubrication which include high viscosity indices (VI), low volatility, higher molecular weight, low vapor pressure and high flash point[3, 8]. They consists of ester bonds which enables the molecules to attach themselves to metal surfaces and provide good lubricity as compared to nonpolar petroleum based mineral oils [7]. In general bio lubricants are renewable, nontoxic to aquatic life and are biodegradable due to which it would be more favorable to use them as an alternate fuel. The reduction in degradation rates is mainly due to higher chemical stability[9]. Plants oil when compared with mineral oils have better chemical properties but due to the reason that they oxidize when exposed to high temperature, they are not tribologicaly favorable to use under high temperature conditions[10].Vegetable oils are mainly composed of triglycerides (TAG) which are esterified to produce three fatty acids shown in Figure 1.1. These glycerol can easily undergo elimination reactions and hence these vegetable oils get unstable at higher temperature[3]. In order to solve this problem the lubricant is chemically modified by replacing glycerol with more suitable alcohol or by addition of additives[2, 11]. Bio-lubricants work really well under boundary lubrication regime but adding certain quantity of ionic liquids can further enhance its tribological properties[12].

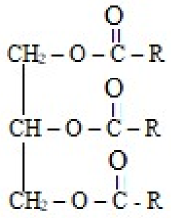


Figure 1.1: Triglyceride molecule. R', R'', R''' represents fatty acids chain[13].

Ionic liquids are organic salts that melt at temperature as low as 100 ˚C and consists of positive and negative ions. Positive ions are called cations and negative ions are called anions[14]. Ionic liquids are low volatile , have low combustibility , higher thermal stability , low melting points , high viscosity , a variety of anion and cations combination, negligible effect to environment and high conductivity which make them suitable for lubrication purposes[15]. They can be used independently as lubricants as well as an additive to any other lubricant. Ionic liquids are highly miscible in polar solvents and hence can be used effectively as an additive to bio lubricants. As ionic liquids can have a large combination of ions and so a variety of ionic liquids has been studied as possible additives to bio lubricants. However Ionic liquids having phosphonium as cations shown in Figure 1.2 are seen to be highly miscible with bio lubricants and hence has a great effect on its tribological properties[16].

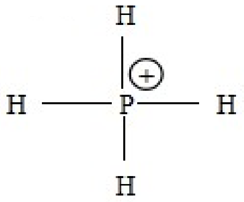


Figure 1.2: Phosphonium cation[13].

1.2 Objectives

In this study a Tri hexyl tetra decyl phosphonium bis (2, 4, 4-trimethylpentyl)phosphinate ionic liquid is checked for its compatibility with one conventional oil polyalphaolefin (PAO) and three bio lubricants Cotton Seed Oil (CSO), Rattan Jot Oil (RJO) and Waste Cooking Oil (WCO). The main objectives of this thesis are:

A. Tribological analysis of $(P_{66614})(^{i}(C_8)_2PO_2)$ ionic liquid based bio lubricant using tribometer
B. Tribological analysis of $(P_{66614})(^{i}(C_8)_2PO_2)$ ionic liquid based PAO using tribometer.
C. Comparison of tribological performance of bio lubricant and PAO.
D. Wear analysis using Olympus microscope.

1.3 General Methodology

In this thesis PAO, RJO, CSO and WCO along with its blend with 1wt% $(P_{66614})(^{i}(C_8)_2PO_2)$ ionic liquid is taken and tested for its tribological characteristics. The bio lubricants and its blend was already studied[1]**.** At first the friction values were measured on a four ball tribotester and then the wear scar on the balls were measured using OLYMPUS microscope at a magnification of 280x.

1.4 Scope in Pakistan

Pakistan is a mineral rich country but due to lack of extraction resources the country petroleum needs are majorly fulfilled through imports which is a real setback for us. Also due to hazardous emissions of these petroleum based products there is an environmental concerns across highly populated areas of Pakistan.

As Pakistan is an agricultural rich country have access to different plants and seeds which can be used to produce bio lubricants which can be used as a more environmental friendly and cheap alternative to these mineral products. This will also help Pakistan achieve growth in local industry, decrease the imports of petroleum products, create more job opportunities and hence step towards achieving a stable economy.

CHAPTER 2: Production of Bio-Lubricants

2.1 Introduction

Bio-lubricants are considered to be one of the best alternatives to mineral based oils due to its great lubricity and biodegradability. Under low temperature, bio lubricants show great properties but the triglycerides (TAG) inside bio- lubricants oxidize when exposed to high temperatures. Form literature it can be seen that thermal stability of those bio lubricants which do not have hydrogen atom on the β-carbon atom of the alcohol in ester molecule are much better[17]. So thermal stability of bio lubricants can be increased by replacing the glycerol molecule which contain β-hydrogen atoms with alcohols which don't contain β-hydrogen atoms i.e. Trimethylopropane (TMP) or neopentylglycol (NPG). In this thesis bio lubricants production from vegetable oils are done in two steps. Production of bio-lubricant is most commonly carried out through esterification process because it can produce more than 90 percent yield[18]. In the first step the vegetable oils are converted into bio diesel and in the second step these bio diesels are than converted into bio lubricants.

Vegetable oils are comprised of triglycerides (TAG) and fats. In order to convert these vegetable oils to bio diesel, the TAGs are converted into fatty acid alkyl ester (FAME) through transesterification. This esterification process occurs in three phases under presence of a catalyst. The final result of this reaction is a free of carbon, renewable and biodegradable fuel. First a reaction takes place between TAGs and alcohol molecule and yields FAME and diglyceride as a product. After this another reaction takes place between the diglyceride produced in the previous step and alcohol molecule to produce FAME and monoglyceride. At last again a reaction takes place between monoglyceride produced in the previous step and alcohol molecule to produce FAME and glyceride. So in transesterification reaction a total of three FAME are produced by reaction of one triglyceride with alcohol molecules[19]. The reaction is represented by the following equation shown in Figure 2.1.

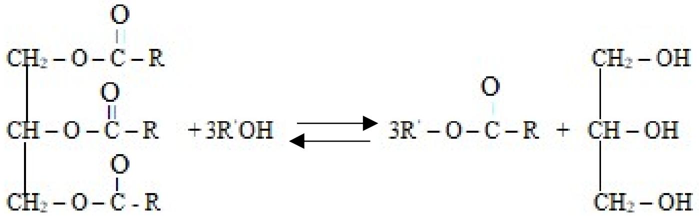


Figure 2.1: Esterification of raw vegetable oil[20].

Transesterification is a reversible process and a lot of factors decides the rate at which this reaction achieves equilibrium. Time, type of catalyst, concentration of catalyst, alcohol to oil molar ratio and mixing intensity are the factors that when combine effects the efficiency of transesterification process[21, 22] . A great variety of catalysts are available that are used to catalyze the reactions, but best results are achieved when a base is used as catalyst in these reactions. Yields of transesterification with 45-60% of reaction time were found to be 90% when reactions were performed in presence of potassium hydroxide as catalyst at concentrations varying from 0.5-2% in methanol with oil to alcohol molar ratio of 1:6 and at 60 ˚C temperature[23, 24]. These results demonstrate the effect on efficiency of reactions when a base is used as catalyst in transesterification reaction.

The product of transesterification is mostly biodiesel and a molecule of glycerol. The feedstock oil and the method of extraction are two main parameters which define the properties of transesterified bio diesel. Triglyceride which is the main building block of raw vegetable oil is mostly comprised of three fatty acids (FA). The chain length of these three fatty acids attached to glycerol may or may not vary. The chains of these fatty acids are either saturated or unsaturated. Poor oxidation stability is seen for feedstocks having more percentage of chains of unsaturated FA than saturated FA due to higher affinity of the double bonded carbon atoms present in it. By transesterification of the methyl ester the favorable properties of base oils such as lubricity and viscosity remains preserved whereas its thermal oxidative stability increases and pour points decreases[25].

After the formation of bio diesel these bio-diesel further undergoes esterification to produce bio-lubricant. In this process a reaction between bio diesel and a polyol e.g. Trimethylolpropane (TMP) takes place which converts the fatty acid methyl ester into TMP based monoester, diester and triester along with chains of fatty acids[26] . The properties of the final products are strongly influenced by the reaction parameters. TMP has high melting points, lacks the beta hydrogen atom and have branched chains due to which it is considered to be ideal for esterification process. For the conversion of bio-diesel to bio-lubricant, bio-diesel reacts with TMP in a molar ratio of methyl ester to TMP of 3:1 and in presence of a catalyst sodium methoxide ($NaOCH_3$). The reaction is shown in Figure 2.2.

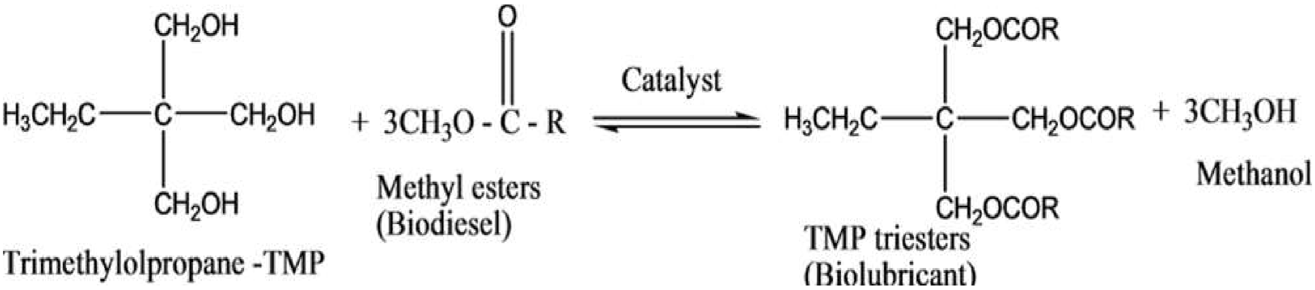


Figure 2.2: Conversion of bio-diesel to bio-lubricant[20].

Rattan jot oil, cotton seed oil and waste cooking oil were selected as feedstock for bio lubricant. These oils are relatively cheaper and are readily available in Pakistan and so were chosen as feedstock. Rattan jot oil and cotton seed oil were procured from local market and were filtered to remove any impurity and waste cooking oil was collected from home[1].

2.2 Material used

Rattan jot oil, cotton seed oil and waste cooking oil were selected as feedstock for bio lubricant[1]. Rattan jot oil and cotton seed oil were procured from local market and were filtered to remove any impurity and waste cooking oil was collected from home. The chemicals used during productions were Methanol, TMP, KOH, $NaOCH_3$ and propanol. All the chemicals required were bought from a manufacturer (Sigma Aldrich)[1].

2.3 Production of Bio-diesel

Production of bio-diesel was done through transesterification process defined in previous section in presence of a basic catalyst and methanol. In the first step a round bottom flask was taken and about 250g of feedstock vegetable oil was added to it. This flask was then placed in a water bath and heated to a temperature of 60 ˚ C. A solution of 56g of methanol and 4.25g of KOH was prepared. Before adding into the oil it was make sure that the KOH is completely dissolved in methanol. This solution is than used in oil at a molar ratio of 6:1. The solution was added to oil that was at 60˚C and for 45 minutes the reaction was allowed to take place in presence of a reflux condenser. A magnetic stirrer was used to continuously stir the solution. After this time had passed, the solution was transferred to a separation flask and allowed to cool down for 7-8 hours. After the above specified time two distinct layers were formed the upper one was impure bio diesel and the lower one was mainly comprised of glycerol. The lower layer has certain amount of methanol and oil that didn't undergo reaction as well. The glycerol layer was then removed. This is shown in following Figure 2.3.

The impure bio-diesel obtained was than purified through water and the impurities like methanol and glycerol was removed. The biodiesel was washed three times with water. At first a 250g of water is added to the separation funnel and was shaken carefully. As bio diesel was lighter in weight as compared to water, all the impurities was dissolved by water and was removed through the bottom of funnel as shown in Figure 2.4. This process was done 3 times until a clear solution was obtained. After this the bio-diesel is heated to 110˚C in a beaker as shown in. All the dissolved water evaporated and the required bio-diesel was obtained. The flow chart of this whole process of production of bio-diesel from vegetable oil is shown in Figure 2.5.

Figure 2.3: Formation of glycerol and impure bio-diesel layer[1].

Figure 2.4: After washing bio-diesel[1].

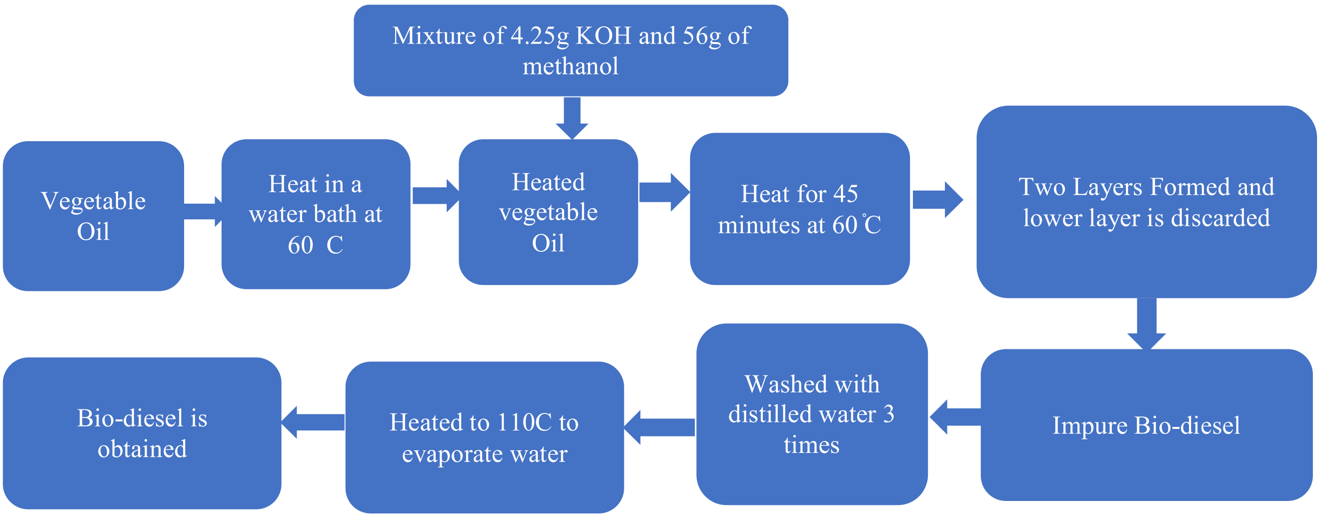


Figure 2.5: Production of bio-diesel from raw vegetable oil.

2.4 Production of Bio-lubricant

Bio-lubricant were produced from further esterification of bio-diesel produced in the previous section. For this purpose 250g by weight bio-diesel were taken in a rounded flask and was subjected to heat at a temperature of 60 ̊C in an oil bath. A 37.5 g by weight TMP was added to this bio-diesel at 140℃ temperature. The temperature was maintained until the TMP was melted. The mixture was continuously stirred during this whole process. After whole TMP was melted, 2.5g of sodium methoxide was added to the above mixture while maintaining the temperature at 140℃ and the pressure was lowered by installing a distillation setup to the reaction flask. After some time bubbles started to form as a result of the reaction and in the condensate flask some substances started to settle. As a result of this reaction between FAME and TMP, Methanol was formed as a by-product. The reaction was allowed for four hours. The product of the reaction was allowed to cool down and then filtered in order to remove any impurities. The remains were TMP bio-lubricant required. The procedure for both bio-diesel production and bio-lubricant production was same. Flow chart for the production of bio-lubricant from bio-diesel is shown in the Figure 2.6.

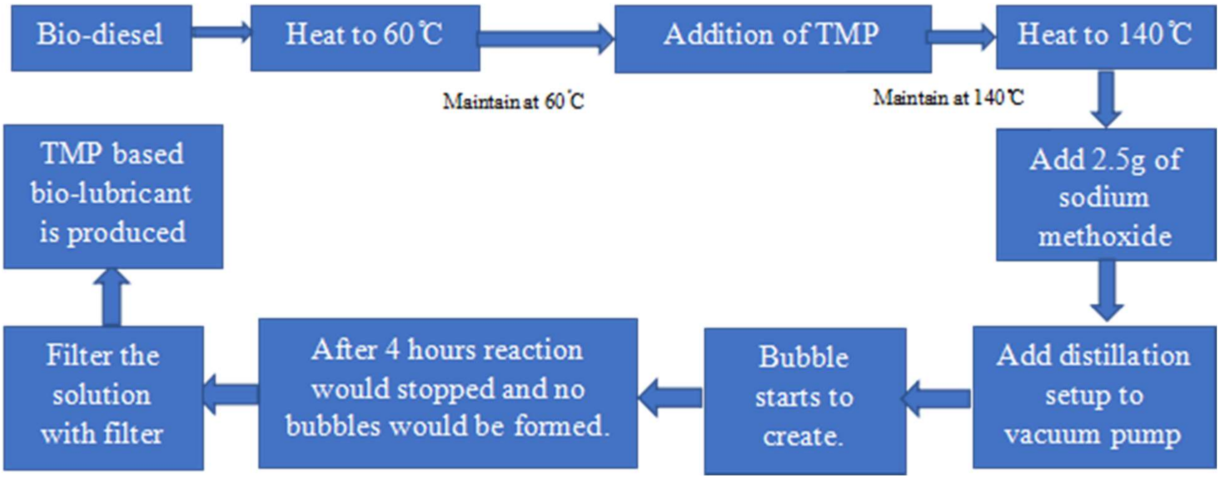


Figure 2.6: Production of bio-lubricant from bio-diesel.

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR) of Bio-lubricant

FTIR analysis is used for identification of different material by scanning through infrared rays. FTIR analysis is used to determine the chemical characteristics of a material such as additives inside it and detects any decomposition or oxidation occurred inside it. FTIR use to identify the different functional groups present inside a material. In FTIR spectrum wavenumbers ranging from $4000cm^{-1}$ to $1500cm^{-1}$ identifies the presence of a functional group and wave numbers ranging from $1500 cm^{-1}$ to $500 cm^{-1}$ identifies the fingerprint region[27]. If there are peaks in the functional group range, it identifies the presence of functional group whereas the peak in fingerprint range identifies the presence of weak functional groups [28, 29].

Figure 2.7 represents the FTIR analysis of bio-lubricants within wavelength range of $4000 cm^{-1}$ to $450 cm^{-1}$ [1]. The FTIR analysis of all the bio lubricants were similar whereas the FTIR of PAO was different from them. At wavenumber of $3500 cm^{-1}$ there is a peak which represents the presence of O-H group due to trace of water present inside the bio-lubricant[30]. Also from the FTIR, the presence of two peaks between 2750-$3000 cm^{-1}$ indicates that there is a carboxyl group present here. In between the region of wavenumber $1750 cm^{-1}$ to $2750 cm^{-1}$ there is stretching vibrations of C=O[31]. In bio-diesel (FAEE) C-O stretching are seen which cannot be seen in TMP based bio-lubricant because it is not its characteristic[32]. Also peaks at wavenumber $1500 cm^{-1}$ is seen in both FAEE and TMP based bio lubricant[33]. This whole FTIR analysis shows us that the bio-lubricant is completely produced and don't have any FAEE in it.

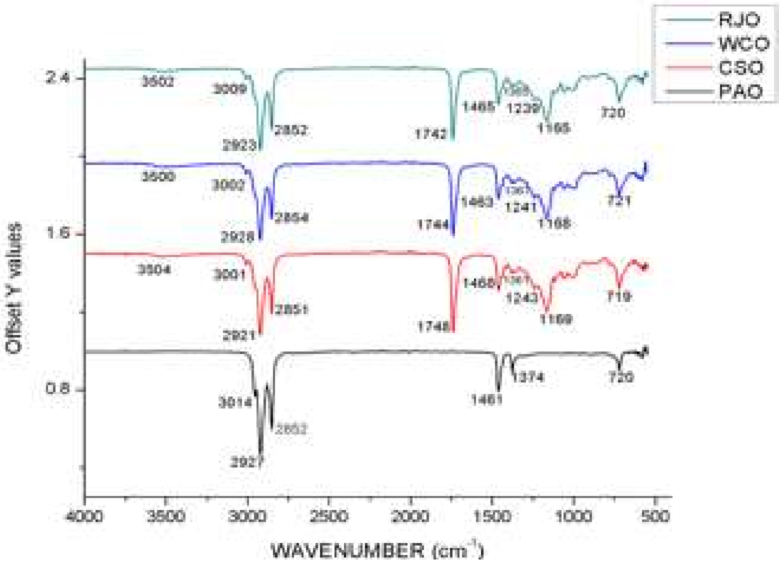


Figure 2.7: FTIR spectrum of bio-lubricant[1].

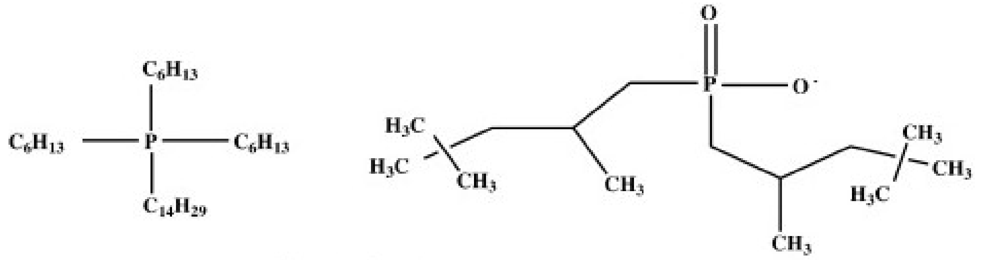
CHAPTER 3: Production of Ionic Liquid Based Bio-Lubricant

3.1 Introduction

Ionic liquids are liquids having low melting temperature as compared to water. Ionic liquid is a subject that is being investigated by researchers now a days for better tribological performances due to the properties like low melting points, non-flammability, environmental friendliness and low volatility[34, 35]. Ionic liquids are generally classified on the basis of cations present in it. Generally ionic liquids have phosphonium, imidazolium, ammonium or pyrolidinium cations in it. A lot of studies has been done on using ionic liquid as a lubricant [36-38]. Ionic liquids when analyzed from tribological point of view outperformed all other conventional lubricants. Ionic liquids although having great tribological properties cannot be used as a lubricant itself because of its high cost, however it can be mixed with other base oils to improve their tribological properties[39, 40]. Till date a lot of ionic liquids is used as an additive to different lubricants and there effect on the tribological behavior of those lubricants have been investigated [11, 41, 42]. There are variety of ionic liquids which can be used as an effective lubricant additive. In some research mixtures of ionic liquid and other particles has been investigated as effective additives to lubricants [43-45]. These additives were investigated at different concentration, different operating conditions and under different applications as a possible additive to lubricants. When the friction and wear behavior of these lubricants were studied they were found to be a lot more effective as compare to lubricants without these additives[46].

The effect of ionic liquids on tribological properties of lubricants depends a lot on its bonding with the lubricants molecule. Solubility of ionic liquids in nonpolar oils is negligible due to which it forms ionic-oil emulsions and does not perform well. However they are miscible in polar base oils [47-50]. Study has shown that the ionic liquids are more soluble in solvents having more polarity and hence the ionic liquids show best performance with base oils that have ester groups in them[51]. Also among ionic liquids, ionic liquids that have cations of phosphonium are found to have outstanding friction and wear characteristics especially in systems under boundary and mixed lubrication regimes[5, 51]. In one study two phosphonium based ionic liquids tri hexyl tetra decyl phosphonium bis (2, 4, 4-trimethylpentyl) phosphinate (IL1) and tri hexyl tetra decyl phosphonium bis(2-ethylhexyl) phosphate (IL2) when used as an additive to Hydrocracked mineral oil (Yubase4/Group III) in two different concentration i.e. 0.5wt% and 1wt%, different operating temperature and different slide to roll ratios(SSR) shows that the mixture of base oil with IL2 has the least values of COF and wear at 1wt% concentration, 100℃ temperature and all SSR[46] . This shows that the phosphonium based ionic liquid strongly effect the stability of base oils even at higher temperature. In another study when two ionic liquids tri hexyl tetra decyl phosphonium bis (2, 4, 4-trimethylpentyl) phosphinate (IL1) and tri hexyl tetra decyl phosphonium bis (2-ethylhexyl) phosphate (IL2) were used as an additive at 1wt% to polyalphaolefin (PAO) and tested at different operating temperatures and slide to roll ratios it was found that base oils with IL1 in it outperformed the other samples in terms of tribological performance under all operating conditions[52]. Similarly in one other study it is shown that when tri hexyl tetra decyl phosphonium bis (2, 4, 4-trimethylpentyl) phosphinate was used as an additive to TMP ester, there was a huge enhancement in frictional properties[16].

From the above literature ionic liquid tri hexyl tetra decyl phosphonium bis (2, 4, 4-trimethylpentyl) phospinate was selected as additive to different bio-lubricants. The structure of this ionic liquid is shown in Figure 3.1.



$(C_{48}H_{102}O_2P_2)$

Figure 3.1: Tri hexyl tetra decyl phosphonium bis (2, 4, 4 trimethylpentyl) phosphinate[5].

3.2 Lubrication Mechanism of Ionic Liquids Based Bio-Lubricants

In mechanical systems lubricants used are majority liquids. Ionic liquids have outstanding effects on the tribological behavior of the base oils when used as additive and has attracted researches towards itself [34, 35]. A boundary lubrication layer is formed between the contact area and ionic liquid base lubricant due to molecular reaction whenever the lubrication regime shifts to mix and elastohydrodynamic lubrication [53]. Covalent bonds are formed between the ions present in ionic liquids and the metal surface, due to which a layer is produced on the metal surfaces which helps to distribute the load among asperities as well as act as a shield to the surfaces[54]. The ionic liquids also form a tribofilm over the metal surfaces by chemisorption[55]. It can be seen from literature that ionic liquids with phosphonium cations can form the tribofilms more rapidly because of its ability to react rapidly with metal surfaces[56].

3.3 Synthesis of Ionic Liquids based Bio-Lubricant

The procedure used for synthesis of ionic liquid is explained in this section. A 250g sample of each bio-lubricant containing 1wt% ionic liquid was made. For this purpose 247.5g of bio-lubricant was taken and then heated to a temperature of 80 ℃. 2.5g of ionic liquid was taken and heated to a temperature of 60℃. After the base oil has achieved the required temperature than it was carefully added to ionic liquid with constant stirring. The process takes up to 30 minutes and then a mixture of bio-lubricant with 1wt% ionic liquid was obtained[1].

3.3.1 Fourier Transform Infrared Spectroscopy of Ionic Liquid Based Bio-Lubricant

In FTIR analysis the intensity of absorption of the functional groups reflects the chemical makeup of the oils[57]. The FTIR spectra of ionic liquid based bio-lubricants are shown in Figure 3.2. From the figure a peak can be seen at $3000cm^{-1}$ representing C=C-H present in trimethylopropane. Similarly from 850-$1400cm^{-1}$, a peak can be seen representing weak C=C due to transesterification process. Peaks at $1750cm^{-1}$ representing weak C=O. The presence of carboxylic ester can be seen in the region between 2850-$2930cm^{-1}$.There is also a characteristic peak of P=O which confirms the presence of ionic liquid.

The overall FTIR spectra of ionic liquid based bio-lubricant is similar to that of TMP based bio-lubricant. There are no visible shifts of peak or peaks representing formation of new bonds which shows us that addition of ionic liquid into bio-lubricant has no effect on the structural composition of bio-lubricants and that there is a physical interaction between ionic liquid and bio-lubricant.

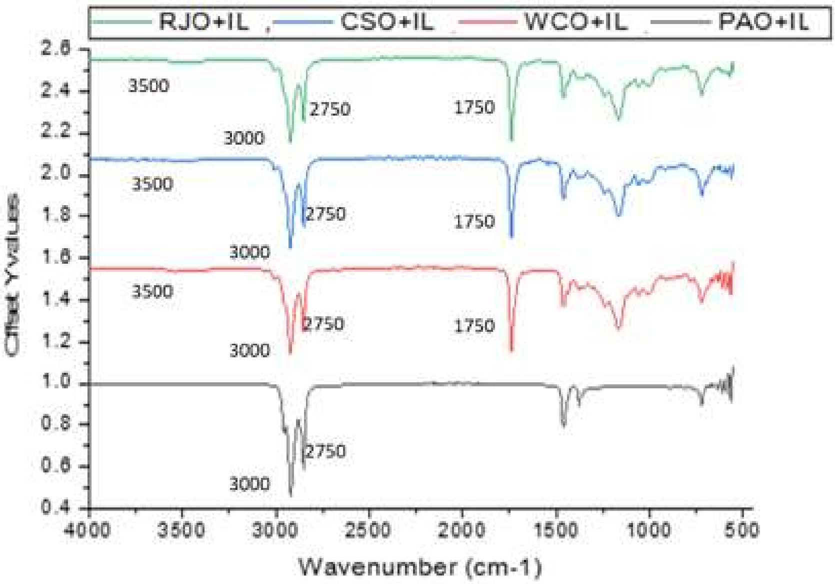


Figure 3.2: FTIR spectra of ionic liquid based bio-lubricant[1].

CHAPTER 4: Physiochemical properties of Lubricant

4.1 Introduction

Mineral oils based lubricants are widely used in industry which are dangerous for the environment due to hazardous emissions. Over the last few years bio-lubricants has emerged as an alternative to these mineral based oils. These bio-lubricants although being environment friendly don't possess the required tribological properties and hence methods are used to improve the tribological performances of these bio-lubricants. Ionic liquids has emerged to be of great potential for this purpose. Ionic liquids are environment friendly and has good miscibility with bio-lubricants. When added to bio-lubricants these ionic liquids has a great effect on the tribological performance of the bio-lubricants[58].

Physiochemical properties of the lubricants directly affect its performance. The addition of ionic liquid into lubricants effect their chemical properties. In this chapter the effect of the selected ionic liquid on the physiochemical properties of lubricants under study will be discussed. All the physiochemical properties were measured according to ASTM standards[1].

4.2 Experimental Setup

All the physiochemical properties of lubricants under study were measured according to ASTM standards. The methodology used for measurement of these properties are represented here.

4.2.1 Density

Density defines how much space has a substance taken in relation to its mass. Simply mass per unit volume of a substance is defined by density. Bio-lubricant are less dense as compared to vegetable oil due to the transesterification reactions that takes place during its production. Less density of bio-lubricant is desirable as it would be easy to transport them. The density of the selected lubricants along with its blend with ionic liquid was measured according to the standard ASTM D1480 in bio-lubricant lab at SMME NUST. This method is used for liquids having vapor pressure values less than 80kPa and viscosities less than 40,000cSt (mm^2/sec). This method is used when dealing with liquids having temperatures in between 20 and 100℃.

In order to find the value of density, sample of each lubricant was added to empty pycnometer whose exact volume is known. Once the pycnometer has been compensated to the required temperature than the weight of pycnometer with lubricant inside it is taken. This value divided by the volume of pycnometer gives us the density of lubricant.

*4.2.2 Kinematic Viscosity (*η)

Kinematic viscosity is the ability of a fluid to resist flow under gravitation. The kinematic viscosity of lubricant is important because it decides the thickness of oil film produced by lubricant between asperities. Lubricants with low kinematic viscosity make a thin oil film between bodies in contact and have low load bearing capacities as compared to lubricants having higher values of kinematic viscosity. In order to measure the value of kinematic viscosity an Ostwald viscometer shown in Figure 4.1 present at bio-lubricant lab SMME was used. The measurement of kinematic viscosity value was done according to standard ASTM 445. In this method the kinematic viscosity of lubricant under study is determined by allowing it to flow under gravity in a calibrated capillary viscometer. A comparative study is done between time taken by lubricant under consideration and a lubricant with known viscosity. In this case PAO was taken as a reference lubricant because its viscosity was provided to us by its manufacturer.

In order to perform the experiment the Ostwald viscometer was filled with lubricant up to the bulb of U shaped tube. After that the lubricant was heated to desired temperature by placing the tube in a liquid and heating it. A pippet sucker was placed on top of the tube and the liquid was sucked till top mark. After it the sucking was stopped and the time taken by oil to move from top mark to the bottom mark was noticed. By comparing this time to the time taken by PAO, the viscosity of lubricant was found. Kinematic viscosity (η) was measured at both 40℃ and 100℃ temperature. Dynamic viscosity (μ) was measured by simply dividing kinematic viscosity (η) of lubricant by its density (ρ).

Figure 4.1: Ostwald Viscometer[1].

4.2.3 Viscosity Index (VI)

Viscosity index tells us that how well does a lubrication perform under high temperature conditions. A greater value of viscosity index means that there is less change in the value of viscosity of lubricant with increase in temperature. Usually with increase in temperature the interaction between molecules of a lubricant decreases and hence its ability to flow also decreases. Lubricants with viscosity index below 100 are not preferable for high temperature conditions. Usually the viscosity index of vegetable oils is approx. 200. The viscosity index for the lubricants under study was measured though an online calculator using standard ASTM D2270.

4.2.4 Flash Point

Flash point is the quantity that defines the lowest temperature at which the lubricant will ignite on exposure to fire. Precautionary measure are taken for handling of lubricants having flash point value <40 ̊C. The measurement of flash point values of the lubricants under study were done using a flash point tester shown in Figure 4.2 available at biofuel laboratory present at USPCASE NUST according to the standard ASTM D92.

In order to measure the flashpoints of lubricants, a 5mL of lubricant was added to the test cup of flash point tester. The temperature of the oil was increased at slow rate. At regular intervals a test flame was passed through the test cup and the point at which the oil ignites was noted as flash point of that oil.

Figure 4.2: Flash point tester[1].

4.2.5 Pour Point

Pour point value defines the lowest temperature at which the lubricant has the ability to flow under gravity. Pour point values are important because it tells us about the performance of lubricants at low operating temperatures. Pour point is also important for the transportation of lubricants. The pour point was determined using Koehler's cloud and pour point tester shown in Figure 4.3 at temperatures from -38℃ to 50℃ in thermodynamics lab of SCME NUST using the standard ASTM D97.

Figure 4.3: Pour point tester[1].

4.2.6 Total Acid Number (TAN)

Total Acid number is the amount of KOH required to neutralize 1g of lubricant. Total Acid number is important because the lubricant having high amount of carboxylic acid are prone to corrosions and hence can have higher value of friction and wear. Bio-lubricants with low value of TAN are preferred. In order to find the Total acid number of lubricants under study a titration setup present at bio-lubricant lab SMME NUST was used. All the values were recorded manual by titration with KOH using standard ASTM D664. Yellow color of solution in presence of an indicator represented the acidic impurity present in it. In total three tests were done for each sample and there average value was reported.

4.2.7 Total Base Number (TBN)

Total base number is the amount of hydrochloric acid required to neutralize 1g of lubricant. In order to find the TBN of lubricant a titration setup present at bio-lubricant lab SMME NUST was used and all the test were carried out with 0.1M hydrochloric acid using standard ASTM D4739. The titration tests were performed manually. Pink color of solution in presence of an indicator represented any basic content present in the solution.

4.3 Results

The results of all the experiments explained above is shown in Table 4.1.

Table 4.1: Physiochemical Properties of Lubricants

Properties	**Standard**	**Units**	**PAO**	**PAO+IL**	**CSO**	**CSO+IL**	**RJO**	**RJO+IL**	**WCO**	**WCO+IL**
Density@20 ℃	ASTM D1480	Kg/m^3	827.6	850.8	904.6	932.8	906.4	927.2	907.8	930.8
Viscosity@40 ℃	ASTM D445	cST	65.1	59	27.7	23.27	29.9	35.85	36.8	25.94
Viscosity@100 ℃	ASTM D445	cST	9.8	15.68	5.94	7.22	6	8.9	7.9	8.17
Viscosity Index	ASTM D2270	-	133	282	167	308	137	243	194	321
Pour Point	ASTM D97	℃	-41		-10.2	-10	-13.2	-12.4	-12.8	-12.2
Flash Point	ASTM D92	℃	230	218	175	155	150	205	155	187
Total Acid Number	ASTM D664	mmKOH/g	0.21	0.3	0.25	0.38	0.29	0.43	0.3	0.38
Total Base Number	ASTM D4739	mmHCL/g	0	0.42	0.14	0.62	0.15	0.44	0.1	0.78

4.4 Analysis of physiochemical properties of Lubricants

Here we will discuss the physiochemical properties of lubricants and its comparison to lubricants with trihexyltetradecylphosphonium bis (2, 4, 4-trimethylpentyl) phosphinate ionic liquid in it. The physiochemical properties of bio-lubricant depends a lot on the type of triglycerides present in it.

Densities of all bio lubricants and its blend with ionic liquids was studied and the results are presented in Table 4.1. Here a comparison between densities of lubricants and its blend with ionic liquid is shown in Figure 4.4. A higher value of density in lubricants means it has very strong chemical interaction between its molecules. The density value of PAO is found to be the least as compare to other bio-lubricants. It can be seen that the addition of ionic liquid has slightly increased the values of density for all lubricants.

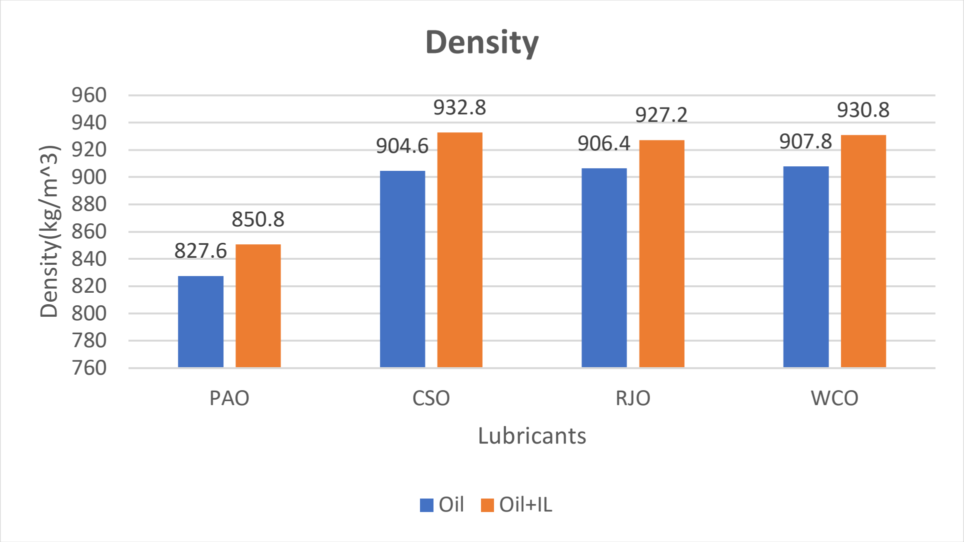


Figure 4.4: Density of lubricants and their blend with ionic liquid[1].

Viscosity of lubricant is important because it tells us how much thick will be the oil film between the bodies in contact. The viscosity of lubricants along with its blend with ionic liquid is shown in Figure 4.5 and Figure 4.6. The kinematic viscosity values for cotton seed oil, waste cooking oil and rattan jot oil at 40 ℃ and 100 ℃ are similar to that reported in literature [59-62]. We can see from Figure 4.5 that there is not much significant change in viscosity of lubricant after addition of ionic liquid at 40 ℃. A significant increase in viscosity of lubricant by addition of ionic liquid can be seen at 100 ℃. This is due to the reason that addition of ionic liquid has a strong effect on the chemical composition and thermal stability of bio-lubricants[45].

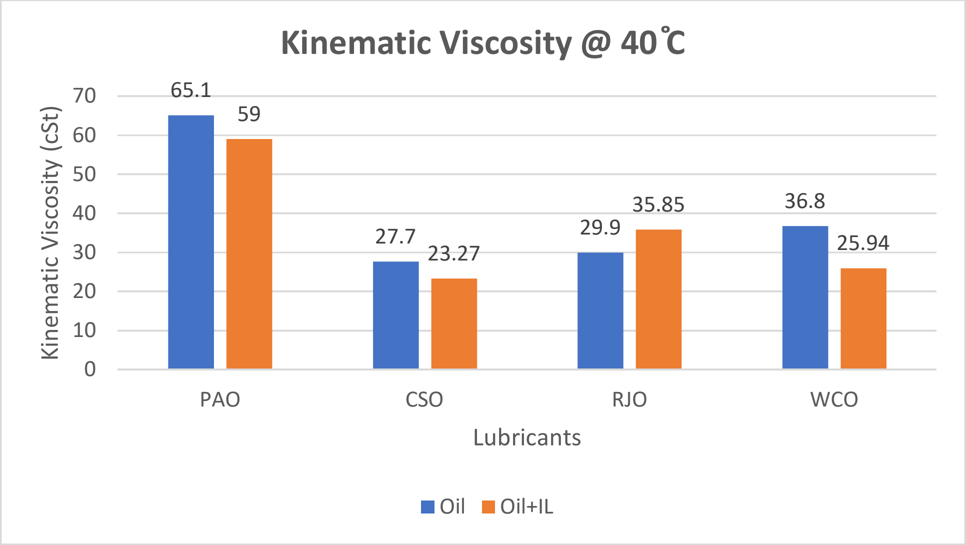


Figure 4.5: Kinematic Viscosity of Lubricants at 40℃ [1].

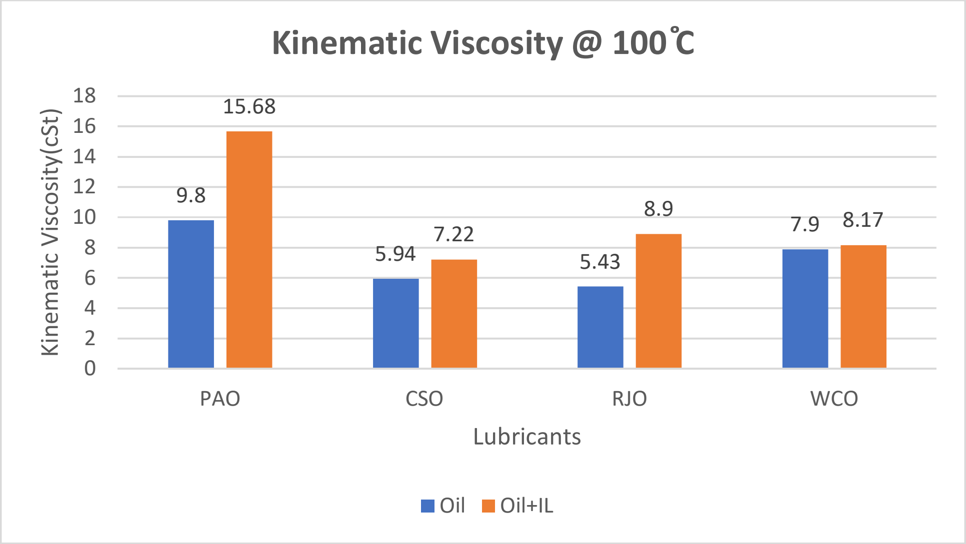


Figure 4.6: Kinematic Viscosity of Lubricants at 100℃[1].

Viscosity index of a lubricant is important as it decides how the lubricant is going to behave with change in temperature. Those lubricants whose protective oil layer does not change in extreme temperatures are best suited for tribological application. Higher viscosity index of oil is preferable as it shows that increase in temperature will have less impact on decline of viscosity of that oil. Figure 4.7 represents the comparison of viscosity index of the lubricants and its blend with ionic liquid. As can be seen from figure 18 that WCO has a viscosity index less than 100, so it is not a suitable option for better tribological performance. As can be seen from the figure that viscosity index of WCO and CSO after the addition of ionic liquid is maximum, so it is best suited for tribological applications. In generic it can be seen that for all lubricants an increase in viscosity index is seen after the addition of ionic liquid into it. The results are in accordance to the literature [59, 62, 63].

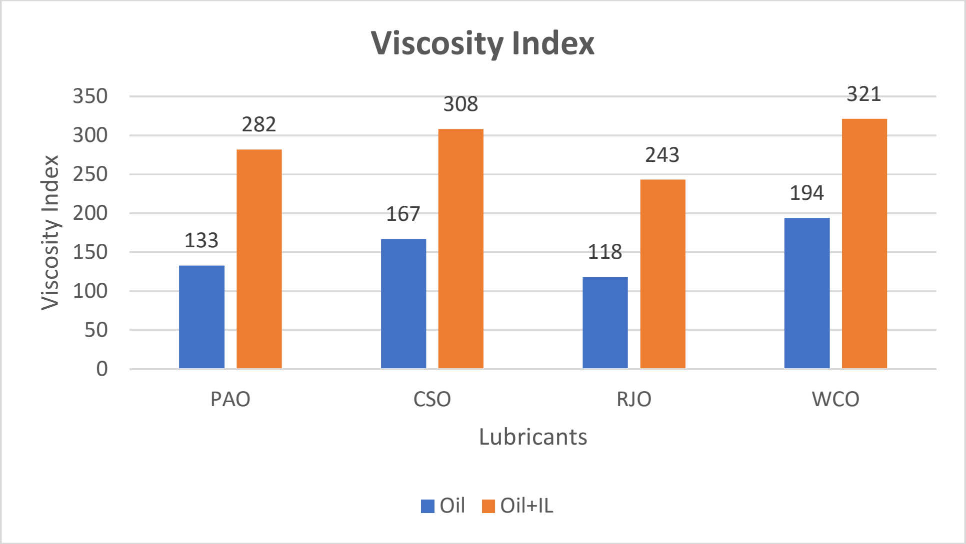


Figure 4.7: Viscosity Index of Lubricants[1].

Flash point and pour point are two factors that has a great effect on the tribological performance of lubricant. The pour point of the lubricant is decided by its viscosity and structure of molecules inside it. Pour point of lubricant is important factor towards its flow ability. The pour point of PAO was already known to us by its manufacturer that is -41 ℃ whereas the pour points of other lubricants and its blend with ionic liquid is shown in Figure 4.8. Pour point of all bio lubricants and its blends were found to be in range of -10.2 ℃ to -13.2 ℃. The pour point of all other bio-lubricants matches with the literature except of WCO. The reason behind this is the presence of crude vegetable oil inside it[64]. As it can be seen from the Figure 4.8 that addition of ionic liquid doesn’t have much effect on the pour point of bio-lubricants.

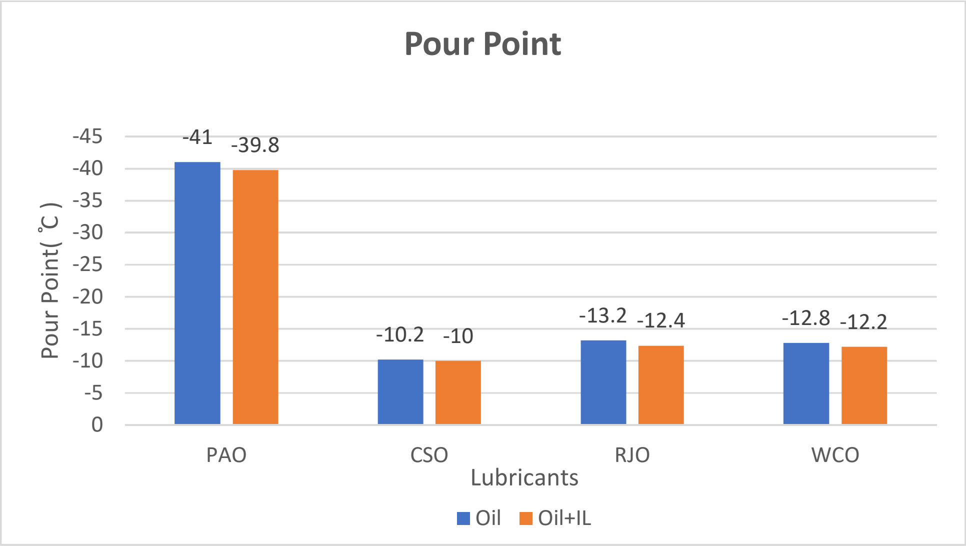


Figure 4.8: Pour Point of Lubricants[1].

Flash point of all the lubricants as well as its blend with ionic liquid is shown in Figure 4.9. Flash point of lubricant is an important factor especially in applications like IC engines where the operating temperatures are very high. For better tribological performances, lubricants with high flash points are preferred. From the figure it can be seen that flash point of PAO with and without the addition of ionic liquid is more than any other lubricant. As ionic liquids are nonvolatile in nature therefore an increase in flash point of all lubricants after addition of ionic liquids can be seen.

The Total Acid number of a lubricants determine the fatty acids present in it. Total acidic numbers of all lubricants along with its blend with ionic liquid is shown in Figure 4.10. The Acid value of bio-lubricants after addition of ionic liquid is found to be slightly higher than that of neat bio-lubricant. The difference in values of acid number of bio-lubricant is very less as shown in Figure 4.10.

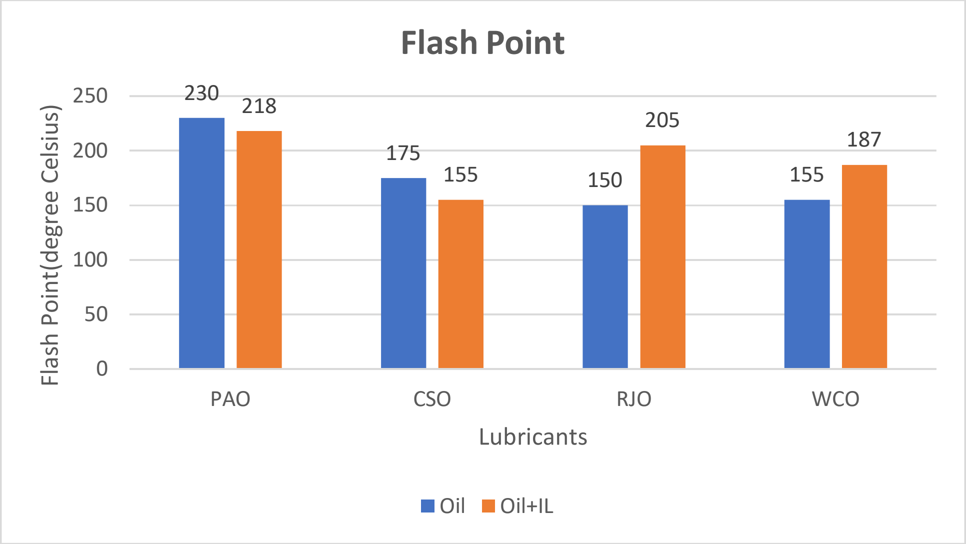


Figure 4.9: Flash Point of Lubricants[1].

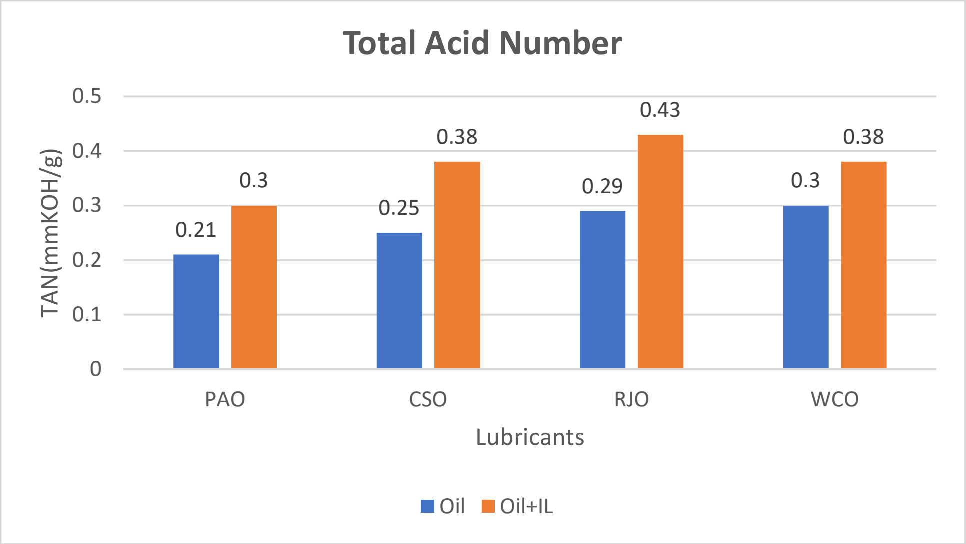


Figure 4.10: Total Acid Number of Lubricants[1].

Total base number of lubricants is shown in Figure 4.11. In case of PAO there was no indication of basic nature of lubricant whereas for bio-lubricant a small value of total base number was recorded. In case of all bio-lubricants the addition of ionic liquids has increased the basic nature of lubricants as shown in Figure 4.11.

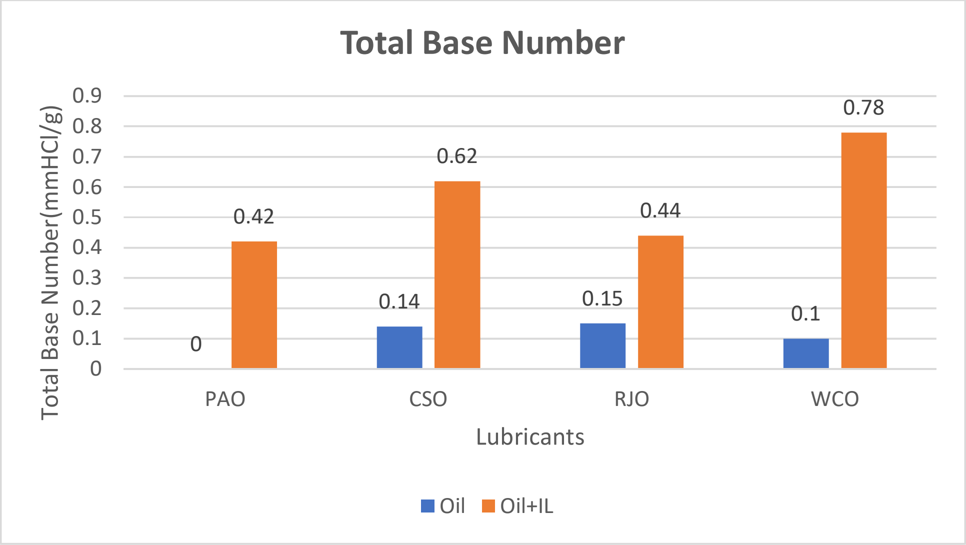


Figure 4.11: Total Base Number of Lubricants[1].

4.5 Discussion

From the above results it can be seen that addition of ionic liquid to bio-lubricants can enhance their physiochemical properties. One of the problems with bio-lubricant is its decreased effectiveness under high temperature conditions. From the above results it can be seen that the addition of ionic liquid has a huge impact on physiochemical properties of bio-lubricant especially under high temperatures. The above results shows that thermal stability of bio-lubricant increases with addition of ionic liquid into it.

From the above results it can be seen that both Cotton seed oil and Rattan Jot oil after the addition of ionic liquid shows better physiochemical properties. Both of these oils can be a used as a lubricant for tribological applications. These oils have the ability to perform well under high operating temperatures and can be used effectively to decrease the friction and wear values in any mechanical system.

CHAPTER 5: Tribological Testing of Bio-Lubricants

5.1 Introduction

In tribological analysis different set of tests are performed on lubricant to see its effect on the values of friction and wear. Different types of tribological configuration are used to determine the tribological behavior of lubricants. Among these tribological configurations the most commonly used are four ball, Pin on disk, Pin on plate and Ball on plate. Sometimes modified test rigs made for a specific applications such as engine test rigs are also used for tribological analysis of lubricant for that specific application. In this chapter we will discuss four ball tests conducted on the lubricants under study and its results. All of these tests were conducted inside Tribology Lab SMME NUST H-12 Islamabad.

5.2 Details of Experiment

Four ball tests were conducted on the selected lubricants using the Vertical Universal Friction Testing Machine (MMW-1A) present in Tribology Lab SMME NUST H-12 shown in Figure 5.2. This four ball configuration consists of four AISI 52100 steel balls with diameter of 12.7mm, out of which three balls were fixed in a fixture containing cavity where the lubricant to be tested was filled and one ball held in a rotating spindle shown in Figure 5.3. All the lubricants were tested at two different loads 147N and 392N, two operating temperatures 75℃ and 100℃ and the spindle rotating at a speed of 1200 rpm. The tests were conducted according to ASTM D4172. The conditions of experiments are listed in Table 5.1. Before start of each experiment the fixture and balls were cleaned with acetone. After that 9mL of sample of oil was taken and added to the cavity of fixture. Three balls were taken and fixed in the fixture having oil inside it and one ball was fixed inside the spindle. Using the PID controller the temperature of the oil was raised at interval of 5℃ to the required temperature. After reaching the required temperature the setup was allowed to maintain the required temperature for a time of about 20 minutes. After that the load was applied and the test was allowed to run for 60 minutes and the data for COF was stored. After completion of the test the setup was unloaded and the balls were taken out of the fixture and cleaned with a tissue paper. The wear scar on the balls were marked with the help of marker to be further studied using a microscope. This whole process is shown by a flow chart shown in Figure 5.1. An electronic microscope OLYMPUS DX-1000 shown in Figure 5.4 was used for the study of wear.

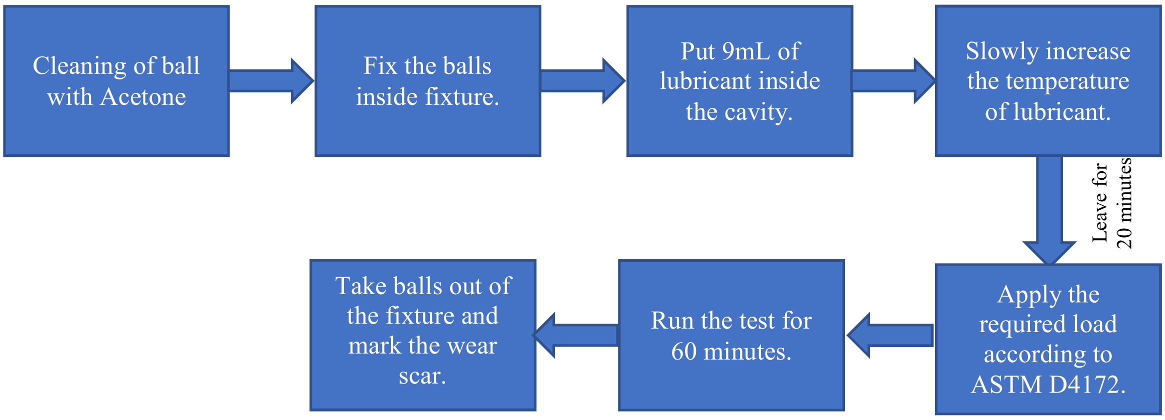


Figure 5.1: Flow chart of four ball test.

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

Figure 5.3: Four Ball Tester Fixture

Figure 5.4: 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	1 Hour.

5.3 Results

All the bio-lubricants along with its blend with ionic liquid were tested at two different loads and two different temperatures to check its tribological behavior and its results are mention in this chapter. The coefficient of friction values for all samples were recorded using 4 ball tribotester at different operating conditions and wear of all samples were analyzed using OLYMPUS microscope. The results are shown in 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 Explanation:

Frictional properties of lubricants were studied using four ball tribometer at multiple loads and operating temperatures and wear scar diameters on the AISI 52100 steel balls were measured with help of an OLYMPUS microscope.

Figure 5.5 shows the average COF results at 75℃. For bare lubricants, CSO has the least value of COF (0.042) whereas WCO has the highest value of COF (0.067) at normal load of 147N. The reason for increased value of COF of WCO can correspond to the fatty acid composites of crude waste cooking oil [64]. These crude waste cooking oils contain saturated fatty acids which can increase friction as compared to monosaturated fatty acids like oleic acid which is present in higher concentration in CSO [65]. At 392N and 75℃, PAO has the highest value of COF (0.069) whereas Rattan Jot Oil shows the least value of COF (0.039). This greater value of COF for PAO as compared to bio lubricants can be explained by its non-polar behavior, resulting in weak interactions with steel surfaces [66].

At 75℃, addition of ionic liquid to PAO has caused an increase of 20.27% and 18.82% at normal load of 147N and 392N as shown in Figure 5.5. This is attributed to the incompatibility of ionic liquid in non-polar base oils [67]. At 75℃, for bio lubricants under normal load of 147N, CSO has encountered an increase of 46.15% when additivated with ionic liquid whereas RJO and WCO shows a decrease of 31.57% and 38.8% in COF as shown in Figure 5.5. The decrease in COF values of RJO and WCO when additivated with ionic liquid can be explained by the rapid formation of tribolayer at this operating condition which effectively separate the asperities from each other. At 75℃ and 392N, a decrease of 8.92% can be seen for CSO when additivated with ionic liquid whereas for RJO, COF value increases. This increase in value of COF attribute to incompatibility of this oil to maintain the protective film at higher loads. For WCO, addition of ionic liquid didn’t show any effect on COF value at 392N.

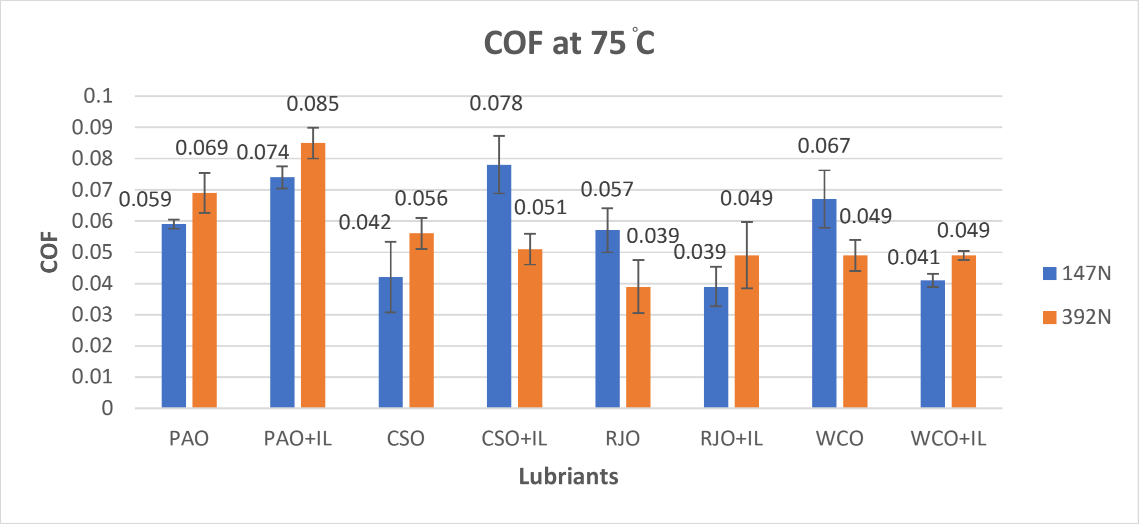


Figure 5.5: Average COF of Lubricants at 75̊C Temperature.

Figure 5.6 shows the average COF of all lubricants at 100̊C. As shown in Figure 5.6 that in case of bare lubricants, PAO shows the highest values of COF at both normal loads 147N and 392N. This is due to the fact that PAO has lower viscosity index as compared to bio-lubricants as shown in Table 4.1. At 100̊C, for bio-lubricants WCO has the least value of COF at 147N normal load whereas at 392N load RJO has the least value of COF. The value of COF at 147N load are in accordance to the viscosity index of lubricants i.e, lubricants with greater viscosity index has less value of COF. The lesser COF value of RJO at 392N corresponds to its better load carrying capacity.

From Figure 5.6, at 100̊C and 147N, the COF values of PAO, CSO and WCO remains almost the same with or without ionic liquid whereas a decrease of 17.3% can be seen for RJO values after addition of ionic liquid to it. At 100̊C and 392N, addition of ionic liquid causes a decrease of 40.38% in COF values for CSO whereas in case of PAO an increase of 6.5% can be seen after addition of ionic liquid. In case of RJO and WCO no significant change in COF values can be seen at 100̊C and 392N load as shown in Figure 5.6.

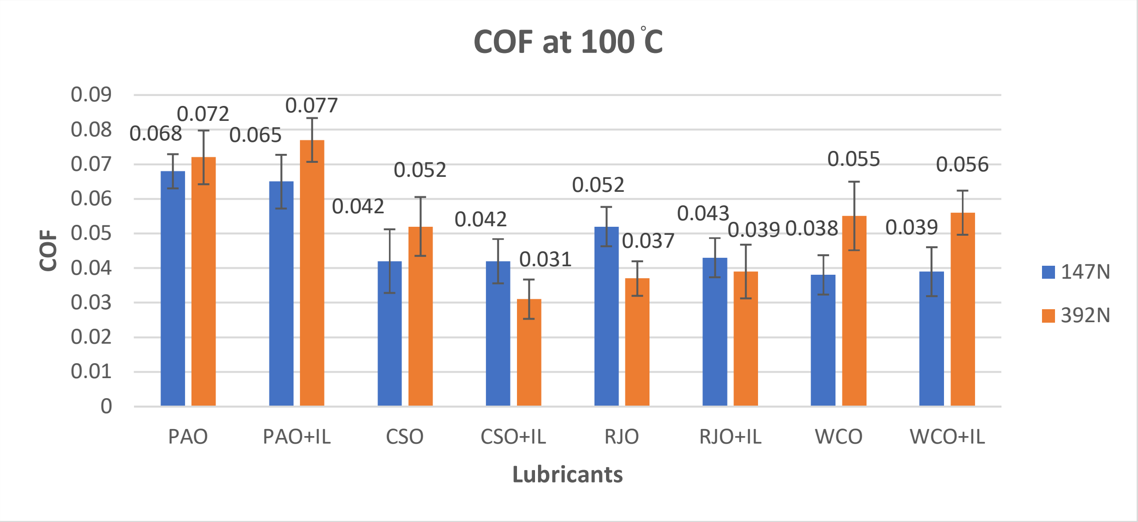
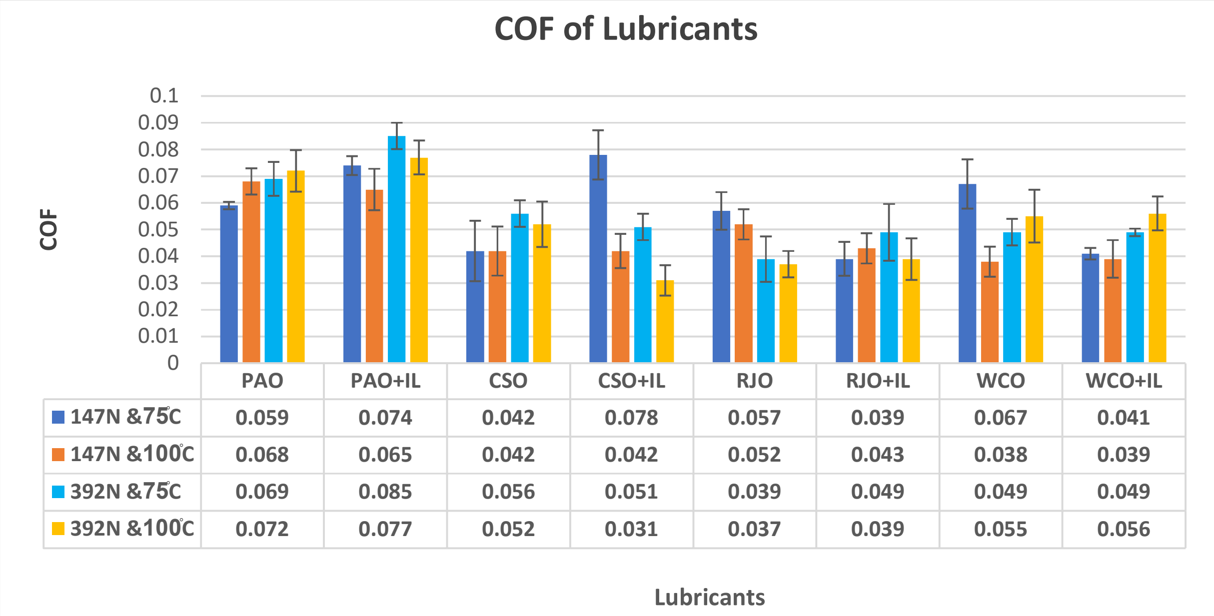


Figure 5.6: Average COF of Lubricants at 100̊C Temperature.

Figure 5.7 shows the COF values for lubricants at all operating conditions. As shown in Figure 5.7 at 75̊C, with increase in load from 147N to 392N, a decrease in COF can be seen for CSO+IL, RJO and WCO. This decrease in COF values is due to the increase in surface roughness and increased amount of wear debris removal [68]. These wear debris act as a filler between the surfaces which reduces the direct contact of asperities and as a result decrease in value of COF can be seen. Similarly at 100̊C same effect of increase in load can be seen for CSO+IL, RJO, RJO+IL. The increase in temperature has caused a decrease in COF values for all lubricants with additives of ionic liquids [69] except for RJO+IL sample at 147N and WCO+IL at 392N as shown Figure 5.7.



	PAO	PAO+IL	CSO	CSO+IL	RJO	RJO+IL	WCO	WCO+IL
■ 147N &75̊C	0.059	0.074	0.042	0.078	0.057	0.039	0.067	0.041
■ 147N &100̊C	0.068	0.065	0.042	0.042	0.052	0.043	0.038	0.039
■ 392N &75̊C	0.069	0.085	0.056	0.051	0.039	0.049	0.049	0.049
■ 392N &100̊C	0.072	0.077	0.052	0.031	0.037	0.039	0.055	0.056

Figure 5.7: Average COF of all lubricants.

Figure 5.8 shows the average WSD of all lubricants at 75̊C temperature. For bare lubricants, it can be seen that PAO has the highest value of WSD as compared to bio lubricants at both normal loads. The better performance of bio-lubricants as compared to PAO can be attributed to the presence of fatty acids molecules in bio-lubricants which reacts with metal surface and form a low shear strength layer over the metallic surfaces [70]. Amongst bio lubricants the least WSD can be seen for WCO samples at both normal loads as shown in Figure 5.8.

At 75̊C, addition of ionic liquid has no significant effect on WSD value of PAO at 147N whereas at 392N load the value of WSD increases by 3.95% for PAO after the addition of ionic liquid. These values represent the ineffectiveness of ionic liquid with PAO because of its non-compatibility with it. At 75̊C temperature and 147N load, addition of ionic liquid has caused a decrease of 9.56% and 1.93% in WSD for RJO and WCO whereas for CSO 6.92% increase in WSD can be seen with addition of ionic liquid. At 75̊C temperature and 392N load, addition of ionic liquid has caused a decrease of 7.8%, 17.7% and 8.44% in WSD for CSO, RJO and WCO respectively. This decrease in WSD represents the enhancement in load carrying capacity of bio-lubricants with addition of ionic liquid.

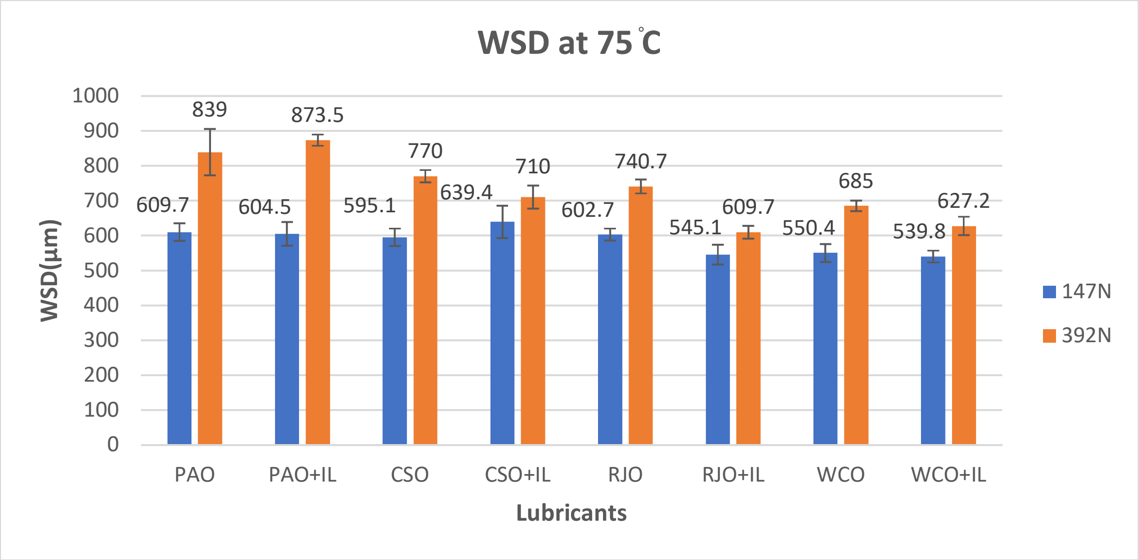


Figure 5.8: Average WSD of Lubricants at 75℃ Temperature.

Figure 5.9 shows average WSD of all lubricants at operating temperature of 100℃. For bare lubricants it can be seen that RJO has the greatest value of WSD at both normal loads. This high value of wear scar diameter shows the lower thermal stability of RJO as compared to other lubricants. For bare lubricants at 100℃ temperature, WCO has the least value of WSD at 147N load whereas PAO has the least value of WSD at 392N load.

At 100℃ temperature, addition of ionic liquid has shown an increase of 28.17% and 21.75% for WCO sample at normal load of 147N and 392N respectively. This increase in WSD values represents the ineffectiveness of ionic liquid in WCO at high temperature. Figure 5.9 shows that CSO when additivated with ionic liquid has caused a decrease of 27.68% and 14% in WSD at 147N and 392N load respectively. Similarly for RJO additivated with ionic liquid a decrease of 63.93% and 22.92% can be seen in WSD at normal load of 147N and 392N respectively. This decrease in WSD values for RJO and CSO additivated with ionic liquid is because of the higher thermal stability of ionic liquid samples.

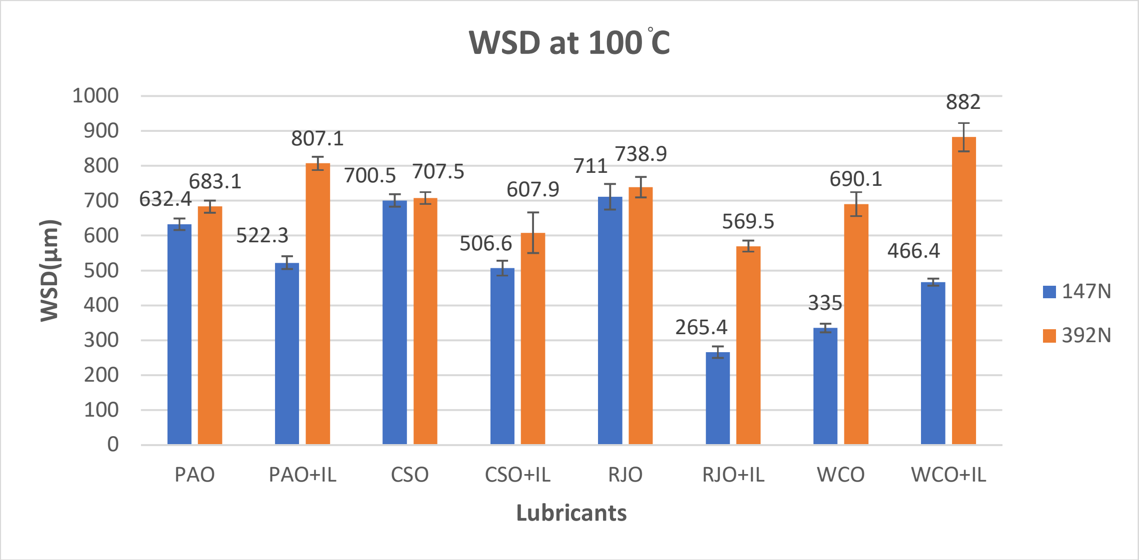
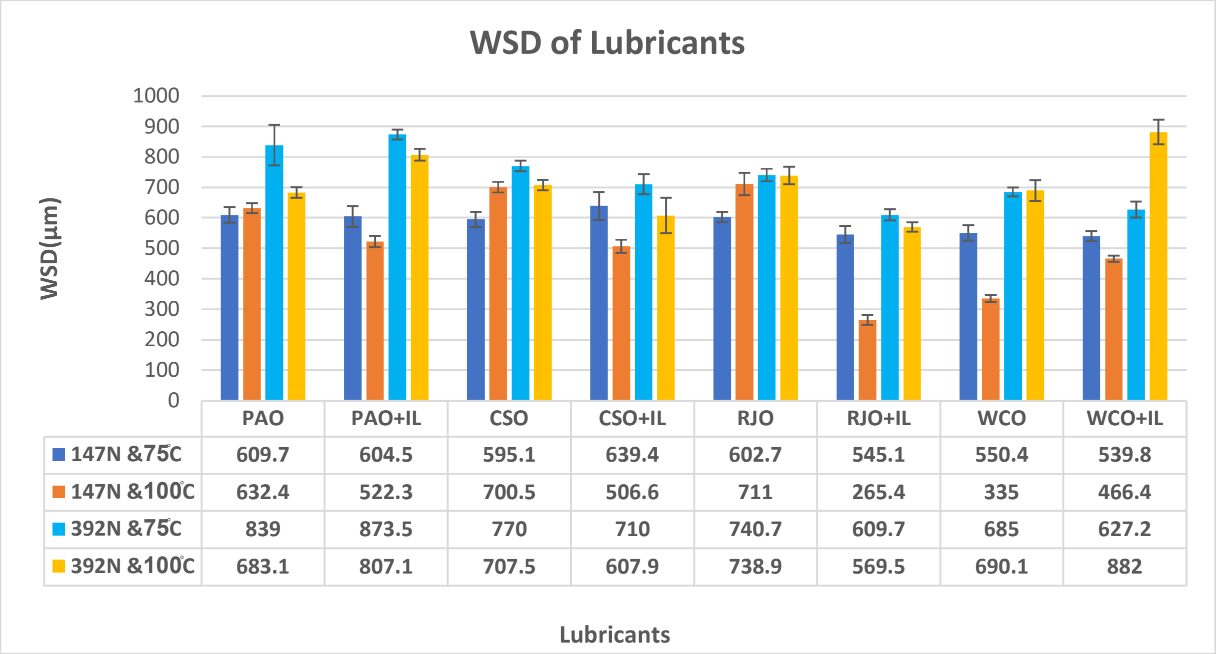


Figure 5.9: WSD of Lubricants at 100℃ Temperature.

Figure 5.10 represent the average WSD values for lubricants under all operating conditions. Form Figure 5.10 it can be seen that RJO+IL samples have the least values of WSD at all operating conditions. With increase in load from 147N to 392N the WSD of all lubricants increased as shown in figure [71]. This increase in WSD can be explained by the decrease in strength of materials with increase amount of heat generation due to increase in load which can cause plastic deformation in material [68]. Also Figure 5.10 shows that with increase in temperature from 75℃ to 100℃, WSD value decreases for all samples containing additives of ionic liquid except for WCO+IL. This can be explained by the fact that by increasing the temperature, viscosity decreases and ionic liquid additives inside the lubricant took the dominant role by forming a protective film over the surface, which leads to decrease in WSD values [69].



	PAO	PAO+IL	CSO	CSO+IL	RJO	RJO+IL	WCO	WCO+IL
🟦 147N &75℃	609.7	604.5	595.1	639.4	602.7	545.1	550.4	539.8
🟧 147N &100℃	632.4	522.3	700.5	506.6	711	265.4	335	466.4
🟦 392N &75℃	839	873.5	770	710	740.7	609.7	685	627.2
🟨 392N &100℃	683.1	807.1	707.5	607.9	738.9	569.5	690.1	882

Figure 5.10: WSD of all Lubricants.

Figure 5.11 shows the values of surface roughness at 75℃. With increase in load from 147N to 392N, an increase in surface roughness values can be seen for CSO+IL, RJO and WCO. On the other hand, as Figure 5.5 shows, these lubricants coefficient of friction (COF) values drop as the load increases. A decrease in surface roughness values can be seen with an increase in load for all other lubricants where the COF increases. These findings show that, in contrast to COF, surface roughness and load variation have an inverse connection. In particular, an increase in surface roughness values was noted for some lubricants with increase in load loads while COF values drop [68].

Figure 5.12 shows the surface roughness values for all lubricants at 100℃. At 75°C, comparable trends between COF and surface roughness values are visible. As shown in Figure 5.12 and Figure 5.6, for CSO+IL, RJO+IL, and RJO, an increase in load causes a rise in surface roughness values while their COF falls. These surface roughness patterns highlight how operating conditions have a major impact on both COF and surface roughness.

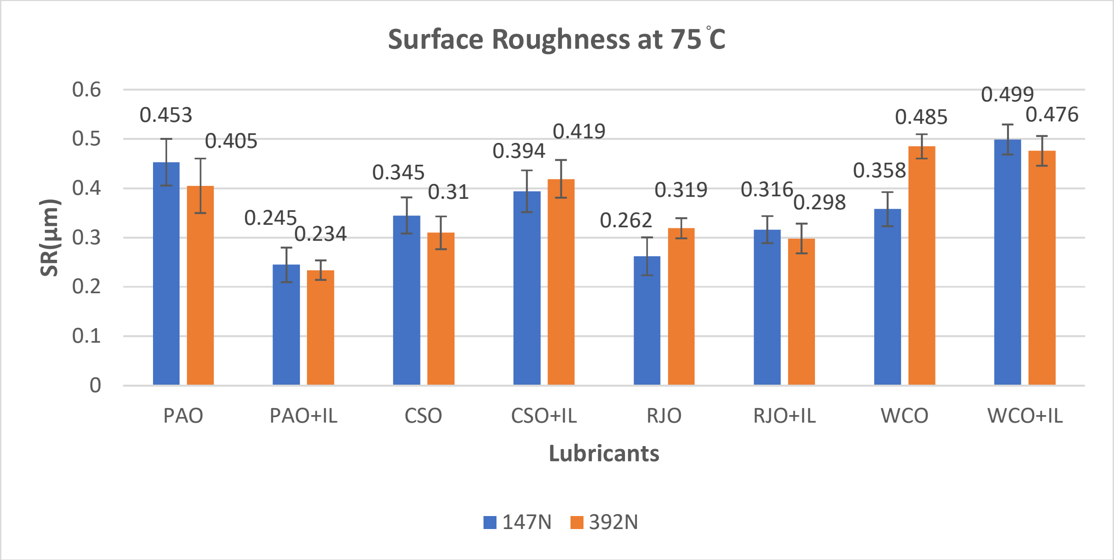


Figure 5.11: Surface Roughness of Lubricants at 75̊C Temperature.

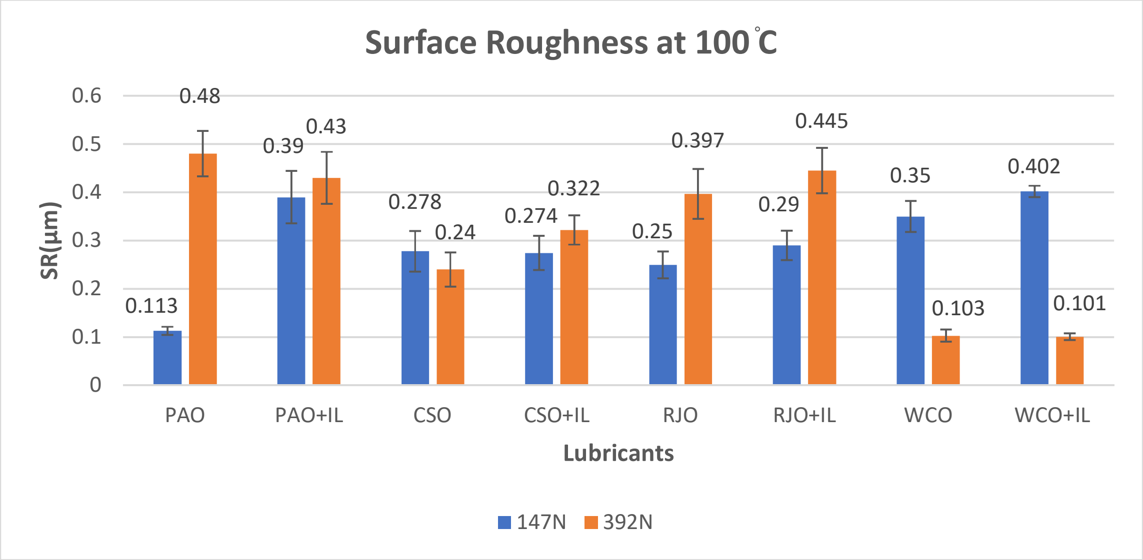


Figure 5.12: Surface Roughness of Lubricants at 100̊C Temperature.

Real time graph of PAO, CSO, WCO and RJO are shown in Figure 5.13, Figure 5.14, Figure 5.15 and Figure 5.17. A distinct initial increase in the coefficient of friction (COF) is observed across all lubricants, followed by a subsequent stabilization at a lower steady-state value, indicative of the running-in process. Notably, PAO exhibits a more stable friction coefficient compared to other lubricants, suggesting rapid tribofilm formation.

Among bio-lubricants RJO has the least stable value of COF throughout the whole test when tested at operating temperature of 100°C and normal load of 147N which could be due to the failure of RJO to separate the interacting surfaces from each other. Ionic liquid-based lubricants exhibit generally stable COF values, because of rapid formation of a tribofilm facilitated by additives. However, CSO+IL samples show less stable values at higher temperatures, indicating potential incompatibility under elevated operating conditions

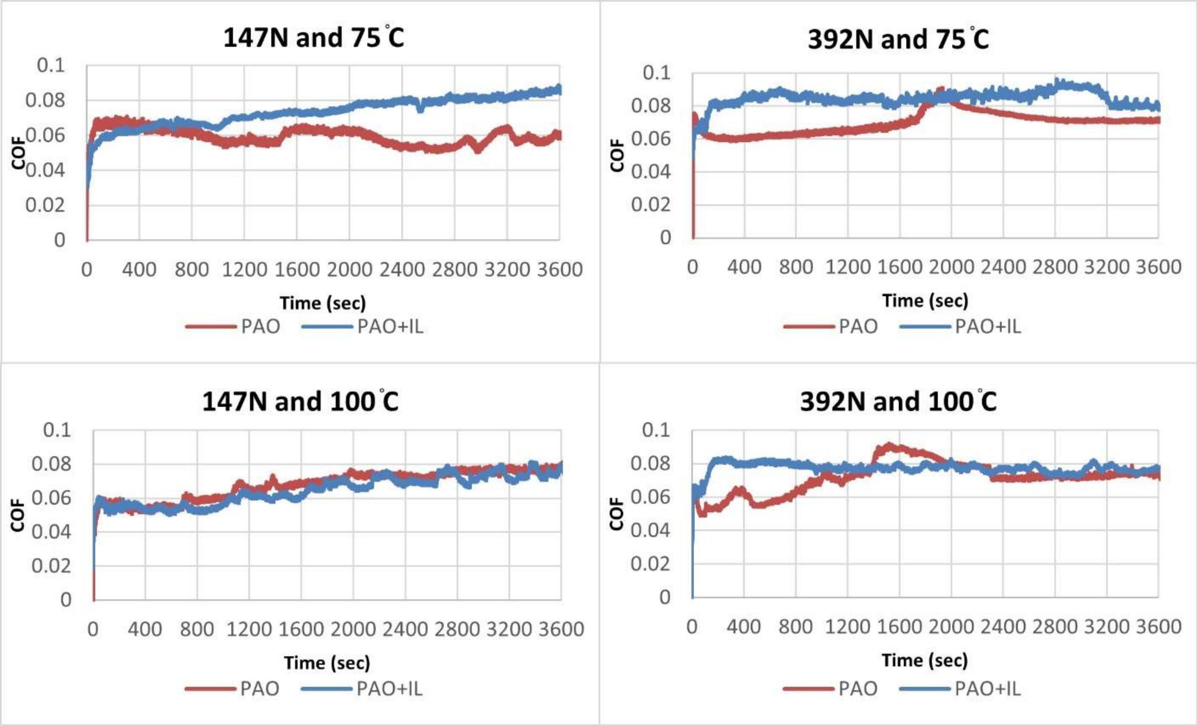


Figure 5.13: COF graph of PAO and PAO+IL

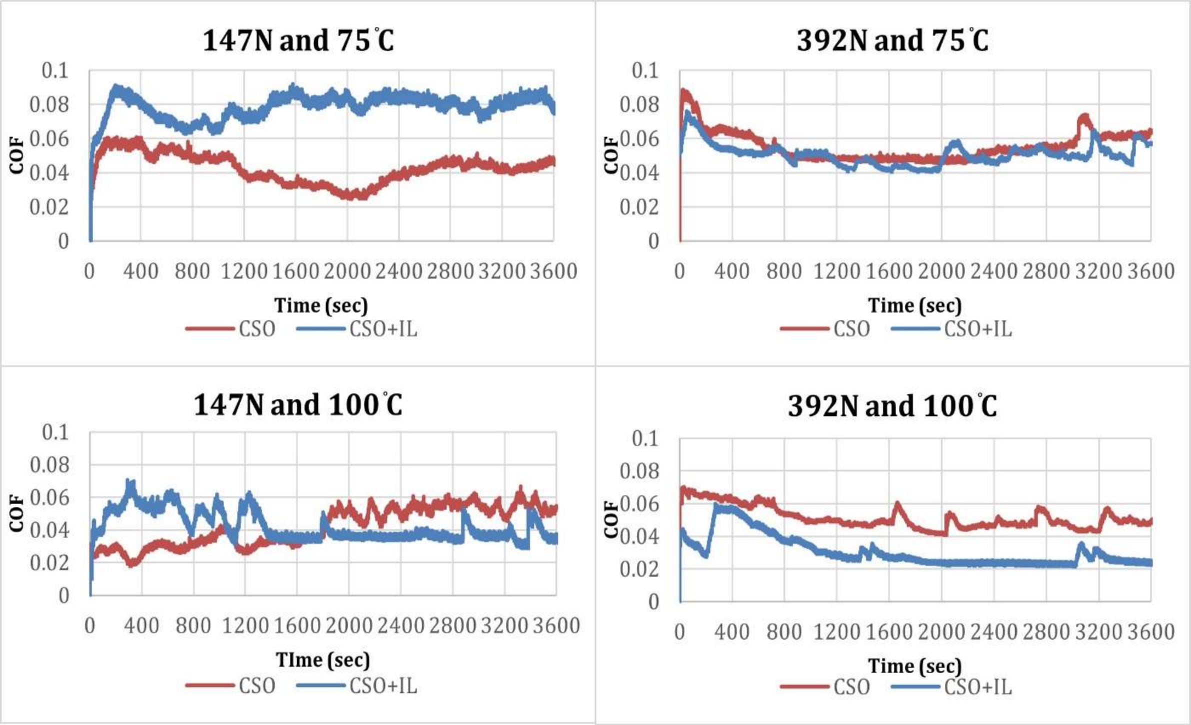


Figure 5.14: COF graph of CSO and CSO+IL

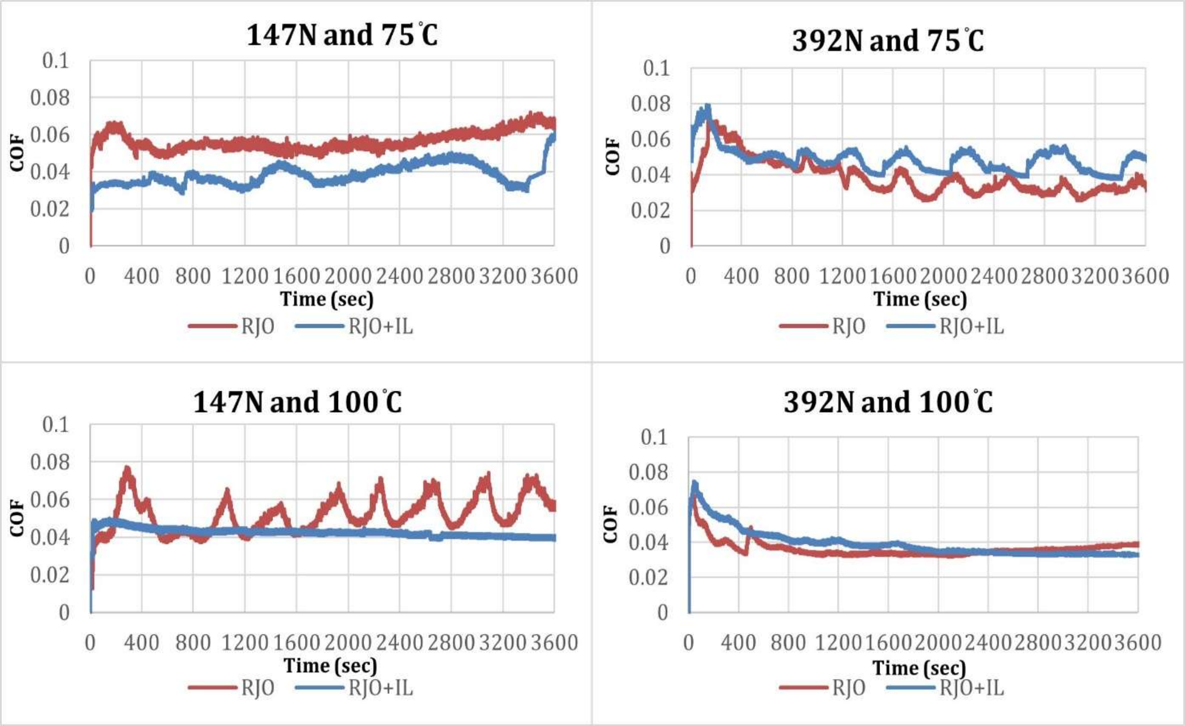


Figure 5.15: COF graph of RJO and RJO+IL

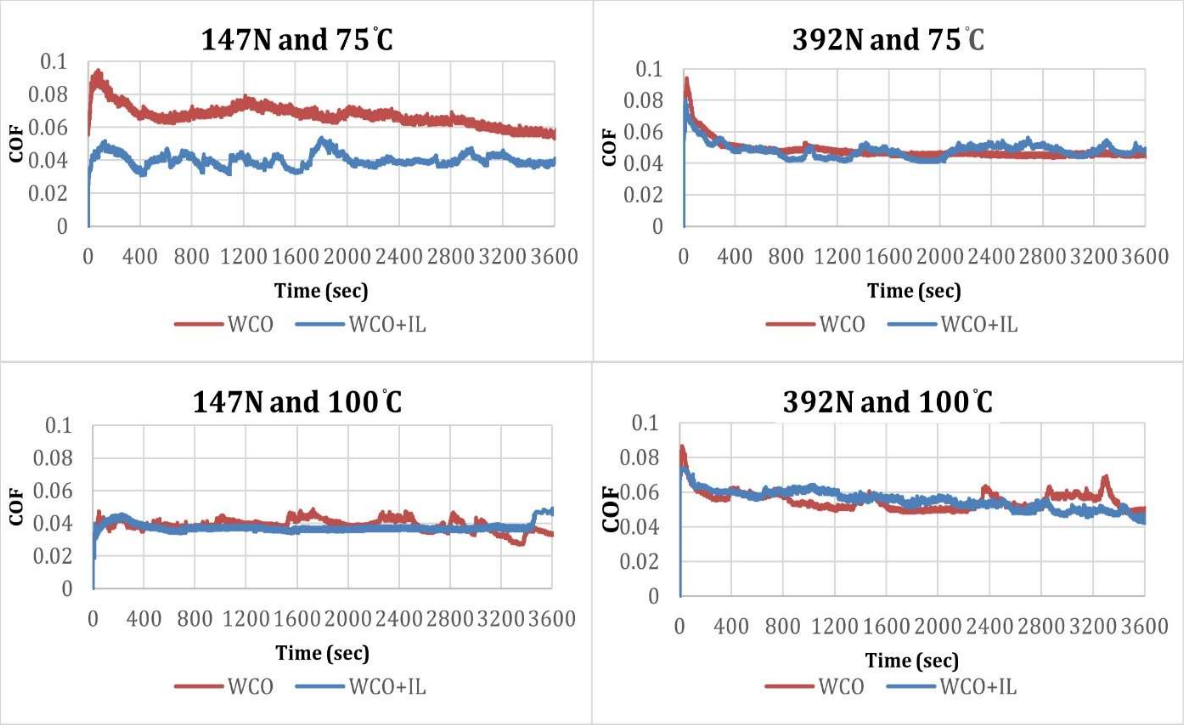


Figure 5.17: COF graph for WCO and WCO+IL

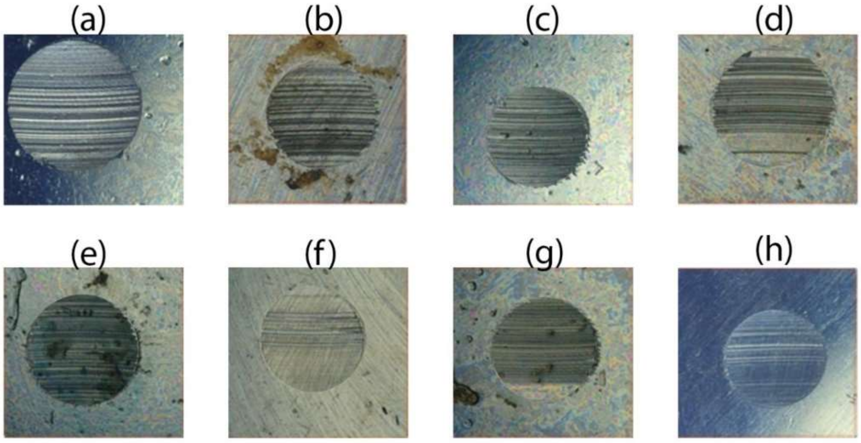


Figure 5.16: WSD at 147N and 75 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

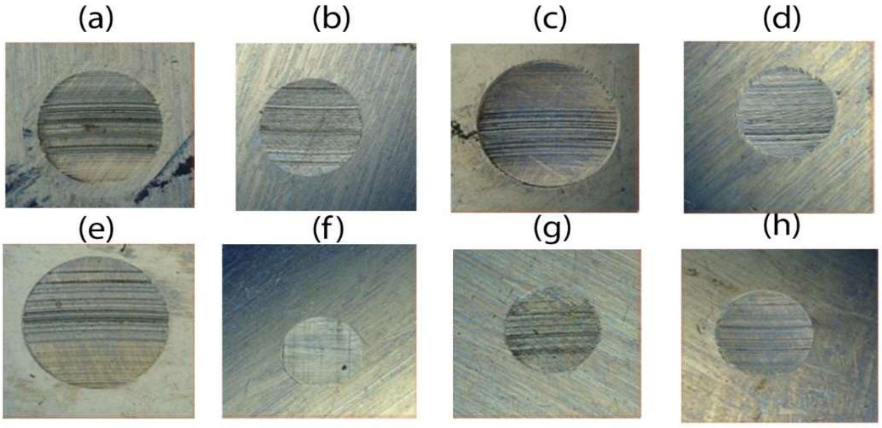


Figure 5.18: WSD at 392N and 75 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

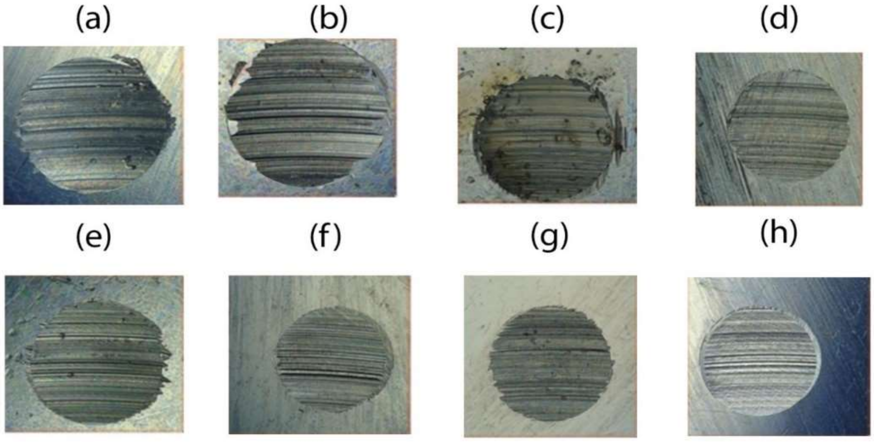


Figure 5.19: WSD at 147N and 100 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

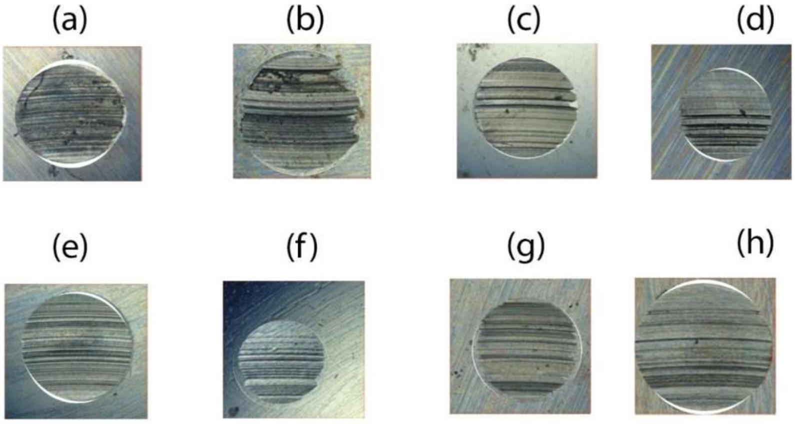


Figure 5.20: WSD at 392N and 100 Degree for (a) PAO (b) PAO+IL (c) CSO (d) CSO+IL (e) RJO (f) RJO+IL (g) WCO (h) WCO+IL

Wear scar images for all lubricants taken with OLYMPUS microscope at a magnifying power of 200x is shown in Figure 5.16 to Figure 5.20. Abrasive wear can be seen for all samples. It can be seen from these images that for higher loads the abrasive wear has increase for all samples. This trend can be explained by the fact that with increase in load more heat is generated causing more removal of material and hence decreasing the strength of material. Also with increase in operating temperature, it can be seen that the wear has increased for all bare lubricants. In case of lubricants containing ionic liquids a trend of decrease for wear scar can be seen. This can be explained by higher thermal stability of ionic liquid based lubricant. It can be observed that the abrasive wear in case of PAO is a little intense as compared to bio-lubricant. Also no much effect of addition of ionic liquids can be seen on PAO samples.

RJO along with its blend with ionic liquid has outperformed all the other lubricants in terms of both COF and WSD under all operating conditions. Also a decrease in COF and wear can be seen for all bio-lubricants when compared with synthetic lubricant PAO. This enhancement in tribological behavior of bio-lubricants is because of its higher thermal stability which is caused by high oleic acid concentration in it[72]. Amongst bio-lubricant RJO shows best results with ionic liquid as compared to WCO and CSO.

CHAPTER 6: Conclusions

Several conclusions regarding the performance of bio-lubricants and its comparison with PAO can be made from this study. The study shows that bio-lubricants when compared with PAO shows better tribological performance under all operating conditions. Moreover the introduction of ionic liquid does not produce a positive effect on the tribological performance of PAO because of its incompatibility with synthetic lubricants. Also it can be seen that bio-lubricants with the incorporation of ionic liquid produces better tribological results especially at higher loads. Additionally, it can be observed that at higher temperatures bio-lubricants containing ionic liquids performed better when compared with untreated lubricants.

In summary, this study highlights the better performance of bio-lubricants over synthetic PAO lubricants and the positive impact of ionic liquids on tribological performance of bio-lubricants under all operating conditions. Furthermore this study tell us that Rattan Jot oil outperformed all the other lubricants in terms of tribological performance both in its pure state as well as after addition of ionic liquid.

Future Recommendation

Tribological performance of three bio-lubricants produced and its blend with ionic-liquid is studied and its result is compared with a synthetic lubricant PAO. According to the results RJO and RJO+IL showed better performance in terms of COF and wear as compared to other lubricants. The following studies can be carried out in the future.

- The effect of these bio-lubricants as a blend to other lubricants can be studied.
- Effect of other additives such as nanoparticles and other ionic liquids can be seen with these bio-lubricants.
- Further studies of tribological performance of these bio-lubricants can be carried out on test rigs.
- Studies on this ionic liquid as an additive to other bio-lubricants can be done in future.

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